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ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

VII *. THE THERMAL AND PHOTOCHEMICAL PROPERTIES OF TRIALKYLLEAD DERIVATIVES OF Cr, Mo AND W

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Summary

Trimethyl- and triethyllead derivatives $(\eta^5\text{-}C_5H_5)M(CO)_3PbR_3$ (M = Cr, Mo, and W) have been synthesized. The trimethyllead derivatives are photochemically, and to a lesser extent, thermally unstable with respect to methyl transfer reactions that yield the corresponding $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$ complex. The related triethyllead complexes behave in a distinctly different fashion exhibiting rearrangements to $[(\eta^5\text{-}C_5H_5)M(CO)_3]_3PbEt_2$ (M = W, Mo). The reactions of the Cr, Mo, and W complexes with SO_2 yielded the corresponding alkyl sulphinato complexes as did the reaction of the related Fe complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}PbEt_3]$.

Introduction

One of us recently reported on the novel rearrangement of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PbMe_3]$ involving a 1,2-methyl migration from Pb to Fe that results in the formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]$, $PbMe_4$ and Pb [2]. This rearrangement takes place both thermally and photochemically, whereas for the triethyllead-iron complex no rearrangement was observed thermally, and only very little photochemically when the reaction was performed in the presence of PPh_3. This observation was the first recorded example of such alkyl migration from Pb to a transition metal in a well characterized and isolated metal lead complex and lent credence to a proposed mechanism for the zinc-based removal of alkyllead pollutants from industrial effluents. This mechanism involved transient (alkyllead)-zinc complexes that were proposed to decompose via alkyl migration to form alkylzinc complexes which react with water to liberate alkanes [3,4]. A related phenyl group migration from an unstable, non-isolable complex for-

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* For part VI see ref. 1.

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mulated as $PtCl(PbPh_3)(PPh_3)_2$ had been reported earlier by Baird [5]. In this paper we report an extension of our investigation to the photochemical and thermal stabilities of trialkyllead complexes of the transition metals to cover Cr, Mo, and W. Chemical properties of the lead complexes, involving reactions with SO_2 are also reported.

Experimental

All experimental procedures involving the various complexes were performed under nitrogen atmospheres using dry oxygen-free solvents. The various transition metallates were prepared using the standard procedures [6], the starting metal carbonyls, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ being purchased from Strem Chemicals. Triethyllead chloride was purchased from Alfa Products, Thiokol/Ventron Division, and the trimethyllead chloride was generously provided by the Ethyl Corporation. A typical preparation and the reactions of the lead complexes are illustrated below.

$[(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3]$

A THF slurry of Et_3PbCl (3.3 g, 10 mmol) was added to 100 ml of a solution of $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-Na^+$ (3.92 g, 11 mmol) cooled to 0°C. The reaction mixture was permitted to warm to room temperature and stirred for 12 h, and then the solvent removed under vacuum, and the resulting gum extracted with hexane. This hexane solution was concentrated to approximately 10 ml and placed upon an alumina column, 2.5 × 100 cm. It was found satisfactory to perform this chromatography in air, but to collect the eluent under nitrogen. Elution of the yellow band with hexane, and removal of solvent yielded a yellow-orange oil

TABLE 1

ANALYTICAL AND SPECTRAL DATA

Complex (Yield)		IR [a] $\nu(CO)$ (cm^{-1})	NMR [b] (ppm)		Analysis [c] Found (calcd.) (%)	
			$(\eta^5\text{-}C_5H_5)$	Pb—R	C	H
1. $(\eta^5\text{-}C_5H_5)Mo(CO)_3PbMe_3$	(80)	1896, 1914, 1985	4.75	8.82	31.7 (31.2)	3.61 (3.73)
2. $(\eta^5\text{-}C_5H_5)Mo(CO)_3PbEt_3$	(74)	1892, 1914, 1985	4.70	8.20(m)	see ref. 7	
3. $(\eta^5\text{-}C_5H_5)W(CO)_3PbMe_3$	(60)	1890, 1908, 1981	4.60	8.79	see ref. 7	
4. $(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3$	(78)	1891, 1910, 1980	4.61	8.20(m)	26.9 (26.8)	3.48 (3.21)
5. $(\eta^5\text{-}C_5H_5)Cr(CO)_3PbMe_3$	(50)	1884, 1895, 2063	5.20	8.74	29.5 (29.1)	2.93 (3.11)
6. $(\eta^5\text{-}C_5H_5)Cr(CO)_3PbEt_3$	(56)	1885, 1896, 2067	5.25	8.20(m)	34.6 (33.9)	4.04 (4.06)
7. $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2$	(58)	(1885, 1967, 1990) 2010, 2005) [d]	4.47	7.52(q) [e] 8.40(t) [e]	25.9 (25.8)	2.04 (2.16)

[a] Recorded in hexane. [b] Recorded in $CDCl_3$. [c] Analyses performed by Canadian Analytical Service, Vancouver, Canada. [d] Recorded in CH_2Cl_2. [e] $J = 7.0$ Hz. [f] M. pts. of complexes (°C) 1, 102—103; 3, 111—113; 5, 118—119; 7, 126—128(d). The other complexes are oils.

(4.4 g, 7.0 mmol, 70%). The spectral and analytical data for the complex, along with that of all other complexes are recorded in Table 1.

Thermal treatment of $[(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3]$

The product from the above reaction was placed in a flask (0.8 g, 1.3 mmol) and heated in vacuo to 60°C for 8 h. During this time the yellow-orange liquid slowly became solid and darker orange in colour. The resulting solid was dissolved in the minimum of a 1/3 CH_2Cl_2/hexane solution and placed upon an alumina column. The column was eluted with hexane to remove any unreacted starting material and then the broad orange band was eluted with a 1/3 hexane/ CH_2Cl_2 solution. The resulting solution was then concentrated to approximately 1/4 of the original volume and placed in a refrigerator. From this solution 0.3 g, 0.32 mmol (58%) of crystalline $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2$ was isolated.

Similar experiments with the Mo and Cr derivatives $[(\eta^5\text{-}C_5H_5)M(CO)_3PbEt_3]$ led to no observable chemical reaction.

Thermal treatment of $[(\eta^5\text{-}C_5H_5)W(CO)_3PbMe_3]$

A hexane solution of the title complex (0.3 g, 0.5 mmol) was refluxed in a Pyrex flask and the solution monitored by infrared spectroscopy. The infrared bands of the title complex began to diminish and two new bands appeared at 2023 and 1930 cm^{-1}. After 100 h the reaction was stopped with approximately 30% conversion and some general decomposition. The solvent was removed under vacuum, and the resulting yellow solid was purified by sublimation (25°C, 10^{-3} mmHg) to yield 0.03 g (0.08 mmol, 16%) of $[(\eta^5\text{-}C_5H_5)W(CO)_3Me]$, characterized by the equivalence of its spectral properties with those published [7].

A similar reaction with the trimethyllead-molybdenum derivative yielded 15% of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Me]$, again characterized by its published spectral data [7]. For the trimethyllead-chromium complex, no purification was attempted of the $[(\eta^5\text{-}C_5H_5)Cr(CO)_3Me]$, but its formation was confirmed by the infrared monitoring procedure.

Photochemical treatment of $[(\eta^5\text{-}C_5H_5)W(CO)_3PbMe_3]$

A hexane solution (0.5 g, 0.85 mmol) of the title complex was irradiated with a 500 watt Hanovia low pressure Hg lamp in a 100 ml quartz flask situated 1 foot from the lamp. After 35 h, infrared monitoring indicated the title complex had reacted and only the corresponding methyl derivative was observed in solution. The solution temperature was $\simeq$40°C. A considerable amount of Pb and other insoluble matter was present. The solution was filtered and the $[(\eta^5\text{-}C_5H_5)W(CO)_3Me]$ purified and recovered in 36% yield using the procedure described above.

For the related trimethyllead-molybdenum complex, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Me]$, was obtained in 40% yield.

Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3PbEt_3]$ *with* SO_2

Liquid SO_2 (10 ml) used directly from a cylinder was added to 0.6 g (1.1 mmol 10^{-3} mmol) of the title complex. A red solution was formed immediately and the system left untouched until the SO_2 had evaporated (leaving a solid residue). At this time 25 ml of hexane was added to the flask and the solid residue stirred. The hexane solution was filtered, and the solid residue dissolved in CH_2Cl_2, and again the solution was filtered to remove insoluble matter. Upon removal of the solvent, the solid residue was purified by crystallization from CH_2Cl_2/hexane to yield $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(SO_2Et)]$ (0.25 g, 0.74 mmol, 66%) characterized by equivalence of its spectral properties with those published [8].

Similar reactions with the following complexes yielded the corresponding known alkylsulphinato complexes [8] in the recorded yields:

$(\eta^5\text{-}C_5H_5)Mo(CO)_3PbMe_3 \rightarrow (\eta^5\text{-}C_5H_5)Mo(CO)_3(SO_2Me)$ (60%)

$(\eta^5\text{-}C_5H_5)W(CO)_3PbMe_3 \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_3(SO_2Me)$ (60%)

$(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3 \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_3(SO_2Et)$ (70%)

$(\eta^5\text{-}C_5H_5)Cr(CO)_3PbMe_3 \rightarrow$ No isolable product .

$(\eta^5\text{-}C_5H_5)Cr(CO)_3PbEt_3 \rightarrow (\eta^5\text{-}C_5H_5)Cr(CO)_3(SO_2Et)$ (65%)

$(\eta^5\text{-}C_5H_5)Fe(CO)_2PbEt_3 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2(SO_2Et)$ (68%)

Discussion

The yellow-orange alkyllead derivatives of the system $[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Cr, Mo, W) are readily prepared in high yield using the standard salt elimination reaction between the metal carbonylate and the trialkyllead chloride. The trimethyllead complexes are crystalline air-stable materials, while the triethyllead complexes are liquids and less air-stable. The spectral and analytical data for these complexes are presented in Table 1.

The trimethyllead complexes may be readily converted to the corresponding methyl complexes $[(\eta^5\text{-}C_5H_5)M(CO)_3Me]$. The reaction is only very moderate in yield when the transformation is performed thermally; thus, refluxing a hexane solution of a trimethyllead complex for five days led to only 30% conversion along with significant decomposition involving Pb formation.

$$2[(\eta^5\text{-}C_5H_5)M(CO)_3PbMe_3] \rightarrow 2[(\eta^5\text{-}C_5H_5)M(CO)_3Me] + Pb + PbMe_4$$

The transformation is more efficiently effected photochemically. Irradiation of a hexane solution by a 500 watt Hanovia low pressure lamp produced considerably higher yields in shorter reaction times.

These results indicate that the trimethyllead complexes reported here for Cr, Mo, and W behave in essentially the same fashion as their $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ analog, but are significantly more thermally stable [2].

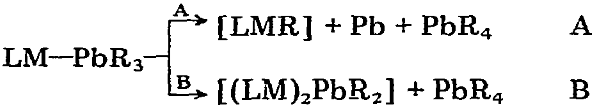
The triethyllead complexes exhibit a markedly different behavior. The W and Mo complexes are readily transformed into the corresponding bis-metal diethyllead complex:

$$[(\eta^5\text{-}C_5H_5)M(CO)_3PbEt_3] \rightarrow [(\eta^5\text{-}C_5H_5)M(CO)_3]_2PbEt_2 + PbEt_4$$

The transformation is particularly facile for the W complex where the reaction occurs almost quantitatively at 60°C, in vacuo, after 8 h. The Mo complex exhibits little rearrangement when treated thermally, but conversion may be effected photochemically, 50% transformation after 12 h irradiation.

The conversions $Et_3PbML \rightarrow Et_2Pb(ML)_2$ reported here are similar to those reported for $[Me_3PbMn(CO)_5]$ and $[(Me_3Pb)_2Fe(CO)_4]$ which yield $Me_2Pb[Mn(CO)_5]_2$ and $[Me_2PbFe(CO)_4]_2$, respectively [9,10].

Overall, we have now demonstrated that there exist two basic modes of chemical disproportionation for trialkyllead derivatives of the transition metals leading to either retention or cleavage of the metal—Pb bond. The two modes are outlined below along with the metal systems that exhibit each type of reactivity:



$$\begin{tikzcd} & {[LMR] + Pb + PbR_4} & A \\ LM{-}PbR_3 \arrow[ur, "A"] \arrow[dr, "B"'] & & \\ & {[(LM)_2PbR_2] + PbR_4} & B \end{tikzcd}$$

A. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (R = Me, Et)

$[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (R = Me, M = Cr, Mo, W)

B. $[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (R = Et, M = W, Mo)

$[Mn(CO)_5]$ (R = Me)

$[Fe(CO)_4]$ (R = Me)

There appears to be no readily understandable correlation between metal and/or alkyl group that determines which mode of reactivity a particular complex exhibits. For a given R group no single metal system exhibits both modes of reactivity, and the only metal system that exhibits both modes with different R groups is the one reported in this paper.

Reactions with SO_2

Studies on the reactions of Group IV-substituted transition metal complexes with SO_2 are reported in the literature for C, Si, Ge, and Sn. No examples have been presented detailing reactions with organolead complexes.

For the series $[(\eta^5\text{-}C_5H_5)Fe(CO)_2EMe_3]$ (E = Si, Ge, Sn) three distinct types of interaction have been reported. Thus, the Si derivative reacts only at elevated temperature, but no isolable complexes could be obtained. The Ge complex exhibits SO_2 insertion into the Fe—Ge bond to yield a $Me_3GeS(O)_2Fe$ linkage, while the Sn complex forms a polymeric material containing Sn—O—S-(O)—Fe linkages [11].

In a different system, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3SnR_3]$ (R = Me and Ph) insertions of SO_2 into the Sn—C bond occur to yield a series of complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_3Sn(SO_2R)_nR_{3-n}$. Similar insertions into the Sn—C bond occurred with the anionic complex $[Mo(CO)_5SnPh_3]^-$ [12], and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SnPh_3]$ [13]. It was also reported that the reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2SnMe_2$ and SO_2 led only to the isolation of trace amounts of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2Me]$ [13].

Several reactions of alkyllead compounds with SO_2 have been reported. In general, insertion into the Pb—C bond occurs. However, the resulting sulphinites are usually unstable with respect to disproportionation involving the reformation of the alkyllead compounds together with lead(II) sulphinites and alkyl sulphones [14].

Reactions between the trialkyllead complexes reported in this paper and SO_2 lead to only a single mode of reactivity as determined by product isolation; namely, formation of the corresponding alkylsulphinato transition metal complexes.

$$[(\eta^5\text{-}C_5H_5)M(CO)_nPbR_3] \rightarrow [(\eta^5\text{-}C_5H_5)M(CO)_nSO_2R]$$

$$(n = 2, M = Fe, R = Et; \quad n = 3, M = Cr, Mo, W, R = Et, Me)$$

$$[(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2 \rightarrow [(\eta^5\text{-}C_5H_5)W(CO)_3SO_2Et]$$

These reactions were carried out in liquid SO_2. These are conditions of temperature under which no rearrangements to the transition metal alkyl complexes are observed. Although we have made no effort to study the SO_2 reactions mechanistically, it seems probable that the reactions proceed via transient $(RSO_2Pb)M$ species, followed by a migration of the RSO_2 group from Pb to the metal. The fact that we obtain very high yields of the $EtSO_2M$ complexes, even though no evidence was obtained for the formation of the related Et—M complexes lends support for this idea.

The fate of the Pb was not ascertained. In each experiment, subsequent to the reactions with SO_2, the solid residue was washed first with hexane, to remove any trace starting complexes then the insoluble material was dissolved in CH_2Cl_2. This process was never complete, i.e. a significant amount of a brown residue was obtained which was insoluble in common solvents. No attempt was made to investigate the material with the exception that the weight was sufficient to account for the Pb portion of the starting material. It is assumed this material represents lead salts, e.g. lead sulphates, sulphinates [14], but no definitive investigations were initiated.

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