chloride showed no absorption. The infrared spectrum, recorded as a carbon tetrachloride solution on a Unicam S.P. 100 spectrometer, showed terminal carbonyl absorption at 2112 (s), 2065 (s), 2048 (s), 2032 (w) and 1992 (w) cm^{-1}.

Department of Chemistry, The University,
Sheffield 10 (England)

S. F. A. Kettle
Irshad A. Khan*

1 S. F. A. Kettle, *Theoret. Chim. Acta*, in press.
2 S. F. A. Kettle, *Theoret. Chim. Acta*, 3 (1965) 282.
3 W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed and B. L. Shaw, *Proc. Chem. Soc.*, (1961) 169.
4 S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, (1962) 82.
5 S. D. Ibekwe and M. J. Newlands, *Chem. Commun.*, (1965) 114.
6 S. F. A. Kettle, *Inorg. Chem.*, 4 (1965) 1661.
7 G. Bor, L. Marko and B. Marko, *Chem. Ber.*, 95 (1962) 333.
8 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, 1962, p. 348.
9 G. G. Hess, F. W. Lampi and L. H. Sommer, *J. Am. Chem. Soc.*, 86 (1964) 3175.

Received November 15th, 1965

---

* Present address: Department of Chemistry, University of Karachi, Karachi 32, West Pakistan.

J. Organometal. Chem., 5 (1966) 588–590

PRELIMINARY NOTES

Addition reactions of the lead–oxygen bond.

Routes to trichloromethyltriphenyllead and tribromomethyltriphenyllead

Organotin alkoxides and oxides add to many types of multiply-bonded acceptor molecules, providing the basis for new organic and organometallic syntheses[1]. Similar reactions (equation 1) have now been established for organolead compounds.

$$R_3Pb{\cdot}OR' + A{=}B \longrightarrow R_3Pb{\cdot}A{\cdot}B{\cdot}OR' \quad (R' = \text{alkyl or } R_3Pb) \qquad (1)$$

Triphenyllead methoxide (m.p. 89–90°; from triphenyllead chloride and sodium methoxide in benzene), tributyllead methoxide (m.p. 46–48°; from the chloride and sodium methoxide in ether), and bistriphenyllead oxide react rapidly and usually exothermically at room temperature with the acceptor molecules shown in the first column of Table 1. The adducts listed in the second column have been isolated with satisfactory analyses.

In the few cases where the reactions are slow enough to allow a comparison to be made, the lead–oxygen bond is clearly more reactive than the corresponding tin–oxygen bond[1,2]. The adducts containing the triphenyllead group are stable under nitrogen, but those with the tributyllead group are thermally or photolytically un-

EAD ADDUCTS

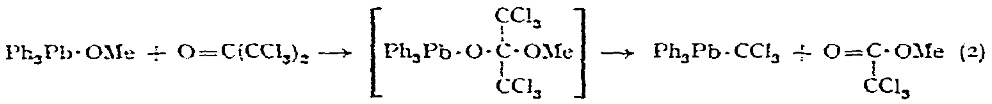
	$R_3Pb\cdot A\cdot B\cdot OR'$	*m.p.*
pNCO[a]	$Ph_3Pb\cdot NNp\cdot CO\cdot OMe$	135–141°d[b]
	$Bu_3Pb\cdot NNp\cdot CO\cdot OMe$	72–75°
hNCS	$Ph_3Pb\cdot S\cdot C(OMe):NPh$	107–120°d
S_2	$Ph_3Pb\cdot S\cdot CS\cdot OMe$	93–95°
$l_3C\cdot CHO$	$Ph_3Pb\cdot O\cdot CH(OMe)\cdot CCl_3$	96–100°d
	$Ph_3Pb\cdot O\cdot CH(O\cdot PbPh_3)\cdot CCl_3$	190–191°d
$l_3C\cdot CN$	$Ph_3Pb\cdot N:C(OMe)\cdot CCl_3$	127–131°
	$Ph_3Pb\cdot N:C(O\cdot PbPh_3)\cdot CCl_3$	137–139°
ıp·NCN·Np	$Ph_3Pb\cdot NNp\cdot C(OMe):NNp$	120–140°d

p = 1-naphthyl. [b] d = with decomposition.

and blacken during a few days. The triphenyllead compounds were stable ı towards hydrolysis to permit their molecular weights to be measured by r pressure osmometry: compounds I–V were monomeric in benzene over the 0.02–0.04 *M*.

A number of catalytic processes can be based on these adducts as intermediates; reactions are similar to those which have been established for the corresponding ɔtin compounds[1a,c]. For example, tributyllead methoxide and triphenyllead ıxide catalyse the trimerization of 1-naphthyl isocyanate, and the addition of ınol to butyl isocyanate and to di-1-naphthylcarbodiimide.

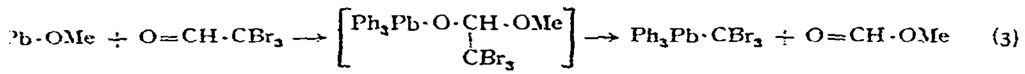
The adducts of organotin oxides and alkoxides with trihalogenomethyl alde- ; and ketones have recently been used as intermediates in the preparation of tri- enomethyltin compounds[3]. Trihalogenomethyllead compounds can be prepared in ilar way. Triphenyllead methoxide reacts exothermically with hexachloroacetone ızene. Thin layer chromatography of the product showed it to consist of a mixture phenyllead chloride (*ca.* 40 %) and a second component which was separated on a nn of silica gel and shown to be trichloromethyltriphenyllead (60 %), m.p. 171.5°.



$$Ph_3Pb\cdot OMe + O{=}C(CCl_3)_2 \longrightarrow \left[Ph_3Pb\cdot O\cdot \underset{CCl_3}{\overset{CCl_3}{C}}\cdot OMe \right] \longrightarrow Ph_3Pb\cdot CCl_3 + O{=}\underset{CCl_3}{C}\cdot OMe \qquad (2)$$

ıe same compound has recently been obtained by Willemsens and van der Kerk[4] ı the reaction between triphenylplumbyllithium and carbon tetrachloride.

Similarly, triphenyllead methoxide reacts with bromal in benzene to give tri- nomethyltriphenyllead, m.p. 135–140°.



$$b\cdot OMe + O{=}CH\cdot CBr_3 \longrightarrow \left[Ph_3Pb\cdot O\cdot \underset{CBr_3}{CH}\cdot OMe \right] \longrightarrow Ph_3Pb\cdot CBr_3 + O{=}CH\cdot OMe \qquad (3)$$

The addition reactions reported here are analogous to those between tributyllead lride and α-olefins, isocyanates, and alkynes[5], and that between triphenyllead lroxide and ketene[6] which have been described elsewhere. Together they make available a wide range of organofunctional lead compounds and suggest the app tion of these compounds in some catalytic processes.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1

ALWYN G. DA
R. J. PUDDEPI

1 A. J. BLOODWORTH AND A. G. DAVIES, *J. Chem. Soc.*, (*a*) (1965) 5238, (*b*) (1965) 6245, (*c*) (6858, (*d*) (1966C) 299.
2 A. G. DAVIES AND P. R. PALAN, unpublished results.
3 A. G. DAVIES AND W. R. SYMES, *J. Organometal. Chem.*, 5 (1966) 394.
4 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, *Investigations in the Field of Organolead Chem* International Lead Zinc Research Organization Inc., 1965, pp. 42, 98.
5 W. P. NEUMANN AND K. KÜHLEIN, *Angew. Chem. Intern. Ed.*, 4 (1965) 784.

Received March 29th, 1966

Some improved preparations of silylmetallic compounds

The preparation of silylmetallic species by the cleavage of polysilanes with al metals in ethereal solvents, generally tetrahydrofuran, is well established and been reviewed[1,7]. However, this work emphasized the fact that whereas lithi potassium, rubidium, and cesium derivatives are relatively easily obtained, the responding silylsodium compounds are almost completely unknown.

Triphenylsilylsodium has been prepared by the cleavage of hexaphenyldisil in 1,2-dimethoxyethane[2] or in liquid ammonia[3]. However, in the ethereal solvent compound is difficult to prepare and unstable, whereas reactions in liquid ammc are complicated by the presence of the highly reactive solvent.

It was reported by Coates and co-workers[4] that solutions of triphenylstanr sodium could be prepared by the action of sodium naphthalenide on hexapher distannane, tetraphenylstannane, or bromotriphenylstannane. In an extension of t work it was shown[5] that triphenylsilylsodium can be prepared in tetrahydrofuran the action of sodium naphthalenide on triphenylsilane, hexaphenyldisilane, or chlc triphenylsilane. However, in all these reactions the stoichiometric quantity of sodi naphthalenide calculated to convert the tin or silicon compounds to the correspond sodium derivatives was employed.

In an excellent investigation, Eisch has shown[6] that solutions of the lithiu biphenyl complexes in tetrahydrofuran are remarkably effective in promoting cert cleavage reactions which proceed only slowly, or not at all, with the bulk metal. this investigation it was shown that catalytic quantities of biphenyl in the presei of the bulk metal were frequently effective.

We are currently undertaking a detailed investigation of the preparation silylmetallic compounds by the treatment of a variety of organosilicon compour with certain aromatic hydrocarbon adducts both preformed and prepared *in situ*.

Results so far obtained appear promising. Treatment of the cyclo- or polysila (x moles) with an excess of sodium in the presence of 0.05–0.3x mole of naphthalene