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TRIHYDROCARBYLTIN COMPLEXES OF TRANSITION METAL CYANIDES

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Summary

Cationic single-bridged trinuclear cyano complexes are obtained by treating trihydrocarbyltin perchlorate $(SnR_3O_2ClO_2)$ (R = alkyl or aryl) with neutral transition metal monocyanides, whereas treatment with the corresponding neutral or anionic transition metal polycyanides gives neutral single-bridged polymeric cyano compounds. In every case the tin atoms are pentacoordinated with the three R groups in the equatorial and two CN groups (or, respectively one CN and one OClO₃ group) in the axial position of a trigonal bipyramid.

Introduction

The synthesis of covalent perchlorato derivatives from the corresponding halo complexes, according to eq. 1 and the subsequent substitution of the perchlorato

$$L_nMX + AgClO_4 \rightarrow AgX + L_nMOClO_3$$

group, (which has a low coordinating capacity) by neutral (eq. 2) or anionic ligands (eq. 3) has frequently been used by us [1] and by others [2] for the

$$L_n MOClO_3 + L' \rightarrow [L_n ML']ClO_4 \tag{()}$$

$$L_n MOClO_3 + M'X \rightarrow M'ClO_4 + L_n MX$$

preparation of neutral and anionic organometallic complexes of gold [1a-1c], nickel [2a-2c], palladium [1d-1g,2d], platinum [1h-1j] and rhodium [1k-11].

If reaction 1 is carried out in a non-donor solvent under anhydrous conditions the intermediate perchlorato complex can sometimes be isolated, but is frequently unstable. Even so, after removal of the precipitated silver halide, the filtrate can in every case be used for processes 2 and 3.

Mainly because of the solubility of L_nMX it is, however, sometimes necessary to work in another type of solvent. In these cases it seems appropriate to employ

(2)

(3)

(1)

acetone, which, though it displaces the perchlorato group giving a (sometimes isolable) cationic perchlorate (eq. 4), can afterwards readily be displaced by

$$L_n MX + AgClO_4 \xrightarrow{Me_2CO} AgX + [L_n M(Me_2CO)_x]ClO_4$$
(4)

reactions of type 2 or 3.

We consider below the reaction of solutions of perchloratotrialkyltin or perchloratotriaryltin compounds with several cyano complexes of transition metals. These behave as a ligand L' (eq. 2) since their cyano group still has a potentially N-donor atom which causes the displacement of the perchlorato group or the acetone. The process allows the preparation of polymeric (finite or infinite) complexes with the cyano group bridging the tin and the transition metal atoms.

Some of these results were the subject of a preliminary communication [3].

Results and discussion

The precursor solutions used in the present study were prepared by treating the organochlorocomplexes SnR_3Cl (R being Me, Bu or Ph) with benzene or acetone solutions of $AgClO_4$, and removal of the AgCl. As reported [4] for the methyl complex [$SnMe_3O_2ClO_2$]_x in the solid state the pentacoordinated tin atoms are bridged by the perchlorato ligands.



This bridging system is cleaved in methanol to give the pentacoordinated cationic perchlorate $[SnR_3S_2]ClO_4$ (S = solvent). Thus, whilst our benzene solutions are likely to contain $[Sn(O_2ClO_2)R_3]$, the acetone solutions are assumed to contain $[SnR_3(Me_2CO)_2]ClO_4$, but the reaction products with cyano-transition metal complexes are in each case the same.

(a) Reactions with monocyanides

$${}^{2} \operatorname{Pd}(CN)(C_{6}F_{5})(\operatorname{PPh}_{3})_{2} + \left[\operatorname{Sn}(O_{2}CIO_{2})R_{3}\right]$$

$$\begin{bmatrix} PPh_{3} & R & PPh_{3} \\ C_{6}F_{5} & Pd & CN & Sn & NC & Pd & C_{6}F_{5} \\ PPh_{3} & R & R & PPh_{3} \end{bmatrix} CIO_{4} \quad (5)$$

$$(I, R = Me; II, R = Bu; II, R = Bu; II, R = Ph)$$

The reaction (1/2) of benzene or acetone solutions of perchlorato trihydrocarbyltin Sn $(O_2ClO_2)R_3$ with cyanopentafluorophenylbis(triphenylphosphine)palladium(II) [Pd(CN)(C₆F₅)(PPh₃)₂] gives cationic trinuclear complexes (see eq. 5). The complexes I and III are precipitated instantaneously whatever the used molar ratio of the reagents used but the butyl complex (II) can only be obtained by use of a 2/1 mole ratio as in eq. 5. A 1/1 mole ratio leads to the

$$Pd(CN)(C_{6}F_{5})(PPh_{3})_{2} + \left[Sr_{1}(O_{2}ClO_{2})R_{3}\right] \longrightarrow O_{3}ClO \longrightarrow Sn \longrightarrow NC \longrightarrow Pd \longrightarrow C_{6}F_{5} \qquad (6)$$

$$R = PPh_{3}$$

$$(\square R = Bu)$$

precipitation of the neutral complex IV, (see eq. 6), which contains a monodentate $(C_{3\nu})$ perchlorato group (see below).

The tendency of tin to adopt a coordination number of 5 means that the reaction of $Sn(O_2ClO_2)R_3$ with di- or poly-cyano-transition metal complexes leads to polymeric end products. Thus the reaction with neutral polycyano complexes yields cationic polymers, whereas anionic polycyanides give neutral polymers.

(b) Reactions with di- and poly-cyanides

The reaction with *trans*-dicyanobis(triphenylphosphine)palladium(II), according to eq. 7 gives rise to the immediate precipitation of the cationic

$$\begin{bmatrix} Pd(CN)_{2}(PPh_{3})_{2} \end{bmatrix} \div \begin{bmatrix} Sn(O_{2}ClO_{2})Ph_{3} \end{bmatrix} \xrightarrow{Ph} \begin{bmatrix} Ph & PPh_{3} \\ & & \\ & & \\ & & \\ & & \\ Ph & Ph & PPh_{3} \end{bmatrix} \xrightarrow{X} (ClO_{4})_{x}$$
(7)

polynuclear complex V. The reactions with other cationic dicyano complexes, such as $(Bu_4N)[Ag(CN)_2]$ or $K[Au(CN)_2]$ (which are very little soluble in benzene require the use of acetone (Me₂CO = S) as reaction medium) also give neutral complexes (eq. 8).

$$Q[M(CN)_{2}] + [SnR_{3}S_{2}]ClO_{4} \rightarrow QClO_{4} + 2S + \begin{bmatrix} R \\ Sn - NC - M - CN \end{bmatrix}_{x}$$
(8)

(VI, M = Ag, $Q = Bu_4N$, R = Me; VII, M = Ag, $Q = Bu_4N$, R = Ph; VIII, M = Au, Q = K, R = Me; IX, M = Au, Q = K, R = Bu; X, M = Au, Q = K, R = Ph)

The complexes separate out upon mixing the two solutions. The simultaneously

precipitated QCIO₄ can be removed by washing with water. No reaction could be observed for M = Ag and R = Bu.

Complex V is decomposed by an acetone solution of NaBPh₄ finally giving trans-Pd(CN)₂(PPh₃)₂. Treatment with tetra- and hexa-cyanometallates gives immediate precipitation of the corresponding neutral polymers.

$$K_{2}[M(CN)_{4}] + 2[SnR_{3}S_{2}]ClO_{4} \rightarrow 2 KClO_{4} + 4 S + \{(R_{3}Sn)_{2}[(\mu - CN)_{4}]\}_{x}$$
(9)

)

(XI, M = Pd, R = Me;XII, M = Pd, R = Bu; XIII, M = Pd, R = Ph; XIV, M = Pt, R = Me; XV, M = Pt, R = Bu;XVI, M = Pt, R = Ph)

In the light of the square planar coordination of Pd or Pt, these polymers can be expected to have an infinite twodimensional structure (Fig. 1).

When $K_3[Fe(CN)_6]$ is used no reaction occurs for R = Me, whereas when R =Bu or Ph it gives neutral polymeric complexes (eq. 10), which are assumed to

 $K_{3}[Fe(CN)_{6}] + 3[SnR_{3}S_{2}]ClO_{4} \rightarrow 3 KClO_{4} + 6 S + \{[R_{3}Sn]_{3}[(\mu-CN)_{6}Fe]\}_{x}$ (10)

have a threedimensional structure.

(c) Solubility and conductivity

As expected for macromolecular substances, all the polymeric complexes (V—XVIII) are insoluble in water and organic solvents. The bi- and tri-nuclear complexes (I-IV) are soluble in chloroform, dichloromethane and nitromethane, and complexes II-IV are also soluble in acetone. All are insoluble in n-hexane



Fig. 1. Proposed structure of the $\{[R_3Sn]_2[(\mu-NC)_4M]\}_{r}$ complexes. (M = Pd or Pt; R = Me, Bu, Ph).

and benzene. The conductivities of the soluble complexes show [5] that they behave as 1/1 electrolytes, in accordance with the proposed formulae.

(d) IR spectra

The discussion above requires that the reaction products contain only bridging CN groups while the starting materials contain only terminal CN groups. In accordance with this, the $\nu(CN)$ stretching vibration of the resulting complexes is always shifted towards higher energy, and only a single band is observed [6]. Table 1 shows the values of $\Delta \nu (\Delta \nu = \nu(CN)_{\text{bridge}} - \nu(CN)_{\text{terminal}})$ for all the new complexes.

All the pentafluorophenyl derivatives exhibit absorption at ~1500vs, 1050s, 950vs and 800s cm⁻¹ due to the C₆F₅ ligand [7] along with those of the two mutually *trans*-PPh₃ groups [8] at 525s, 515s and 502s cm⁻¹ (complexes I–IV).

All the methyl derivatives show a strong absorption at 560—555 cm⁻¹ assignable to the $\nu_{as}(Sn-C)$ stretching mode, and only complex XIV also shows a very weak band at 505 cm⁻¹ assignable to $\nu_{asym}(Sn-C)$. This is in good agreement with the proposed trigonal bipyramidal structure, with the three methyl groups in equatorial position and the two cyano groups at axial sites. This agrees with the structure proposed for other trimethyl derivatives of SnR₃X, with X being a bridging ligand (X = F [9]; Cl, Br [10]; ClO₄ [4,11]; BF₄ [12], AsF₆, SbF₆ [13]; RCOO [14] or alkyl- and aryl-imidazole [15]).

The corresponding absorptions for the butyl derivatives located in the 650–600 cm⁻¹ region, which are always weak [16] are in our complexes masked by bands due to the PPh₃, ClO₄ or CN group. Our phenyl derivatives show two medium bands at 280–270 and 240–230 cm⁻¹, assignable to symmetric and assymetric ν (Sn–C) [17], showing that the Sn–C bonds are not coplanar.

Finally, all the ionic complexes (I, II, III and V) show absorptions at 1100s and 630m cm⁻¹ assignable, respectively, to v_3 or v_4 vibrations of the perchlorato group (T_d). In complex IV the bands expected at 1100 and 630 cm⁻¹ are split, and are located, respectively, at 1140 and 1040 cm⁻¹ and at 615 and 625 cm⁻¹, corresponding to the v_1 , v_4 and v_3 , v_5 vibrations of the OClO₃ group (C_{3v}). This complex shows another band (A_1) at 915 cm⁻¹ assignable to v(Cl-O), which would be IR active for C_{3v} symmetry, and this confirms the formulation proposed for this compound [18].

Experimental

C, H and N analyses were carried out with a Perkin—Elmer 240 microanalyzer. Melting points were measured on a Buchi apparatus (model Dr. Tottoli) and are uncorrected. Conductivities were determined in approximately $5 \times 10^{-4} M$ solutions with a Philips PW 9501/01 conductimeter. IR spectra were recorded (over the range 4000—200 cm⁻¹) on a Perkin—Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates.

 $Pd(CN)(C_6F_5)(PPh_3)_2$ was prepared as described elsewhere [19]. $Pd(CN)_2$ -(PPh_3)₂ was obtained by treating a solution of $PdI_2(PPh_3)_2$ (9.01 g, 10 mmol) in 2C0 ml of acetone with freshly prepared AgCN (2.60 g, 20 mmol) for 60 min at room temperature with exclusion of light. The AgI was filtered off and

I N on the transport on the transportex on the transport on the tra	Complex		Foun. (cal	cd.) %		A _M (ohm ⁻¹	μ(CN)	Δν 	M.p.
I [(Masjan]u-NC)g1Pu(GeFg(PPi3_j)g1S(O_4 64.76 3.76 1.46 1.16 11.7 4.7 4.7 1.46 1.16 2.177 4.7 1.46 1.13 12.6^{10} 2.177 4.7 1.46 1.14^{10} 11.2^{10} 2166 26 106 106 106 106 106 11.47 11.2^{10} 2166 28 106 1166 1166 1166 1066 <			O,	Н	Z	(, 10H - HD	complex (cm ⁻¹)	(- III)	3
II (Busahle-NC)_[PB(GeF3)(PFb3)J_1)C(0.4 (55.83) (3.34) (1.41) 112 215 25 119 (dac) III ([Ph3shle-NC)_[PB(GeF3)(PFb3)J_1)C(0.4 (55.83) (3.00) (1.36) 22.9° 2155 25 119 (dac) V ([Ph3shle-NC)_[PB(GeF3)(PFb3)J_1)C(0.4), (55.83) (3.00) (1.36) 22.9° 2155 25 179 (dac) V ([Ph3shle-NC)[PB(GeF3)(PFb3)J_1) (54.43) (1.13) 22.9° 2156 26 179 (dac) VI ([Ph3shle-NC)[Ad(Perb3)J_1) (54.43) (1.13) 2100 2156 26 179 (dac) VI ([Ph3shle-NC)[Ad(U-CN)]_x (54.43) (1.13) 2160 20 100 2156 26 109 (dac) VI ([Ph3shle-NC)[Ad(U-CN)]_x (1.41) 2.60 266 26 216 26 266 266 266 266 266 266 266 266 266 266 266 266 266 266 266 266 <td>I</td> <td>{[Me₃Sn](µ-NC)₂[Pd(C₆F₅)(PPh₃)₂]₂]ClO₄</td> <td>64.75</td> <td>3.76</td> <td>1.45</td> <td>115 b</td> <td>2177</td> <td>47</td> <td>164(dec.)</td>	I	{[Me ₃ Sn](µ-NC) ₂ [Pd(C ₆ F ₅)(PPh ₃) ₂] ₂]ClO ₄	64.75	3.76	1.45	115 b	2177	47	164(dec.)
II (Busjanilu-NC) ₂ [Pu(GF5)(TPh3)2] (04, 77.73) 5.30 1.31 1.20° 2156 25 195 (dec) III (Prisaniu-NC) ₂ [Pu(GF5)(TPh3)2] (Co1, 95.83) 3.30 1.37 3.41 1.13 21.55 25 195 (dec) V (Prisaniu-NC) ₂ [Pu(GF5)(TPh3)2] (Co1, 13 54.43 (1.31) 62.9 21.55 25 193 (dac) V (Prisaniu-NC)[Pu(GF5)(TPh3)2] (Co1, 13 54.43 (1.31) (1.31) 21.60 2 25 193 (dac) VI (Prisaniu-NC)[Au(UCN)] _x (71.1) (7.31) (1.31) 21.60 2 21.60 2 28			(55.93)	(3.64)	(1.47)	-			
III ([Paysin(u-NC)][Pa(Ge ² /s)(PPh3)1] (57.77) (4.30) (1.37) (2.30) (1.37) (2.30) (1.37) (2.30) (2.31) <	II	{[Bu3Sn](µ-NC)2[Pd(C6F5)(PPh3)2]2}CIO4	57.62	4,31	1,41	112 ⁰	2166	26	195 (dec.)
III (Preparitu-NO), Pa(Ge ² S) (Prepariti), PCO 55.60 1.35 62.9 ⁴ 215.6 25 176 (dau) V (Pregenic-NO), Pa(Ge ² S) (Prepariti), PCO 65.60 1.35 62.90 215.6 25.6 178 (dau) V (Pregenic-NO), Pa(Ge ² S) (Prepariti), PCO 65.44 1.13 1.13 1.16 216.0 20 203 66.0 VI (Pregenic-NO) Pa(Perbay) (PreON) 17.33 1.4.33 (.1.16) 2.4.4 2.16 2.16 2.03 1.03 0.040 VI (Pregenic-NO) Pa(Perbay) (PreON) 17.13 2.86 6.4.9 2.16 2.4.4 2.16 2.4.4 2.1.6 <td></td> <td></td> <td>(57.77)</td> <td>(4.30)</td> <td>(1.37)</td> <td></td> <td></td> <td></td> <td></td>			(57.77)	(4.30)	(1.37)				
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	III	{[Ph ₃ Sn](µ-NC) ₂ [Pd(C ₆ F ₅)(PPh ₃) ₂] ₂ } ₂ C!O ₄	58,69	3,60	1.35	62.9 ^đ	2155	26	1.79 (dec.)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$			(69.55)	(3.60)	(1.34)	4			-
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	IV	[Bu3(03Cl0)Sn](#-NC)[Pd(C6F5)(PPh3)2]	3772	1017	1.18	130 0	21.65	26	203 (doc.)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$:		(64.44)	(4.73)	(1.16)	c		4	
VI [me_ssniu_WC)[Ag](ω -CN)]_x (79.3) (70.3)	>	{ Ph3Sh](µ-NC) [Pd(PPh3)2](µ-CN)] _X (ClO4) _X	59,11 /50,201	4.04	2.69	L.	2150	30	192 (dıc.)
VII (Fh35n](ω -NC)[As](ω -CN)]x (18.6b) (2.80) (8.6b) (2.90) (3.6b) (2.90) (3.6b) (2.9b) (3.7b)	IV	[[Messulti-NC)[Aelti-CN]].	17 91	2 60	(Z.4 1) R 5 R		9188	96	963
VII $[[Ph_35n](\omega \cdot VC)[Ag](\omega \cdot CV)]_x$ $\overline{4}7.02$ $\overline{2}92$ $\overline{6}.13$ 2160 20 >300 VIII $[[Me_35n](\omega \cdot VC)[Au](\omega \cdot CN)]_x$ 14.711 $(\overline{2}.961$ $(\overline{6}.49)$ 2171 26 202 201 X $[[Me_35n](\omega \cdot VC)[Au](\omega \cdot CN)]_x$ 14.516 (2.20) $(\overline{6}.77)$ 2170 26 200 X $[[Me_35n]_2(\omega \cdot VC)_4n](\omega \cdot CN)]_x$ 31.193 5.06 5.200 2170 26 200 XI $[[Me_35n]_2(\omega \cdot VC)_4n](\omega \cdot CN)_r^{1}$ 31.193 5.06 5.200 2170 216 293 206 XII $[[Me_35n]_2(\omega \cdot VC)_r^{1}M]_1^{1}$ 22.36 3.275 (10.24) 2170 216 293 <td< td=""><td></td><td></td><td>(18.66)</td><td>(2.80)</td><td>(8.65)</td><td></td><td></td><td>2</td><td></td></td<>			(18.66)	(2.80)	(8.65)			2	
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X ([Ph3sh]g(μ -NC)[Au](μ -CN)] _x 40.56 2.65 4.82 2.170 25 220 (dec.) XI [[Me35h]g((μ -NC)] _q Pd1]] _x 2.3.56 (10.24) 2.165 2.9 2.43 (dec.) XII [[Me35h]g((μ -NC)] _q Pd1]] _x 2.2.36 3.2.75 (10.41) 2.165 2.9 2.84 (dec.) XIII [[Ph35h]g((μ -NC)] _q Pd1]] _x 2.2.36 3.2.76 (3.6.9) (7.09) 2.165 2.9 2.84 (dec.) XIII [[Ph35h]g((μ -NC)] _q Pd1]] _x 2.2.36 3.2.76 2.86 5.77 2.165 2.9 2.87 (dec.) XIV [[Me35h]_g((μ -NC)]_qP1]] _x 3.3.25 (1.0.9) (7.09) 2.166 2.9 2.90 (dec.) XV [[Me35h]_g((μ -NC)]_qP1]] _x 19.74 2.916 9.25 2166 27 290 XVI [[Ph35h]_g((μ -NC)]_qP1]] _x 3.8.78 6.2.19 (3.8.94) 2166 27 290 XVI [[Ph35h]_g((μ -NC)] _q P1]] _x 3.8.78 6.2.19 (3.6.19) 21.40 <td< td=""><td></td><td></td><td>(31.19)</td><td>(0.06)</td><td>(6.20)</td><td></td><td></td><td></td><td></td></td<>			(31.19)	(0.06)	(6.20)				
XI [[Me_35n]_2[(μ -NC)_4Pd]]_x (40.10) (2.53) (4.68) 216 29 243 (dec.) XII [[Jbu_35n]_2[(μ -NC)_4Pd]]_x 22.36 3.25 10.24 2165 29 243 (dec.) XII [[Jbu_35n]_2[(μ -NC)_4Pd]]_x (22.32) (3.37) (10.41) 2165 29 243 (dec.) XII [[Ph_35n]_2[(μ -NC)_4Pd]]_x (22.32) (3.32) (6.16) (7.09) 2165 29 240 (dec.) XIV [[Ph_35n]_2[(μ -NC)_4Pt]]_x (22.71) (3.32) (6.15) (7.09) 2165 32 280 (dec.) XV [[Pu_35n]_2[(μ -NC)_4Pt]]_x 19.74 2.98 9.25 (6.16) 2165 32 280 (dec.) XVI [[Pu_35n]_2[(μ -NC)_4Pt]]_x 18.74 2.98 9.25 (dec.) 2166 27 280 (dec.) XVI [[Pu_35n]_2[(μ -NC)_4Pt]]_x 18.74 2.98 9.25 (dec.) 2166 27 280 (dec.) XVII [[Pu_35n]_3[(μ -NC)_6Pt]]_x 48.62 3.	×	{[bh3sn](4-NC)[Au](4-CN)}	40.59	2,65	4.82		2170	26	220 (dee.)
XI {[Me_3Sn]_2[(μ -NC)_APd]]_x 22.36 3.25 10.24 2.9 248 (dec.) XII {[Pu_3Sn]_2[(μ -NC)_APd]]_x 22.32 (3.27) (10.41) 2165 29 287 (dec.) XII {[Pu_3Sn]_2[(μ -NC)_APd]]_x 22.85 (5.77 2.66) (3.89) (7.09) 2165 29 287 (dec.) XIV {[Me_3Sn]_2[(μ -NC)_APt]]_x 2.86 (5.77 2.66) (5.15) 2165 29 210 (dec.) XV {[Bu_3Sn]_2[(μ -NC)_APt]]_x 2.89 (6.32) (6.16) 2.77 2.165 29 210 (dec.) XV {[Bu_3Sn]_2[(μ -NC)_APt]]_x 2.88 (5.77 2.98 2.56) (6.15) 2.90 216 2.9 200 (dec.) XV {[Bu_3Sn]_2[(μ -NC)_APt]]_x 2.89 (6.29) (6.39) (6.37) 2165 29 210 (dec.) XVI {[Ph_3Sn]_2[(μ -NC)_APt]]_x 48.62 3.21 4.76 2.90 216 2.7 500 (dec.) XVI {[Ph_3Sn]_2[(μ -NC)_6Pt]]_x 48.62 3.21 4.76 2.80 (dec.) 2.160 27 500 (dec.) XVII {[Ph_3Sn]_3[(μ -NC)_6Ft]]_x 7.7 2.66 (dec.) 2.7 1.7 (dec.) 2.160 2.7 2.160 2.7 2.160 2.7 2.100 2.1 2.100 2.7 2.100 2.1 2.100 2.7 2.100 2.1 2.100 2.1 2.100 2.7 2.100 2.1 2.100 2.1 2.100 2.1 2.100 2.1 2.100 2.1 2.100 2.1 2.100 2.1 2.1 2.1 0.2 2.1 1.2 (dec.) 2.1 2.1 0.2 2.1 1.2 (dec.) 2.1 1.7 2.1 0.2 2.1 1.2 (dec.) 2		, - , -	(40.10)	(2.62)	(4.68)				٠
XII $[IBu_3Sn]_2[(\mu-NC)_4Pd]]_x$ (22.32) (3.27) (10.41) 2165 29 287 (dec.) XIII $[IPa_3Sn]_2[(\mu-NC)_4Pd]]_x$ (42.54) (6.89) (7.09) 5.77 (20) 2165 29 210 (dec.) XIV $[Im_3Sn]_2[(\mu-NC)_4Pt]]_x$ (42.54) (6.89) (7.09) 2.76 2.9 210 (dec.) XIV $[Im_3Sn]_2[(\mu-NC)_4Pt]]_x$ (5.77) (3.32) (6.15) (7.79) 2165 32 >800 XVI $[IPa_3Sn]_2[(\mu-NC)_4Pt]]_x$ (38.26) (6.19) (8.94) 2.165 32 >800 XVI $[IPa_3Sn]_2[(\mu-NC)_4Pt]]_x$ (38.25) (6.19) (6.37) 2.165 27 >800 XVII $[IPa_3Sn]_2[(\mu-NC)_6Pt]]_x$ (38.25) (6.19) (6.37) 2.160 27 >800 XVII $[IPa_3Sn]_3[(\mu-NC)_6Ft]]_x$ (48.08) (3.09) (5.61) (7.77) 2.160 27 >800 XVIII $[IPa_3Sn]_3[(\mu-NC)_6Ft]]_x$ (48.08) (3.09) (5.61) (7.77) 2.160 27 >800 XVIII $[IPa_3Sn]_3[(\mu-NC)_6Ft]]_x$ (6.646 3.59 7.16 2.163 (6.60) 2.140 22 163 (40c.)	XI	{[Me3Sn]2[(µ-NC)4Pd]] _x	22.36	3.25	10.24		2165	29	243 (dec.)
XII $([Bu_3Sn]_2[(\mu \cdot NC)_q Pd])_x$ (42.64) (6.89) (7.09) 2166 29 287 (dec.) XII $[[Ph_3Sn]_2[(\mu \cdot NC)_q Pd]]_x$ (42.64) (6.89) (7.09) (7.09) 2165 29 210 (dec.) XIV $[[Ma_3Sn]_2[(\mu \cdot NC)_q Pt]]_x$ (52.77) (3.32) (6.15) 2.16 2.9 210 (dec.) XV $[[Bu_3Sn]_2[(\mu \cdot NC)_q Pt]]_x$ (19.26) (2.89) (8.94) 2.165 21 200 27 200 XVI $[[Ph_3Sn]_2[(\mu \cdot NC)_q Pt]]_x$ (19.26) (2.19) (6.37) 2160 27 200 XVI $[[Ph_3Sn]_2[(\mu \cdot NC)_q Pt]]_x$ (38.25) (6.19) (6.37) 2160 27 200 XVI $[[Ph_3Sn]_2[(\mu \cdot NC)_q Pt]]_x$ (38.25) (6.19) (6.37) 2160 27 200 XVII $[[Ph_3Sn]_3[(\mu \cdot NC)_6 Pt]]_x$ (48.62 3.21 4.76 2.89 (6.61) 2140 27 200 XVII $[[Ph_3Sn]_3[(\mu \cdot NC)_6 Fe]]_x$ (46.22) (7.75) (7.77) 2140 22 183 (dec.) XVIII $[[Ph_3Sn]_3[(\mu \cdot NC)_6 Fe]]_x$ (66.0) 2140 22 163 (dec.)			(22.32)	(3.27)	(10.41)				
XIII $\left[[Ph_3Sn]_2[(\mu-NC)_4Pd] \right]_x$ (42.64) (6.89) (7.09) XIV $\left[[Ma_3Sn]_2[(\mu-NC)_4Pt] \right]_x$ (52.75 2.85 6.77 (3.32) (6.15) XV $\left[[Ma_3Sn]_2[(\mu-NC)_4Pt] \right]_x$ (52.77) (3.32) (6.15) XV $\left[[Ph_3Sn]_2[(\mu-NC)_4Pt] \right]_x$ (19.26) (2.89) (8.94) XVI $\left[[Ph_3Sn]_2[(\mu-NC)_4Pt] \right]_x$ (19.26) (2.89) (6.37) XVI $\left[[Ph_3Sn]_2[(\mu-NC)_6Pt] \right]_x$ (38.25) (6.19) (6.37) XVII $\left[[Pu_3Sn]_3[(\mu-NC)_6Ft] \right]_x$ (38.25) (6.19) (6.37) XVII $\left[[Ph_3Sn]_3[(\mu-NC)_6Ft] \right]_x$ (38.25) (7.19) (6.37) XVII $\left[[Ph_3Sn]_3[(\mu-NC)_6Ft] \right]_x$ (38.25) (7.17) XVII $\left[[Ph_3Sn]_3[(\mu-NC)_6Ft] \right]_x$ (38.26) (7.77) (6.64) 3.59 7.16 (6.64) (7.77) 2.16 (6.64) 2.10 22 163 (6.64) (7.77) (7.77) 2.16 (6.64) 2.10 22 163 (6.64) (7.77) (7.77) 2.16 (6.64) 22 163 (6.64) 2.16 (6.64) 2.16 (6.64) 2.16 (6.66) (7.77) 2.16 (6.64) 2.16 (6.66) (7.77) 2.16 (6.66) (7.77) 2.16 (6.66) (7.77) 2.16 (6.66) (7.77) 2.16 (6.66) (7.77) (7.77) 2.16 (6.66) (7.77) (7.77) (7.16 (7.16) (7.77) (7.16 (7.16) (7.77) (7.16 (7.16) (7.17) (7.16 (7.16) (7.16) (7.17) (7.16 (7.16) (7.16) (7.16) (7.17) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.17) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (7.16) (7.16) (7.16) (7.16) (7.16 (7.16) (ЛХII	{[Bu ₃ Sn] ₂ [(µ-NC) ₄ Pd]} _x	42.30	6.69	6,96		2165	20	287 (dec.)
XIII {[Ph3Sn]2[(μ -NC)_{q}Pd]] _x 52.75 2.85 5.77 2.86 5.77 2165 29 210 (dec.) XIV {[Me3Sn]2[(μ -NC)_{q}Pt]] _x (52.77) (3.32) (6.15) 32 2165 32 2800 XV {[Bu3Sn]2[(μ -NC)_{q}Pt]] _x 2.89 (8.94) 2.98 9.25 (6.19) (8.94) 2160 27 2800 XVI {[Ph3Sn]2[(μ -NC)_{q}Pt]] _x (19.26) (2.89) (8.94) (8.94) 2160 27 2800 XVI {[Ph3Sn]2[(μ -NC)_{q}Pt]] _x (3.8.25) (6.19) (6.37) (3.03) (6.10) (6.37) 2160 27 2900 XVII {[Ph3Sn]3[(μ -NC)_{6}Po]] _x (48.08) (3.03) (5.61) (7.71 2160 27 2900 XVII {[Ph3Sn]3[(μ -NC)_{6}Po]] _x (46.22) (7.755) (7.77) 7.78 2146 28 182 (dec.) XVII {[Ph3Sn]3[(μ -NC)_{6}Po]] _x (46.22) (7.75b (7.77) 2160 22 163 (dec.) XVII {[Ph3Sn]3[(μ -NC)_{6}Po]] _x (46.22) (7.75b (7.77) 216 28 182 (dec.)		, -	(42.64)	(6,89)	(40,7)				
XIV $\left[[Me_3Sn]_2[(\mu \cdot NC)_q Pt] \right]_X$ $\left[(B_2.77) \left(52.77 \right) \left(5.32 \right) \left(6.15 \right) 2165 32 > 300$ XV $\left[[Bu_3Sn]_2[(\mu \cdot NC)_q Pt] \right]_X$ $\left[19.74 2.98 9.25 \left(5.94 \right) 2160 27 > 300$ XVI $\left[[Ph_3Sn]_2[(\mu \cdot NC)_q Pt] \right]_X$ $\left[38.78 6.27 6.05 \left(5.19 \right) \left(6.37 \right) 3.73 \right] 2160 27 > 300$ XVII $\left[[Bu_3Sn]_3[(\mu \cdot NC)_6 Po] \right]_X$ $\left[48.68 3.21 4.76 \left(5.61 \right) 2.160 27 > 300 2.7 \right] 3.03 \left(5.61 \right) 3.03 \left(5.61 \right) 2.160 27 > 300 2.7 \right] 3.03 \left(5.61 \right) 2.160 2.7 \left(3.00 \right) 2.7 \right] 3.00 2.7 \left(3.03 \right) \left(5.61 \right) 2.7 \left(7.73 \right) 2.146 2.8 182 \left(4ec. \right) 3.03 \left(5.61 \right) 2.7 \left(7.77 \right) 2.146 2.8 182 \left(4ec. \right) 3.59 \left(7.77 \right) 2.16 2.140 2.2 163 \left(4ec. \right) 3.59 \left(7.16 \right) \left(5.61 \right) 2.140 2.2 163 \left(4ec. \right) 3.59 \left(5.61 \right) \left(5.66 \right) \left(5.66 \right) 3.59 \left(7.16 \right) \left(5.66 \right) 2.140 2.2 163 \left(4ec. \right) 3.59 \left(5.66 \right) \left(5.$	XIII	[[Ph ₃ Sn]2[(µ·NC)4Pd]] _x	52.75	2.85	6.77		2165	29	210 (dec.)
XIV [[Me ₃ Sh] ₂ [(μ -NC) ₄ Pt]] _x 19.74 2.98 9.25 2165 32 >800 XV [[Bu ₃ Sh] ₂ [(μ -NC) ₄ Pt]] _x (19.26) (2.89) (8.94) 2160 27 >800 XVI [[Ph ₃ Sh] ₂ [(μ -NC) ₄ Pt]] _x (3.8.25) (6.19) (6.37) (3.37) XVII [[Ph ₃ Sh] ₂ [(μ -NC) ₆ Pe]] _x (3.02) (6.19) (6.19) (6.37) (3.03) (6.61) 2160 27 >800 XVII [[Bu ₃ Sh] ₃ [(μ -NC) ₆ Pe]] _x (48.08) (3.03) (5.61) (4.76 2160 27 >800 XVII [[Ph ₃ Sh] ₃ [(μ -NC) ₆ Pe]] _x (46.22) (7.55) (7.71) 2146 28 182 (dec.) XVIII [[Ph ₃ Sh] ₃](μ -NC) ₆ Pe]] _x (46.22) (7.55) (7.77 716 2140 22 163 (dec.) XVIII [[Ph ₃ Sh] ₃](μ -NC) ₆ Pe]] _x (6.71) (3.59) (6.66)			(52.77)	(3.32)	(6.15)				
XV $\left[[Bu_3Sn]_2[(\mu \cdot NC)_4 Pt] \right]_x$ (19,26) (1,289) (1,944) XVI $\left[[Ph_3Sn]_2[(\mu \cdot NC)_4 Pt] \right]_x$ (38,25) (1,9) (1,9) (1,37) XVII $\left[[Bu_3Sn]_3[(\mu \cdot NC)_6 Po] \right]_x$ (38,25) (1,9) (1,9) (1,17) XVII $\left[[Bu_3Sn]_3[(\mu \cdot NC)_6 Po] \right]_x$ (48,08) (3.03) (1,61) XVIII $\left[[Ph_3Sn]_3[(\mu \cdot NC)_6 Po] \right]_x$ (46,22) (7,55) (7,77) XVIII $\left[[Ph_3Sn]_3[(\mu \cdot NC)_6 Po] \right]_x$ (36,0) (3.59) (1,77) (6,64) (1,77) (1,69) (2,140) 22 163 (46c.) (6,64) (1,77) (1,69) (2,140) 22 163 (46c.)	XIX	[[M035n]2[(µ-NC)APt]] _X	19.74	2.98	9,26		2165	32	>800
XV [[Bu ₃ Sh]2[(μ -NC) ₄ Pt]] _X 38.78 6.27 6.05 21 2160 27 >300 XVI [[Ph ₃ Sh]2[(μ -NC) ₄ Pt]] _X (38.25) (6.19) (6.37) (3.37) XVII [[Bu ₃ Sh]3[(μ -NC) ₆ Po]] _X (3.03) (5.61) (3.03) (5.61) XVII [[Bu ₃ Sh]3[(μ -NC) ₆ Po]] _X (46.22) (7.55) (7.71) (7.71 2146 28 182 (dec.) XVIII [[Ph ₃ Sh]3[(μ -NC) ₆ Po]] _X (46.22) (7.55) (7.77) 2140 22 163 (dec.) (66.46 3.59 7.16 2140 22 163 (dec.)			(19.26)	(2.89) 2.55	(8,94)			1	
XVI $\left[[Ph_3Sn]_2[(\mu-NC)_4Pt] \right]_x$ (38.25) (6.19) (6.37) (3.03) (5.61) 2160 27 >300 XVII $\left[[Bu_3Sn]_3[(\mu-NC)_6Fo] \right]_x$ (48.08) (3.03) (5.61) 2146 28 182 (dec.) (46.22) (7.55) (7.71) 2146 28 182 (dec.) XVIII $\left[[Ph_3Sn]_3[(\mu-NC)_6Fo] \right]_x$ (67.11) (3.59) (7.66) (7.77) 2140 22 163 (dec.)	XV	[[Bu3Sn]2[(µ-NC)4Pt]] _X	38.78	6.27	6.05		2160	21	>300
XVI {[[Ph ₃ Sn] ₂ [(μ-NC) ₄ Pt]] _x 21.0 27 >300 XVII {[[Bu ₃ Sn] ₃ [(μ-NC) ₆ Fo]] _x (48.08) (3.03) (5.61) XVII {[[Bu ₃ Sn] ₃ [(μ-NC) ₆ Fo]] _x (46.01) 7.07 7.78 XVIII {[[Ph ₃ Sn] ₃](μ-NC) ₆ Fo]] _x (46.22) (7.55) (7.77) XVIII {[[Ph ₃ Sn] ₃](μ-NC) ₆ Fo]] _x (46.22) (7.55) (7.77) (46.22) (7.55) (7.77) 2140 22 163 (dec.) (7.16 2140 22 163 (dec.) (67.11) (3.59) (6.66)			(38.25)	(6.19)	(6.37)				
XVII {[Bu ₃ Sn] ₃ [(μ·NC) ₆ Fo]} _X (48.08) (3.03) (5.61) 45.61 7.07 7.78 2146 28 182 (dec.) XVIII {[Ph ₃ Sn] ₃](μ·NC) ₆ Fo] _X (6.Fo] (4.52) (7.55) (7.77) XVIII {[Ph ₃ Sn] ₃](μ·NC) ₆ Fo] _X (7.70 21 163 (dec.) (6.7.11) (3.59) (6.66)	XVI	[[Ph ₃ Sn]2[(µ-NC) ₄ Pt]] _X	48.62	3.21	4.76		2160	21	>300
XVII {{Bu ₃ Sn}a{(u-NC) ₆ ^{Fo}]} _x 45.61 7.07 7.78 2146 28 182 (dec.) (46.22) (7.55) (7.77) 2146 28 182 (dec.) XVIII {{Ph ₃ Sn}a{(u-NC) ₆ ^{Fe}]} _x 66.46 3.59 7.16 2140 22 163 (dec.) (67.11) (3.59) (8.66)		,	(48.08)	(3.03)	(2,61)				
XVIII {[Pʰ͡ ₃ Sn] ₃](ພ·NC) ₆ Fe]} _# (46.22) (7.55) (7.77) 56.46 3.59 7.18 2140 22 163 (dec.) (57.11) (3.59) (8.68)	плх	{[Bu ₃ Sn] ₃ [(µ-NC) ₆ Fo] } _X	45.61	7.07	7.78		2146	28	182 (dec.)
XVIII {[[Ph ₃ Sn] ₃](µ-NC) ₆ Fe]} _x 56.46 3.59 7.16 21 40 22 163 (dec.) (57.11) (3.59) (8.68)			(46.22)	(1.55)	(7.7.)				
(67.11) (3.59) (8.68)	XVIII	{[Ph ₃ Sn] ₃ [(µ-NC) ₆ Fe]} _X	56.46	3.59	7,16		2140	22	163 (dec.)
			(67.11)	(3.59)	(8,66)				

^a In nitromethane. ^b In acctone. ^c Insoluble.

TABLE 1 ANALYTICAL AND OTHER DATA FOR POLYNUCLEAR COMPLEXES

.

364

the filtrate evaporated to dryness. The residue was recrystallized from dichloromethane/ethanol.

K[Au(CN)₂], (BuN₄)[Ag(CN)₂], K₂[Pd(CN)₄] and K₂[Pt(CN)₄] were prepared by standard procedures [20,21]. K₃[Fe(CN)₆] was acquired from commercial sources.

(i) Preparation of the organotin perchlorate complexes $[Sn(O_2ClO_2)R_3]$ (R = Me, Bu, Ph)

Depending on their subsequent use these complexes were prepared either in benzene or acetone by treating stoichiometric amounts of the organotin complex SnR_3Cl with $AgClO_4$ for 30 min at room temperature. After removal of the AgCl the filtrate was used for further reactions without additional treatment.

(ii) $\{[R_3Sn](\mu-CN)_2[Pd(C_6F_5)(PPh_3)_2]_2\}ClO_4$ (I, R = Me; II, R = Bu, III, R = Ph)

Addition of $Sn(O_2ClO_2)R_3$ (0.25 mmol) in 40 ml of benzene to a stirred solution of $Pd(CN)(C_6F_5)(PPh_3)_2$ (0.4120 g, 0.5 mmol) in 40 ml of benzene immediately gave a white microcrystalline precipitate which was filtered off and repeatedly washed with hexane (yields: Complex I 84%, complex II 75%, complex III (61%).

(iii) { $[Bu_3(O_3ClO)Sn](\mu-NC)[Pd(C_6F_5)(PPh_3)_2]$ } (IV)

Complex IV was similarly prepared but using a different molar ratio: Pd(CN)- $(C_6F_5)(PPh_3)_2$ (0.4120 g, 0.5 mmol) in 20 ml of benzene and $Sn(O_2ClO_2)Bu_3$ (0.5 mmol) in 40 ml of benzene (84% yield).

(iv) { $[Ph_3Sn](\mu-CN)[Pd(PPh_3)_2](\mu-CN)]_x(ClO_4)_x$ (V)

To a solution of $Sn(O_2ClO_2)Ph_3$ (0.5 mmol) in 25 ml of benzene was added $Pd(CN)_2(PPh_3)_2$ (0.3415 g, 0.5 mmol) in 40 ml of dichloromethane. The microcrystalline precipitate, which was difficult to filter off, was separated by centrifugation and washed with hexane (70% yield).

(v) $\{[R_3Sn](\mu-NC)[M(\mu-CN)]\}_x$ (VI, M = Ag, R = Me; VII, M = Ag, R = Ph; VIII, M = Au, R = Me; IX, M = Au, R = Bu; X, M = Au, R = Ph)

To a solution of $Q[M(CN)_2]$ (M = Ag, Q = Bu₄N; M = Au, Q = K) (1 mmol) in 25 ml of acetone was added an equimolecular solution of $Sn(O_2ClO_2)E_3$ in 25 ml of acetone. The immediately precipitated white (or in the case of VIII yellowish) solid was filtered off and repeatedly washed with water/acetone (yields: complex VI, 63%; VII, 76%; VIII, 66%; IX, 64%; X, 81%).

(vi) $\{[R_3Sn]_2[(\mu-NC)_4]\}_x$ (XI, M = Pd, R = Me; XII, M = Pd, R = Bu; XIII, M = Pd, R = Ph; XIV, M = Pt, R = Me; XV, M = Pt, R = Bu; XVI, M = Pt, R = Ph)

To a solution of $K_2[M(CN)_4]$ (1 mmol) in 10 ml of H_2O and 15 ml of acetone was added a solution of $Sn(O_2ClO_2)R_3$ (2 mmol) in acetone (1/2 mole ratio). Stirring was continued for 30–60 min. The white precipitate was filtered off and washed with benzene or acetone and then with hexane (yields: complex XI, 81%; XII, 88%; XIII, 85%; XIV, 91%; XV, 81%; XVI, 93%). (vii) $\{[R_3Sn]_3[(\mu-NC)_6Fe]\}_x$ (XVII, R = Bu; XVIII, R = Ph)

The reaction was carried out as before by treating 1 mmol of the iron complex with 3 mmol of the organotin perchlorato complex. The resulting compounds were washed with acetone (yields; XVII, 95%; XVIII, 96%).

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