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ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

X *. PHOTOCHEMICAL, THERMAL, AND SO_2 INDUCED 1,2-PHENYL AND 1,2-SULPHINATOPHENYL MIGRATIONS FROM LEAD TO TRANSITION METALS IN THE SYSTEM $[(\eta^5\text{-}C_5H_5)M(CO)_nPbPh_3]$ (M = Fe, Cr, Mo, W)

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Summary

The complexes $[(\eta^5\text{-}C_5H_5)M(CO)_nPbPh_3]$ (M = Fe, Cr, Mo, W) have been studied with respect to their thermal and photochemical stability and their reactivity with respect to SO_2. The iron complex is the only complex that exhibits the ability to decompose via a 1,2-phenyl migration to the transition metal under thermal conditions, but photochemically the tungsten complex also exhibits this behaviour. All complexes react readily with SO_2 to yield the corresponding sulphinatophenyl complexes, $LM{-}SO_2{-}Ph$, in high yield.

Introduction

We have recently reported that trialkyllead complexes of the general system $[(\eta^5\text{-}C_5H_5)M(CO)_n]$ (M = Cr, Mo, W, Fe) readily rearrange upon both photochemical and thermal treatment to produce the corresponding alkyl metal complexes, or dialkyl(dimetal)lead complexes as shown in eq. 1 [2,3].

$$\mathrm{LM{-}PbR_3}\begin{cases}\xrightarrow{\mathrm{A}}\mathrm{LM{-}R + Pb + PbR_4}\\[2ex]\xrightarrow[\mathrm{B}]{}\mathrm{(LM)_2PbR_2 + PbR_4}\end{cases}\tag{1}$$

$LM = [(\eta^5\text{-}C_5H_5)M(CO)_n]$;
Route A: R = Me, M = Fe, Cr, Mo, W; R = Et M = Fe;
Route B: R = Et, M = Mo, W

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* For parts VIII and IX see ref. 1.

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While route B had been previously established for the complexes $Mn(CO)_5PbMe_3$ and $Fe(CO)_4(PbMe_3)_2$ [4,5], the 1,2-migrations had not been previously observed. Such possibilities had, however, been suggested from studies on zinc catalysed removal of organolead compounds from aqueous solutions [6].

We also reported that the same complexes reacted with SO_2 to yield only the corresponding alkylsulphinato complexes, probably via the intermediacy of unstable $LMPbSO_2R$ complexes [3]. Such reactivity is in direct contrast to the general reactions of SO_2 with other Group IV (C, Si, Ge, Sn) metal derivatives $LMER_3$ where $LMSO_2E$ and $LMESO_2R$ complexes have been reported [7].

There are several reports in the literature concerning the synthesis and spectral properties of triphenyllead transition metal complexes [8,9], but no study of their photochemical, and thermal properties. An early report by Baird on the attempted synthesis of $PtCl(PbPh_3)(PPh_3)_2$ stated that the complex could not be isolated pure, but that the related phenylplatinum complex was obtained, $PtCl(Ph)(PPh_3)_2$ [10]. This result suggested that 1,2-phenyl migrations may be a general property of triphenyllead complexes of the transition metals.

It is the purpose of this article to report on a study of such complexes to determine if this reactivity is observed, coupled with a study of their reactions with SO_2.

Experimental

All manipulations were carried out under nitrogen atmospheres, using dry oxygen free solvents. The various triphenyllead complexes were synthesized using the published procedures [8,9]. Analytical determinations were provided by the Canadian Microanalytical Service, Vancouver, Canada. Some typical reactions are outlined below.

Thermal treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}PbPh_3]$

A 50 ml toluene solution of the title complex (0.31 g, 0.5 mmol) was refluxed in a pyrex flask, and monitored by infrared spectroscopy. The infrared bands of the starting complex (1995, 1945 cm^{-1}) gradually diminished over a 90 h period, with the concommitant growth of two new bands at 2014 and 1956 cm^{-1}. Along with this transformation much metallic lead was precipitated. After 90 h the solution was filtered and the solvent removed under reduced pressure. The residue was stirred in 25 ml of hexane for 30 min, and the solution refiltered to yield 0.02 g (7%) of a white solid shown to be tetraphenyllead, m.p. 225 °C, lit. [11] 227.7 °C, and infrared comparison with diagnostic bands at 993, 768, 725 and 694 cm^{-1} (Nujol). The hexane was removed under reduced pressure to yield 0.03 g of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph]$ (24%), identified by the coincidence of its spectral data with those published [12].

Similar treatment of the related Cr and Mo complexes led to a gradual disappearance of the starting material, but with no characterizable new products. In the case of the W complex, no change in the system was observed indicating this to be a very thermally stable complex.

Photochemical treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PbPh_3]$

A 200 ml toluene solution of the title complex (0.18 g, 0.29 mmol) was irradiated in a quartz tube situated 5 inches from a water cooled Hanovia 450 watt low

TABLE 1

SPECTRAL AND ANALYTICAL DATA FOR THE $[(\eta^5\text{-}C_5H_5)M(CO)_nSO_2Ph]$ COMPLEXES (M = Cr, Mo, W, Fe)

Complex	Yield	IR [a]	NMR [b] C_5H_5; Ph	Analysis [c] (Found (calcd.) (%))		
				C	H	S
$[(\eta^5\text{-}C_5H_5)Cr(CO)_3SO_2Ph]$	73	2042, 1977	5.4(s); 7.6(m)	48.25	3.14	8.61
				(49.12)	(2.94)	(9.36)
$[(\eta^5\text{-}C_5H_5)Mo(CO)_3SO_2Ph]$	80	2052, 1969	5.84(s); 7.6(m)	43.56	2.50	8.24
				(43.52)	(2.60)	(8.30)
$[(\eta^5\text{-}C_5H_5)W(CO)_3SO_2Ph]$	82	2042, 1955	5.84(s); 7.4(m)	35.31	1.91	6.75
				(35.46)	(2.12)	(6.76)
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2Ph]$	77	2053, 2009	4.90(s); 7.4(m)	Ref. 15		

[a] Recorded in CH_2Cl_2, $\nu(CO)$ in cm^{-1}. [b] δ relative to TMS, recorded in $CDCl_3$. [c] The Cr complex is light and heat sensitive, and the analytical data reflect this feature.

pressure lamp, and the reaction was monitored by infrared spectroscopy. After a very short time, 30 min, significant amounts of lead were deposited as a lead mirror, and the infrared indicated that the same reaction observed thermally was occurring, but at a much more rapid rate. After 2 h the reaction was complete and no more starting complex was present in solution. Removal of the solvent, and purification by column chromatography, elution with hexane, led to a 60% yield of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph]$.

Similar treatment of the Cr complex led, as with the thermal reaction of this complex, to total decomposition, with no observable products. In the case of the W complex, work up as described for the Fe complex yielded 45% of $[(\eta^5\text{-}C_5H_5)W(CO)_3Ph]$, ($\nu$(CO), hexane: 2024, 1940, 1930 cm^{-1}) after 4 h irradiation time. The complex was identified on the basis of its published spectral properties [13].

In the case of the Mo complex, no evidence was obtained for the formation of the related phenyl complex, only the Mo–Mo dimer, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, was recovered in 35% yield after 3 h irradiation.

Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3PbPh_3]$ with SO_2

Liquid SO_2 (20 ml) was distilled directly from a cylinder into a flask containing 0.4g (0.58 mmol) of the title complex under a nitrogen atmosphere. This solution was left untouched until all the SO_2 had evaporated, 2–3 h. The resultant solid material was stirred with 25 ml of CH_2Cl_2 after completely drying on a high vacuum line. The solution was filtered, the solvent removed under vacuum, and the resultant solid was recrystallized from a CH_2Cl_2/hexane (3/1) mixture to yield 0.18 g (80%) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3SO_2Ph]$. The spectral and analytical data for the various sulphinatophenyl complexes are recorded in Table 1.

Results and discussion

From the results delineated in the experimental section it is apparent that only the Fe complex exhibits the ability to rearrange thermally via a 1,2-phenyl migration to the corresponding aryl complex $[(\eta^5\text{-}C_5H_5)M(CO)_nPh]$. It is also noted that this reaction takes a considerable time period, and the yields are only moderate. Along with the iron complex, Pb, and $PbPh_4$, are produced illustrating that the decomposition is similar to the pathway A outlined in the introduction.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2PbPh_3] \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph] + \tfrac{1}{2}Pb + \tfrac{1}{2}PbPh_4 \qquad (2)$$

In the case of the Group VI elements Cr, Mo, and W, both the Cr and Mo complexes decompose over a 36 h time period in refluxing toluene but with no observable transition metal complexes. In both cases Pb and $PbPh_4$ are observed, suggesting that the same type of chemistry is occurring, but that under the reaction conditions the related σ-aryl complexes are unstable. By contrast the triphenyllead-tungsten complex is very stable; no observable thermal decomposition was observed even after 4 days in refluxing toluene.

Photochemical treatment of the complexes in toluene and hexane had a pronounced effect upon the stability of the complexes. Both the Fe and W complexes readily decomposed via the 1,2-phenyl shift mechanism after short irradiation periods using a 450 watt Hanovia low pressure mercury lamp. As in the thermal reaction with the Fe complex, Pb and $PbPh_4$ were also produced in this reaction. In the case of the Cr complex, a reaction exactly analogous to the thermal reaction was observed in which decomposition of the starting complex occurred with no characterizable Cr product being formed. The Mo complex exhibited a different behaviour producing a very high yield of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. It is unclear from our studies whether the Mo dimer derives directly from the primary photochemical process or via the transient intermediacy of the MoPh complex. This latter complex has been reported to be unstable with respect to migration of the phenyl group to the cyclopentadienyl ring to form $[(\eta^5\text{-}Ph\text{-}C_5H_4)Mo(CO)_3]_2$ [13]. We have been unable to definitively observe this latter complex during our studies.

The photochemical enhancement of the rearrangement reactions for Fe and W, and the observation of the $[Mo]_2$ complex strongly suggest that the reactions occur subsequent to the initial elimination of CO in the primary photochemical process. Overall it is clear that the triphenyllead complexes are significantly more stable than their trialkyl counterparts with respect to rearrangement processes. No evidence has been obtained in this study for the formation of products derived from pathway B, i.e. formation of $(LM)_2PbPh_2$.

The reactions of the various triphenyllead complexes with SO_2 were the same for all the complexes studied, resulting in high yields of the sulphinatophenylmetal complexes (eq. 3).

$$[(\eta^5\text{-}C_5H_5)M(CO)_nPbPh_3] + SO_2 \rightarrow [(\eta^5\text{-}C_5H_5)M(CO)_nSO_2Ph] + \text{Pb salts} \qquad (3)$$

This behaviour is the same as that observed for the trialkyl complexes. We have no evidence for the intermediacy of complexes containing the $LMPbSO_2Ph$ moiety, but suggest that this must be the initially formed species since the isolated sulphinato complexes are formed under reaction conditions where 1,2-phenyl migrations do not occur. Thus, as in the case of the trialkyl complexes, facile migration of the sulphinatophenyl group from lead to the transition metal is occurring. Insertion into Pb–Ph bonds has been observed in organolead compounds, but the resulting compounds are very unstable [14]. No effort has been made to identify the exact nature of the insoluble lead salts also formed during this reaction.

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