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Preliminary communication

Some reactions of di-π-cyclopentadienyllead(II)

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SUMMARY

$(C_5H_5)_2Pb$ reacts with HX to give $(C_5H_5)PbX$ or PbX_2, X = Cl,Br,CH_3CO_2, with $BF_3 \cdot Et_2O$ to give $(C_5H_5)_2Pb{-}BF_3$ and with TCNE to give $(C_5H_5)_2Pb \cdot 0 \cdot 5TCNE$ or $(C_5H_5)_2Pb \cdot TCNE$.

Di-π-cyclopentadienyllead, $(C_5H_5)_2Pb$, is the only well-characterised organolead(II) compound, but although its structure has been determined in both the gas and solid phases and other physical properties have been measured, no chemical reactions have been reported[1]. As part of a wider study of organolead(II) compounds we have investigated the reactions of $(C_5H_5)_2Pb$ with some protic reagents, reactive unsaturated compounds and some simple Lewis acids.

With anhydrous acids the cyclopentadienyl groups of $(C_5H_5)_2Pb$ can be cleaved in a stepwise manner. Thus the new compounds $(\pi\text{-}C_5H_5)PbX$, where X = Cl,Br or CH_3CO_2, are formed from HCl, HBr or CH_3CO_2H respectively; they are insoluble in non-polar organic solvents and are probably polymeric with bridging X groups. Treatment of $(C_5H_5)_2Pb$ with excess protic reagents leads to cleavage of both cyclopentadienyl groups, and provides convenient syntheses of lead(II) dimethoxide, bis(acetylacetonate) and bis(hexafluoroacetonate) which are difficult to prepare in pure form by other methods. However very weak acids such as phenylacetylene fail to react with $(C_5H_5)_2Pb$, so that this route is not available for the preparation of σ-bonded alkynyllead(II) compounds.

The lone pair of electrons on the lead atom of $(C_5H_5)_2Pb$ enables it to act as a Lewis base, and a very stable complex, $(\pi\text{-}C_5H_5)_2Pb \cdot BF_3$, is formed with the Lewis acid, BF_3; however, no adducts could be isolated with the weaker acceptors trimethylaluminium dimer or triphenylboron. With transition metal halides, transfer of one cyclopentadienyl group from lead to the transition metal takes place rather than simple complex formation. Thus $TiCl_4$ gives $(C_5H_5)PbCl$ and $(C_5H_5)TiCl_3$ or $(C_5H_5)TiCl_2$ while Me_3TaCl_2 gives

TABLE 1

REACTIONS OF $(C_5H_5)_2Pb$

Reagent	*mol*[a]	*Product*[b]	*Yield (%)*	*M.p. (°C)*
HCl	1	$(C_5H_5)PbCl$	87	330 (dec.)
HBr	1	$(C_5H_5)PbBr$	82	360 (dec.)
CH_3CO_2H	1	$(C_5H_5)PbO_2CCH_3$	70	180 (dec.)
AcacH	>2[c]	Pb(Acac)$_2$	80	
HfacacH	2[d]	Pb(Hfacac)$_2$	88	
CH_3OH	excess	$Pb(OCH_3)_2$	80	
$BF_3 \cdot OEt_2$	1	$(C_5H_5)_2Pb \cdot BF_3$	85	>360
$TiCl_4$	1	$(C_5H_5)PbCl$	88	
		$(C_5H_5)TiCl_3$	48	180–190
		$(C_5H_5)_2TiCl_2$	23	290
$TiCl_4$	0.5	$(C_5H_5)_2TiCl_2$	50	290
Me_3TaCl_2	2	$Me_3(C_5H_5)TaCl$		*e*
TCNE	0.5	$(C_5H_5)_2Pb \cdot O \cdot 5TCNE$	71	180 (dec.)
TCNE	1	$(C_5H_5)_2Pb \cdot O \cdot 5TCNE$	60	180 (dec.)
TCNE	4	$(C_5H_5)_2Pb \cdot TCNE$	84	180 (dec.)

[a] Mol reagent/mol $(C_5H_5)_2Pb$. [b] Satisfactory analyses have been obtained for all new compounds. [c] AcacH = acetylacetone. [d] HfacacH = hexafluoroacetylacetone. [e] Subl. 50°C (10^{-3} mm Hg).

$Me_3(C_5H_5)TaCl$.

With tetracyanoethylene (TCNE) an adduct of composition $(C_5H_5)_2Pb \cdot O \cdot 5TCNE$ is formed when equimolar amounts of the two reagents are mixed in benzene solution, and a 1/1 adduct is formed when $(C_5H_5)_2Pb$ is added slowly to a large excess of TCNE in benzene. In solution these compounds appear to be simple charge transfer complexes, with the cyclopentadienyl groups acting as electron donors to TCNE. In other charge transfer complexes of TCNE[4], such as $(C_5H_5)_2Fe \cdot TCNE$[5,6], the C≡N stretching frequencies are only slightly lower than those for free TCNE (2255 and 2216 cm^{-1}); however in each of our complexes the corresponding frequencies of solid samples are very much lower (2175 and 2100 cm^{-1}), and close to those for $TCNE^{2-}$ (2160 and 2095 cm^{-1}). This strongly suggests that the compounds contain Pb–TCNE–Pb groupings in the solid state[7]; but their detailed structures are not yet known.

The above reactions suggest that $(C_5H_5)_2Pb$ may prove to be a versatile reagent in organometallic synthesis.

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