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Preliminary communication

REACTIONS OF HEXAMETHYLDILEAD WITH 7,7,8,8-TETRACYANOQUINODIMETHANE (TCNQ) AND TETRACYANOETHYLENE (TCNE)

A.W.S. DICK, A.K. HOLLIDAY and R.J. PUDDEPHATT*

Donnan Laboratories, The University of Liverpool, Grove Street, P.O. Box 147, Liverpool L69 3BX (Great Britain)

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Summary

Hexamethyldilead reacts with TCNQ to give $Pb(TCNQ)_2$ and tetramethyllead and with TCNE to give Pb(TCNE).

Hexamethyldisilane [1] forms a charge-transfer complex with tetracyanoethylene, $Me_6Si_2 \cdot TCNE$, but hexaalkylditins [2,3] give complete electron transfer to yield the radicals $[R_3SnN{=}CC(CN)C(CN)_2]^{\cdot}$, which may be considered to be complexes of R_3Sn^+ with $TCNE^{\overline{\cdot}}$ radical anion. 7,7,8,8-Tetracyanoquinodimethane, TCNQ gives similar reactions [3]. We have now studied the corresponding reactions of hexamethyldilead and find a quite different behaviour.

The reaction of TCNQ with excess hexamethyldilead in benzene gave a deep blue precipitate of $Pb(TCNQ)_2$, characterised by elemental analysis and also as follows: (1) The presence of the radical anion $TCNQ^{\overline{\cdot}}$ was proved by the characteristic IR, UV and ESR spectra [4]; (2) the presence of Pb^{II} rather than methyllead(IV) species was proved by characterising the dithizone complex [5], and was also indicated by the absence of $Pb—CH_3$ stretching vibrations in the infrared spectrum.

Using excess of TCNQ the same product formed, but crystallised with free TCNQ (indicated by the UV spectra and by broadening of the ESR signal of $TCNQ^{\overline{\cdot}}$); thus a reaction with a 2/1 mol ratio of $TCNQ/Me_6Pb_2$ gave $Pb^{2+}(TCNQ^{\overline{\cdot}})_2(TCNQ)$. Under these conditions about 33% of the lead was accounted for as this product, the remainder being present as tetramethyllead; some methane (but no ethane) was also identified. It seems that the expected product $Me_3PbTCNQ$ is not formed even as an intermediate, since the reaction of trimethyllead bromide with $Li^+TCNQ^{\overline{\cdot}}$ did not give $Pb(TCNQ)_2$, although $Me_3PbTCNQ$ is expected to be present in the reaction mixture [6]. The reaction products are most readily explained by the mechanism shown in Scheme 1.

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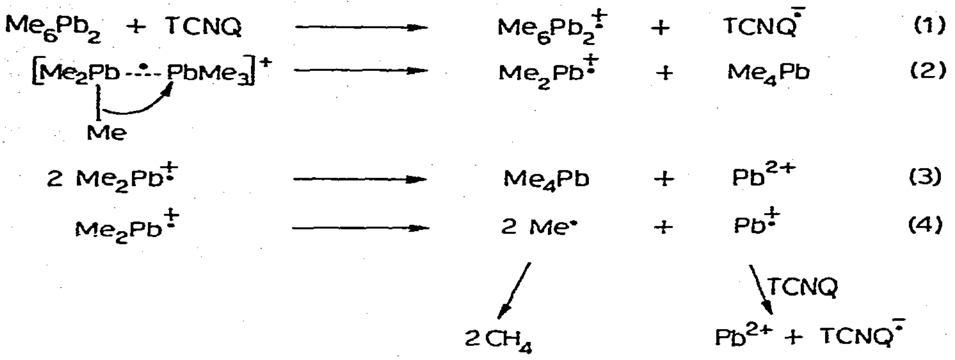
*To whom correspondence should be addressed.

SCHEME 1



Reaction 1 is completely analogous to the corresponding reaction of Me_6Sn_2 with TCNE or TCNQ; involving transfer of an electron from the Pb—Pb bond to TCNQ; however, instead of further loss of an electron to give $2Me_3Pb^+$, a methyl group transfer takes place (eqn.2) to give tetramethyllead and the new cation radical $Me_2Pb^{+\cdot}$. This can then either disproportionate (eqn. 3) or lose methyl radicals (which then give methane) according to eqn. 4. A satisfactory mass balance is obtained if decomposition of the proposed $Me_2Pb^{+\cdot}$ takes place in equal amounts according to eqns. 3 and 4.

Tetracyanoethylene with Me_6Pb_2 gave a dark red complex which analysed as PbTCNE. The presence of lead(II) was confirmed by conversion to the dithizone complex, so that a similar reaction mechanism to the above is suggested. However the IR and UV spectra and the absence of an ESR signal show that no $TCNE^{-\cdot}$ is present. The IR spectrum is similar to that reported [7] for $TCNE^{2-}$ and for $(\eta\text{-}C_5H_5)_2PbTCNE$ suggesting the formulation Pb^{2+} $TCNE^{2-}$, but since the product is formed in the presence of free TCNE, under which conditions the radical anion should be formed exclusively, it is possible that a rearrangement or cleavage of the TCNE structure has occurred.

The different reactions of the compounds Me_6M_2 where M = Si, Sn and Pb can therefore be rationalised in the following terms: (1) The electrons in the metal—metal bond are more easily removed when M = Sn or Pb than when M = Si, (2) methyl transfer reactions take place more readily when M = Pb than when M = Sn.

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