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Single-bridged Pseudohalide Complexes

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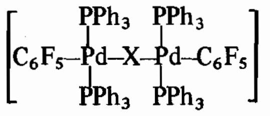
The very poor coordination capacity of the perchlorato ligand, which determines its facile substitution by other groups, makes perchlorato complexes very useful precursors for the synthesis of even fairly unstable complexes [1–7].

In the present paper we report the results obtained on studying reactions in which the perchlorato group is displaced by bidentate ligands which, by one of their donor atoms, are already attached to another metal atom; their free donor atom reacts with transition or post-transition perchlorato complexes, such as $[Pd(OClO_3)(C_6F_5)(PPh_3)_2]$ or $[Sn(O_2ClO_2)(C_6H_5)_3]_x$, to give cationic polynuclear homo- or heteroatomic complexes.

Thus, if equimolar mixtures of benzene solutions of $PdX(C_6F_5)(PPh_3)_2$ (X = CN or SCN) and $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ are stirred for several hours a white precipitate is formed, which has been identified as the product of reaction (1):

$$PdX(C_6F_5)(PPh_3)_2 + Pd(OClO_3)(C_6F_5)(PPh_3)_2 \longrightarrow$$



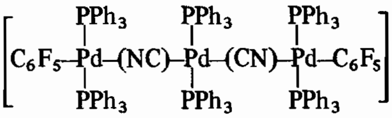
$$\left[C_6F_5-\overset{PPh_3}{\underset{PPh_3}{Pd}}-X-\overset{PPh_3}{\underset{PPh_3}{Pd}}-C_6F_5\right]ClO_4 \qquad (1)$$

X = CN (I) or SCN (II)

If the above described process is to be a general one the choice of the used donor complex should be almost unlimited, and it would accordingly offer a new route for the preparation of polynuclear compounds.

In fact, the addition of a dichloromethane solution of $Pd(CN)_2(PPh_3)_2$ to a benzene solution of $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ (in 1:2 molar ratio) leads to the instantaneous precipitation of a white product, which has been identified as the trinuclear complex $\{(PPh_3)_2Pd(\mu\text{-}CN)_2[Pd(C_6F_5)(PPh_3)_2]_2\}(ClO_4)_2$, (III), formed according to eqn. (2):

$$Pd(CN)_2(PPh_3)_2 + 2Pd(OClO_3)(C_6F_5)(PPh_3)_2 \longrightarrow$$



$$\left[C_6F_5-\overset{PPh_3}{\underset{PPh_3}{Pd}}-(NC)-\overset{PPh_3}{\underset{PPh_3}{Pd}}-(CN)-\overset{PPh_3}{\underset{PPh_3}{Pd}}-C_6F_5\right](ClO_4)_2 \qquad (2)$$

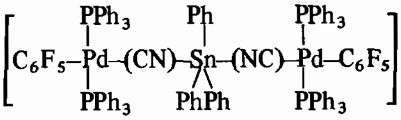
(III)

Similarly, the reaction of a benzene solution of $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ with a suspension of $K_2Pd(CN)_4$ in dichloromethane yields the pentanuclear complex $\{Pd(\mu\text{-}CN)_4[Pd(C_6F_5)(PPh_3)_2]_4\}(ClO_4)_2$ (IV).

The method can also easily be extended to the preparation of polynuclear heteroatomic complexes and therefore if, for instance, benzene solutions of $[Pd(CN)(C_6F_5)(PPh_3)_2]$ and of $Pt(OClO_3)(C_6F_5)(PEt_3)_2$ are reacted a white precipitate is obtained, which has been identified as $\{(\mu\text{-}CN)[Pd(C_6F_5)(PPh_3)_2][Pt(C_6F_5)(PEt_3)_2]\}(ClO_4)$, (V).

The addition of a benzene solution of $[Sn(O_2ClO_2)Ph_3]_x$ to one of $Pd(CN)(C_6F_5)(PPh_3)_2$ in the same solvent leads, according to eqn. (3), to the formation of a white precipitate, which has been identified as $\{(Ph_3Sn)(\mu\text{-}NC)_2[Pd(C_6F_5)(PPh_3)_2]_2\}ClO_4$, (VI).

$$2Pd(CN)(C_6F_5)(PPh_3)_2 + 1/x[Sn(O_2ClO_2)]_x \longrightarrow$$



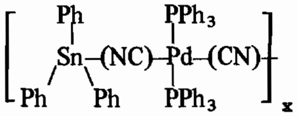
$$\left[C_6F_5-\overset{PPh_3}{\underset{PPh_3}{Pd}}-(CN)-\overset{Ph}{\underset{PhPh}{Sn}}-(NC)-\overset{PPh_3}{\underset{PPh_3}{Pd}}-C_6F_5\right]ClO_4 \qquad (3)$$

(VI)

The same product is obtained even if the reagents are used in a 1:1 molar ratio. This is not altogether surprising if we take into account that, as is well known, tin tends to adopt coordination numbers higher than four [8–10] and that the hitherto-known tin perchlorato complexes are pentacoordinated, with their perchlorato groups bridging two metal atoms [11, 12].

Finally, if a dichloromethane solution of *trans*-$Pd(CN)_2(PPh_3)_2$ is added to a benzene solution of $[Sn(O_2ClO_2)Ph_3]_x$ almost instantaneous precipitation of the white microcrystalline product (VII) can be observed. The reaction yields in every case the same product, regardless of whether a 1:1 or 1:2 molar ratio is used. We formulate it as a polymer according to eqn. (4):

$$Pd(CN)_2(PPh_3)_2 + 1/x[Sn(O_2ClO_2)Ph_3]_x \longrightarrow$$



$$\left[\overset{Ph}{\underset{Ph\quad Ph}{Sn}}-(NC)-\overset{PPh_3}{\underset{PPh_3}{Pd}}-(CN)-\right]_x (ClO_4)_x \qquad (4)$$

(VII)

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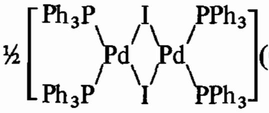
TABLE I. Analytical and Other Data for Polynuclear Complexes.

	Complex	Analysis found (calcd) %			Λ_M (ohm^{-1} cm^2 mol^{-1})	ν(CN)^d cm^{-1}
		C	H	N		
I	$\{(\mu\text{-CN})[Pd(C_6F_5)(PPh_3)_2]_2\}ClO_4$	58.94	3.65	0.82	129^a	2139(2130)
		(59.32)	(3.51)	(0.82)		
II	$\{(\mu\text{-SCN})[Pd(C_6F_5)(PPh_3)_2]_2\}ClO_4$	58.10	3.50	0.85	132^a	2105(2070)
		(58.23)	(3.45)	(0.80)		
III	$\{[(PPh_3)_2Pd](\mu\text{-CN})_2[Pd(C_6F_5)(PPh_3)_2]_2\}(ClO_4)_2$	59.61	3.95	1.08	221^a	2157(2120)
		(59.13)	(3.66)	(1.13)		
IV	$\{Pd(\mu\text{-CN})_4[Pd(C_6F_5)(PPh_3)_2]\}(ClO_4)_2$	56.66	3.89	1.48	202^a	2170(2140)
		(57.36)	(3.36)	(1.55)		
V	$\{[(PPh_3)_2(C_6F_5)Pd](\mu\text{-CN})[Pt(C_6F_5)(PEt_3)_2]\}ClO_4$	49.16	3.89	0.90	131^a	2155(2130)
		(48.14)	(3.97)	(0.92)		
VI	$\{[Ph_3Sn](\mu(NC)_2[Pd(C_6F_5)(PPh_3)_2]_2\}ClO_4$	58.59	3.60	1.35	62.9^b	2155(2130)
		(59.55)	(3.60)	(1.34)		
VII	$\{[Ph_3Sn](\mu\text{-NC})[Pd(PPh_3)_2](\mu\text{-CN})\}_x(ClO_4)_x$	59.11	4.04	2.59	c	2150(2120)
		(59.39)	(4.01)	(2.47)		
VIII	$\{(\mu\text{-I})_2[Pd(PPh_3)_2]\}(ClO_4)_2$	49.52	3.51		232^a	
		(49.48)	(3.52)			

[a] In acetone. [b] In nitromethane. [c] Insoluble. [d] In parentheses ν(CN) for the starting compounds.

In order to establish whether the perchlorato group of palladium complexes can be displaced by halide, which is also capable of bridging two metal atoms, we have tested the analogous reaction of $PdI(C_6F_5)(PPh_3)_2$ with $Pd(OClO_3)(C_6F_5)(PPh_3)_2$. If stoichiometric benzene solutions of these compounds are used no reaction can be observed, and the unchanged starting complexes are recovered. However, the reaction of a dichloromethane solution of $PdI_2(PPh_3)_2$ with a benzene solution of $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ in 1:2 molar ratio leads to the formation of a binuclear compound, which has been identified as $[(PPh_3)_2Pd(\mu\text{-}I)_2Pd(PPh_3)_2](ClO_4)_2$ (VIII).

$$PdI_2(PPh_3)_2 + 2Pd(OClO_3)(C_6F_5)(PPh_3)_2 \longrightarrow$$



$\frac{1}{2}$ $(ClO_4)_2 + PdI(C_6F_5)(PPh_3)_2$

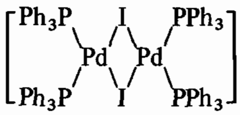
(VIII) $+ Pd(OClO_3)(C_6F_5)(PPh_3)_2$ (5)

The formation of the cationic complex (*cf.* eqn. (5)) can be conceived of as the result of the metathesis (6)

$$Pd(OClO_3)(C_6F_5)(PPh_3)_2 + PdI_2(PPh_3)_2 \longrightarrow PdI(C_6F_5)(PPh_3)_2 + Pd(OClO_3)I(PPh_3)_2 \quad (6)$$

and the subsequent transformation (eqn. 7) of the mononuclear perchlorato- complex into the doubly-bridged cationic dinuclear complex

$$2Pd(OClO_3)(I)(PPh_3)_2 \longrightarrow$$



$(ClO_4)_2$ (7)

Similar complexes have also been obtained by treatment of $PdCl_2L_2$ ($L = PR_3$ or AsR_3) with $AgClO_4$ in a 2:1 molar ratio [13].

The C, H and N analyses of all the reported complexes are in satisfactory agreement with the proposed formulae (*cf.* Table I). The IR spectra and conductivities are consistent with the respective structures. The Table I lists also the Λ_M along with the vibrations due to ν(CN); the latter are, as expected, shifted towards higher energies with respect to the starting compounds.

To explore the generality of the process further work is in progress and our studies are being extended to compounds with other halogen or pseudohalogen bridging atoms as well as to the synthesis of polynuclear complexes of other metals.

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