Journal of Organometallic Chemistry, 67 (1974) C43—C44

Preliminary communication

THE OXIDATION OF DISTANNANES BY TETRACYANOETHYLENE AND 7,7,8,8-TETRACYANOQUINODIMETHANE

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(Received January 21st, 1974)

Summary

The reaction of tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with distannanes result in the formation of complexes of the types $R_3Sn(TCNE)$ and $R_3Sn(TCNQ)$ (R = Me, Bu). Hexaphenylditin and TCNQ give the complex $(Ph_3Sn)_2 \cdot (TCNQ)$.

The recent reports by Traven and West [1] and Sakurai et al. [2] concerning the formation of ($\sigma \rightarrow \pi$) charge transfer complexes between di- and polysilanes and tetracyanoethylene (TCNE) prompt us to communicate our investigations into the interaction of the latter compound and the similar reagent 7,7,8,8-tetracyanoquinodimethane (TCNQ) with distannanes. We have previously [3] reported the synthesis of Me_3SnCl and LiTCNQ in water, but the use of this solvent restricts this method as a general route to this family of compounds. Metallic TCNQ derivatives are also available by the oxidation by the reagent of the corresponding metal iodide, but in the present case no reaction could be detected between any organotin iodide and TCNQ or TCNE. The ease of oxidative cleavage of the Sn—Sn bond in hexaorganodistannanes has proved useful in the synthesis of several organotin derivatives. In the present case, reaction of TCNE or TCNQ with hexamethyl- or hexabutyldistannane in THF resulted in the slow formation of the complexes I and II as intensely coloured solids

$$R_3SnSnR_3 + 2TCNE \xrightarrow{THF} \underset{(I)}{2R_3Sn(TCNE)}$$

$$R_3SnSnR_3 + 2TCNQ \xrightarrow{TCNQ} \underset{(II)}{2R_3Sn(TCNQ)}$$

R = Me, Bu

TABLE 1

	Compound	m.p. (°C)	Colour	ν(C≡N)
I	$Me_3Sn(TCNE)$	ca. 180 (dec.)	black	2200 s (br)
I	$Bu_3Sn(TCNE)$	ca. 180 (dec.)	red-brown	2220 s (br)
II	$Me_3Sn(TCNQ)$	ca. 200 (dec.)	pale brown	2222 mw, 2201 s, 2144 s
II	$Bu_3Sn(TCNQ)$	ca. 200 (dec.)	pale green	2183 s, 2102 vs
III	$(Ph_3Sn)_2(TCNQ)$	ca. 200 (dec.)	blue	2222 mw, 2193 mw

Hexaphenyldistannane is inert to TCNE under the same conditions, but with TCNQ the complex $(Ph_3Sn)_2\cdot(TCNQ)$ (III) is formed. It seems likely that this latter compound is analogous to the ($\sigma\to\pi$) charge transfer compounds observed by West [1] and Sakurai [2], whilst the compounds I and II contain the radical anions $(TCNE)^{\overline{\bullet}}$ and $(TCNQ)^{\overline{\bullet}}$ respectively. Some corroboration for these formulations comes from the tin-119*m* Mössbauer spectral data. The spectrum for Compound III consists of a single sharp (Γ 0.84 mm/s) resonance at 1.46 mm/s (relative to $\delta(SnO_2) = 0$). In contrast, the spectra for I and II exhibit large quadrupole splittings (> 3.3 mm/s). This together with the observation of only a single Sn—C stretching mode in the infrared for the trimethyltin derivatives, is indicative of a trigonal bipyramidal arrangement at tin with alkyl groups occupying equatorial positions. Some details of compounds I—III are presented in Table 1.

Acknowledgements

We thank the S.R.C. for support.

References

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