Easy Access to a New Class of Anionic Cyano-bridged Di- and Tri-nuclear Organotin Adducts. Crystal Structure of $[N(PPh_3)_2][ClPh_3Sn(\mu\text{-}NC)Ag(CN)]$

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Cyanometallates $[N(PPh_3)_2][Ag(CN)_2]$ **1** and $[N(PPh_3)_2]_2[Pd(CN)_4]$ **2** reacted with $SnPh_3Cl$, producing anionic complexes characterized by IR and ^{119}Sn NMR spectroscopy, an X-ray structural analysis of the silver complex evidencing a Sn–NC–Ag bridging interaction; the crystal structure of **1** has also been determined for comparison.

Cyanide complexes are attracting increasing interest in organometallic chemistry owing to the ability of the cyanide ligand to bind different metal centres and to act as a charge-transfer mediator.[1] Furthermore, cyanometallate compounds of the type $M_x[M'(CN)_6]_y$ have been found to show molecular sieving properties[2] and, more recently, Fischer and co-workers[3] have shown that organometallic polymers of the type $[(R_3Sn)_3\text{-}M(CN)_6]_\infty$ are effective three-dimensional host systems, being able to act as efficient ion exchangers and receptors for organic and organometallic cations.

These organometallic polymers are generally obtained when di- or tri-organotin chlorides are treated with potassium hexacyanometallates. Nevertheless, the use of $[N(PPh_3)_2]^+$ instead of K^+, as counter cation for cyanometallate anions, permits variation of the reactivity of the latter species towards electrophilic compounds such as organotin halides. Indeed, by using $[N(PPh_3)_2]^+$, the unusual trinuclear dianion $[(ClPh_3Sn)_2\text{-}(\mu\text{-}NC)_2Fe(CN)_2(dmso)_2]^{2-}$ (dmso = dimethyl sulfoxide) has been obtained (and characterized by a single-crystal X-ray diffraction analysis),[4] instead of the polymeric material produced by the corresponding potassium hexacyanoferrate.[5]

This result stimulated us to test if similar reaction pathways could be extended to different $[N(PPh_3)_2]^+$ cyanometallates, such as $[N(PPh_3)_2][Ag(CN)_2]$ 1 and $[N(PPh_3)_2]_2$ $[Pd(CN)_4]$ 2.† A dichloromethane solution of 1 and $SnPh_3Cl$ gives, by treatment with diethyl ether, a white crystalline solid, identified as $[N(PPh_3)_2][ClPh_3Sn(\mu\text{-}NC)Ag(CN)]$ 3 by elemental analysis data. A bridging Sn–NC–Ag interaction in the solid state is suggested by the presence, in the IR spectrum, of two CN-stretching bands at 2131 and 2143 cm^{-1}, the second band being shifted slightly to higher wavenumber with respect to those found for 1. The same interaction should be present also in chloroform solution, as the ^{119}Sn NMR spectrum of 3 exhibits a single resonance at δ −82.1 ($SnMe_4$ as external reference), significantly shifted to higher field with respect to pure $SnPh_3Cl$ in the same solvent (δ −44.7), as a consequence of an increase in co-ordination number.[6]

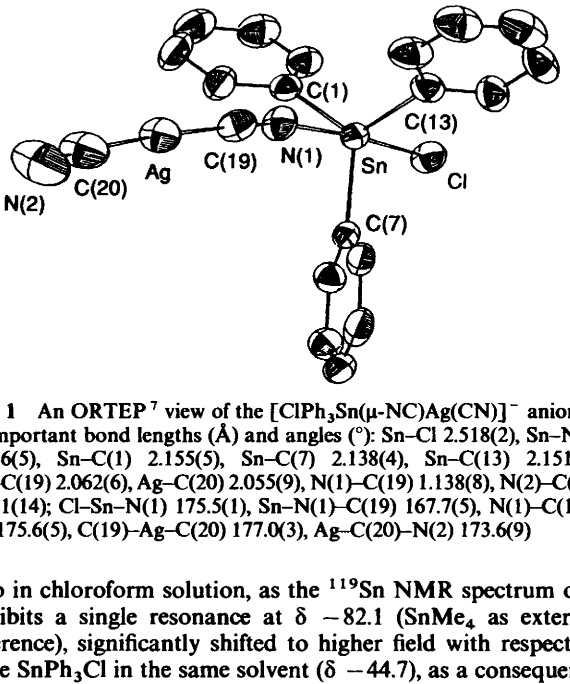

Fig. 1 An ORTEP[7] view of the $[ClPh_3Sn(\mu\text{-}NC)Ag(CN)]^-$ anion in 3; important bond lengths (Å) and angles (°): Sn–Cl 2.518(2), Sn–N(1) 2.436(5), Sn–C(1) 2.155(5), Sn–C(7) 2.138(4), Sn–C(13) 2.151(6), Ag–C(19) 2.062(6), Ag–C(20) 2.055(9), N(1)–C(19) 1.138(8), N(2)–C(20) 1.131(14); Cl–Sn–N(1) 175.5(1), Sn–N(1)–C(19) 167.7(5), N(1)–C(19)–Ag 175.6(5), C(19)–Ag–C(20) 177.0(3), Ag–C(20)–N(2) 173.6(9)

The bridging behaviour of one CN group was confirmed by an X-ray structural analysis carried out on 3.‡ Its structure is built up by discrete $[ClPh_3Sn(\mu\text{-}NC)Ag(CN)]^-$ anions and $[N(PPh_3)_2]^+$ cations. In the anion (shown in Fig. 1), the silver atom is linearly co-ordinated by two cyano groups with the Ag–C bond distances practically identical and apparently

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† Compounds 1 and 2 are prepared by adding warm aqueous solutions (30 cm^3) of $K[Ag(CN)_2]$ (2.3 g) and $K_2[Pd(CN)_4]$ (1.0 g) to aqueous solutions of $[N(PPh_3)_2]Cl$ (3.3 g) (dissolved in a minimum amount of warm water) in a 1:1 and 1:2 molar ratio, respectively. In both cases, white precipitates are obtained, which are filtered off, washed with warm water and dried *in vacuo* (90% yields). They are well soluble in acetone, tetrahydrofuran and light chlorinated solvents. IR (KBr): ν(CN) 2131 and 2138 cm^{-1} **1**; 2124 and 2130 cm^{-1} **2**.

‡ Crystal data for 3: $C_{56}H_{45}AgClN_3P_2Sn$, $M = 1083.95$, monoclinic, space group $P2_1$, $a = 9.522(5)$, $b = 18.286(9)$, $c = 14.076(7)$ Å, $\beta = 90.63(2)°$, $U = 2451(2)$ Å^3, $Z = 2$, $D_c = 1.47$ g cm^{-3}, $F(000) = 1092$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 10.65$ cm^{-1}. Intensity data collected using a Philips PW1100 diffractometer, graphite-monochromatized Mo-Kα radiation, ω–2θ scan technique, 5754 reflections measured to 2θ(max) 54°, 4945 observed with $I > 2\sigma(I)$; no crystal decay.

insensitive to the different nature (terminal or bridging) of the cyano group. Of particular interest are two weaker interactions between the silver atom and the two phenyl rings, one from the $SnPh_3Cl$ moiety at $x - 1, y, z$ [Ag $\cdots$ C(15) 3.510(7) Å] and the other from the $[N(PPh_3)_2]^+$ cation at $-x, y - \frac{1}{2}, 1 - z$ [Ag $\cdots$ C(34) 3.374(5) Å], which deform the silver environment towards distorted square planar.

The tin atom adopts a slightly distorted trigonal-bipyramidal co-ordination geometry, being bonded to three phenyl carbon atoms in the equatorial plane, and a chlorine atom and the nitrogen atom from the bridged cyano group in the axial positions. The whole assembly of the Cl–Sn–NC–Ag–CN system is almost linear, the bond angles in it ranging from 167.7 to 177.0°. It is interesting to note that the Sn–N bond distance is significantly longer [2.436(5) Å] than the corresponding one [2.340(7) Å] found in the ditin–iron trinuclear dianion.[4]

To our knowledge, this structure represents the second example of a compound containing silver and tin in the same complex unit, the first one being $[AgL(SnCl_3)]$ {L = 2,11-bis[(diphenylphosphino)methyl]benzo[*c*]phenanthrene},[8] where a chlorine atom acts as a bridge between the two metal centres. Moreover, so far as we know, only two examples of silver cyano-bridged compounds have been structurally characterized, namely the monomeric Δ-*cis*-$[Cr(NCAgCN)_2(en)_2]^+$ (en = ethane-1,2-diamine) cation[9] and the infinite positively charged chains of the $[Zn(NCAgCN)(en)_2]_n^{n+}$ type.[10]

The structure of **1** also exhibits ionic character, the building units being $[Ag(CN)_2]^-$ anions (Fig. 2), $[N(PPh_3)_2]^+$ cations and tetrahydrofuran (thf) molecules.* The structural parameters of the former agree well with two previous X-ray determinations of this anion.[10] In both **1** and **3**, the $[N(PPh_3)_2]^+$ cation shows no unusual features.

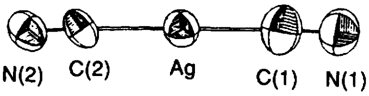

Fig. 2 An ORTEP[7] view of the $[Ag(CN)_2]^-$ anion in **1**, bond lengths (Å) and angles (°): Ag–C(1) 2.03(2), Ag–C(2) 2.05(2), C(1)–N(1) 1.16(3), C(2)–N(2) 1.11(3); C(1)–Ag–C(2) 176(1), Ag–C(1)–N(1) 176(2), Ag–C(2)–N(2) 178(2)

Finally, the palladium compound **2** reacts with $SnPh_3Cl$ in the same way as **1**, producing a white crystalline precipitate, identified as $[N(PPh_3)_2]_2[(ClPh_3Sn)_2(\mu\text{-}NC)_2Pd(CN)_2]$. Spectroscopic evidence supports the existence of Sn–NC co-ordinative interactions: IR (KBr), ν(CN) 2129 and 2145 cm^{-1}; ^{119}Sn NMR ($CHCl_3$), δ −173.5.

In conclusion, these preliminary results clearly indicate that a large lipophilic cation, such as $[N(PPh_3)_2]^+$, allows the facile synthesis of a new family of non-polymeric tin derivatives cyano-bridged to transition metals. In these compounds the electron-rich cyanometallate anion interacts with $SnPh_3Cl$ without causing the loss of the chloride ion.† Di- or tri-nuclear compounds can be obtained depending on the nature of the cyanometallate anion.

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* Crystal data for **1** (thf solvate): $C_{42}H_{38}AgN_3OP_2$, $M = 770.60$, monoclinic, space group $P2_1/c$, $a = 9.182(5)$, $b = 24.412(10)$, $c = 17.081(8)$ Å, $\beta = 101.31(3)°$, $U = 3754(3)$ Å^3, $Z = 4$, $D_c = 1.36$ g cm^{-3}, $F(000) = 1584$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 6.49$ cm^{-1}. Intensity data collected using a Siemens AED diffractometer, niobium-filtered Mo-Kα radiation, ω-2θ scan technique, 6650 reflections measured to 2θ(max.) 54° initially, successively reduced to 48° in view of the weak diffracting power of the crystal, 1659 observed with $I > 3.5\sigma(I)$; no crystal decay.

Data processed in both cases with the peak-profile analysis procedure and corrected for Lorentz, polarization and absorption effects. Both structures were solved by the heavy-atom technique and refined by full-matrix least-squares procedures. A weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$ was applied in the last stages of both refinements. Compound **3**: final $R = 0.0294$, $R' = 0.0428$, 723 parameters, max. Δρ 0.2 e Å^{-3}. Compound **1**: final $R = 0.0794$, $R' = 0.1157$, 165 parameters, max. Δρ 0.6 e Å^{-3}.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

† On the contrary, by reaction of $SnPh_3Cl$ with $K[Ag(CN)_2]$ in water–ethanol, a white precipitate is quickly obtained, insoluble in almost all common solvents; it exhibits only one CN-stretching band at 2159 cm^{-1} which suggests a bridging behaviour for all the CN groups. It has been recognized as $[(Ph_3Sn)Ag(CN)_2]$, probably containing polymeric –SnNCAgCN– chains.