Palladium(0) *Compounds. Part I. Di*iso*nitrilopalladium*(0) *Compounds.*

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The preparation and properties of diamagnetic di*iso*nitrilopalladium(0) complexes, $(R{\cdot}NC)_2Pd^0$ ($R = C_6H_5$, *p*-C_6H_4Me, and *p*-$C_6H_4{\cdot}OMe$), are described. $(R{\cdot}NC)_2Pd^0$ reacts with one mole of iodine to give $(R{\cdot}NC)_2PdI_2$, and with triaryl phosphites to give $[(RO)_3P]_3(R{\cdot}NC)Pd$.

It is well known that, as the –NC group in *iso*nitriles possesses an electronic structure analogous to that of carbon monoxide, it is capable of forming co-ordination compounds of carbonyl type, with the central metal atom in a formally zero oxidation state.

The tetrakisaryl*iso*nitrilo-nickel compounds, $(Ar{\cdot}NC)_4Ni$, were first obtained by Hieber and Böckly (*Z. anorg. Chem.*, 1950, **262**, 344) and by Klages and Mönkemeyer (*Ber.*, 1952, **85**, 109) by the action of *iso*nitriles on nickel tetracarbonyl, and later by Malatesta and Sacco (*Accad. naz. Lincei, Rend. classe Sci. fis. mat. nat.*, 1951, **11**, 379) by direct reduction of nickel(II) salts in the presence of excess of *iso*nitrile. Also the nitrosyl*iso*nitrile compounds, $(NO)_2(R{\cdot}NC)_2Fe$, can be prepared by direct action of *iso*nitriles on the nitrosyl carbonyl $(NO)_2(CO)_2Fe$ as well as by treatment of Roussin's red or black salt with *iso*nitriles. They can be obtained even by addition of hydroxylamine to an alcoholic suspension of $(Ph{\cdot}NC)_4FeCl_2$ (*idem, Z. anorg. Chem.*, 1953, **273**, 247). Pure *iso*nitrile complexes of Group VIA metals (Cr, Mo, and W) cannot be obtained by the action of *iso*nitriles on the corresponding carbonyls; they are, however, obtained by reduction of suitable salts in the presence of excess of *iso*nitrile (see *idem, Ann. Chim., Italy*, 1953, **43**, 622, and previous reference quoted therein). Moreover Sacco (*Gazzetta*, 1953, **83**, 632) has shown that on treatment of dicobalt octacarbonyl with *iso*nitriles only compounds of the type $[(R{\cdot}NC)_5Co]^+[Co(CO)_4]^-$ are obtained.

The ability of *iso*nitriles to give remarkably stable zero-valent complexes, and the ease with which they are obtained by reduction of a suitable metal salt in the presence of excess of *iso*nitrile, prompted the author to attempt the preparation of zero-valent metal *iso*nitriles of metals whose pure carbonyls are not known. Of these, palladium appeared to be the most promising in view of its ability to form carbonyl and nitrosyl halides and the hitherto unknown di*iso*nitrilopalladium dihalides recently prepared in this department (Angoletta, *Ann. Chim. Italy*, in the press). By analogy with $(R{\cdot}NC)_4Ni$, the palladium(0) *iso*nitrile complex should be $(R{\cdot}NC)_4Pd$.

Attempts to prepare ions of the type $[(R{\cdot}NC)_4Pd]^{++}$ showed that they are unstable, and hence it was attempted to reduce the complex $(R{\cdot}NC)_2PdI_2$ in the presence of excess of *iso*nitrile, this complex being chosen owing to its ease of preparation. A large number of reducing agents were tried under widely different conditions, and finally a product of composition $(R{\cdot}NC)_2Pd$, and not the expected $(R{\cdot}NC)_4Pd$, was isolated.

The conditions under which reduction takes place are rather unusual. The compounds $(R{\cdot}NC)_2PdI_2$, which could not be reduced to the zero-valent state by strong reducing agents in acid, neutral, or slightly alkaline solution, are easily reduced in strongly alkaline solution (alcoholic potassium hydroxide) but only if more than 2 moles of *iso*nitrile per mole of $(R{\cdot}NC)_2PdI_2$ are present. In fact, if slightly less than 2 moles of *iso*nitrile are used not even traces of $(R{\cdot}NC)_2Pd$ are obtained, whereas a 5% excess over 2 moles results in a 50% yield. The reaction sequence can be represented as follows:

$$\begin{aligned}
&(1)\ (R{\cdot}NC)_2PdI_2 + 2R{\cdot}NC + 2KOH \longrightarrow [(R{\cdot}NC)_4Pd](OH)_2 + 2KI\\
&(2)\ [(R{\cdot}NC)_4Pd](OH)_2 + R{\cdot}NC \longrightarrow (R{\cdot}NC)_4Pd + R{\cdot}NCO + H_2O\\
&(3)\ (R{\cdot}NC)_4Pd \longrightarrow (R{\cdot}NC)_2Pd + 2R{\cdot}NC
\end{aligned}$$

The phenyl, *p*-tolyl, and *p*-methoxyphenyl compounds were prepared by this method. They are remarkably stable, and are precipitated from the reaction mixture in the pure state, in black-brown leaflets with metallic reflexes. They are diamagnetic, and practically insoluble in all solvents. They dissolve in pyridine and nitrobenzene with complete decomposition.

The ratio *iso*nitrile : metal is 2 : 1 as shown by elementary analysis and by titration with an alcoholic iodine solution : reaction is quantitative according to $(R{\cdot}NC)_2Pd + I_2 \longrightarrow (R{\cdot}NC)_2PdI_2$.

On reaction with tervalent phosphorus derivatives, *e.g.*, tri-*p*-chlorophenyl phosphite, di*iso*nitrilopalladium(0) yields tetraco-ordinated palladium(0) complexes of the conventional type :

$$(R{\cdot}NC)_2Pd + 3(RO)_3P \longrightarrow [(RO)_3P]_3(R{\cdot}NC)Pd + R{\cdot}NC$$

Compounds of the latter type, which are now under investigation in these laboratories, constitute an important development in the complex chemistry of palladium.

The insolubility of the di*iso*nitrilopalladium(0) compounds suggests that they have a polymeric structure, and if so, this would be the first example of a polymeric *iso*nitrilo-complex.

It is well known that the pure carbonyls of Group VIIIA (Fe, Ru, and Os) and VIIIB (Co, Rh, and Ir) show a tendency to be more stable in the polynuclear form as the group is descended. Structural studies of polynuclear carbonyls, *e.g.*, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, show that the metal atoms are joined by bridging CO molecules acting as bidentate ligands, forming metal-to-carbon bonds of organometallic type.

If the carbon atom in the *iso*nitrile group were to function as a bidentate ligand, and this would be the first example of such a bond type, these palladium(0) complexes would form linear macromolecules in which *all* the bonds are of organometallic type. This seems highly improbable in view of the instability of organo-palladium compounds, the method of preparation of the palladium(0) *iso*nitriles, and their reaction with phosphites. Moreover, such a structure would leave palladium co-ordinatively unsaturated, as only four electrons would be donated to the central metal atom.

An alternative structure, with a co-ordinatively saturated palladium atom, could be envisaged as follows : each palladium atom forms four metallic bonds to other palladium atoms and two co-ordinate bonds to *iso*nitrile molecules. This would lead to a layer structure, with a monoatomic layer of palladium atoms sandwiched between *iso*nitrile molecule layers [something intermediate between the metal and the hypothetical $(R{\cdot}NC)_4Pd$], in which the central metal atom would have the effective atomic number of xenon.

The elucidation of the stereochemistry of these interesting compounds must, however, await an *X*-ray structure determination, and the author is prepared to supply samples to those interested in such a study.

EXPERIMENTAL

Palladium was determined as metal, carbon, and hydrogen by the Liebig method, and nitrogen by the Dumas method.

Di(*phenyl*iso*nitrilo*)*palladium*(0), $(C_6H_5{\cdot}NC)_2Pd$.—Di(phenyl*iso*nitrilo)di-iodopalladium (1·13 g., 2 mol.) and phenyl*iso*nitrile (0·433 g., 4·1 mol.) in ethanol (15 ml.), in a 100-ml. flask, were heated to boiling and 20% alcoholic potassium hydroxide (1 ml.) was then added gradually. The clear, brownish-yellow solution obtained was again warmed to boiling and more alcoholic potassium hydroxide (3 ml.) added gradually. At this point a vigorous reaction set in : the solution became brown, then green, and finally green-brown, while dark brown leaflets begin to separate. After 15 min., reaction is complete and the solid is collected at the pump, washed with warm ethanol, cold water (to remove the residual KI), and then cold ethanol, and dried in a vacuum-desiccator [yield 0·4 g. (50%) ; decomp. 170—190°]. *Di*(*phenyl*iso*nitrilo*)*palladium*(0) is diamagnetic ($\chi_M = -40 \times 10^{-6}$). It is insoluble in all solvents except *iso*nitriles, quinoline, pyridine, and nitrobenzene, but it cannot be recrystallised from these solvents (Found : C, 53·8 ; H, 3·3 ; N, 9·1 ; Pd, 34·3. $C_{14}H_{10}N_2Pd$ requires C, 53·75 ; H, 3·2 ; N, 9·0 ; Pd, 34·1%).

Reaction with iodine. The complex (0·310 g.) and alcoholic N/10-iodine (25 ml.) were shaken for 1 hr. and then titrated with N/10-thiosulphate ; 5·3 ml. of solution were used, *i.e.*, 19·7 ml. of iodine [Calc. for reaction $(C_6H_5{\cdot}NC)_2Pd + I_2 \longrightarrow (C_6H_5{\cdot}NC)_2PdI_2$: 19·88 ml.]. The reaction product was collected (0·51 g., theor. 0·56 g.) and after recrystallisation proved to be identical with an authentic sample of $(C_6H_5{\cdot}NC)_2PdI_2$.

Di-(p-*tolyl*iso*nitrilo*)*palladium*(0).—This was prepared similarly in 55% yield from (p-$C_6H_4Me{\cdot}NC)_2PdI_2$ (1·1 g.) and p-tolyl*iso*nitrile (0·5 g.); decomp. 150—160° (Found: C, 56·0; H, 4·1; N, 8·1; Pd, 31·1. $C_{16}H_{12}N_2Pd$ requires C, 56·4; H, 4·1; N, 8·2; Pd, 31·6%). The *complex* (0·375 g.) and N/10-alcoholic iodine (25 ml.) were titrated as before and required 3·52 ml. of thiosulphate (calc., 3·00 ml.).

Di-(p-*methoxyphenyl*iso*nitrilo*)*palladium*(0).—By a similar method, this *complex* was obtained in 45% yield from (p-$MeO{\cdot}C_6H_4{\cdot}NC)_2PdI_2$ (1·25 g.) and p-methoxyphenyl*iso*nitrile (0·558 g.); decomp. 160—170° (Found: C, 51·5; H, 3·9; N, 7·3; Pd, 29·0. $C_{16}H_{12}O_2N_2Pd$ requires C, 51·3; H, 3·8; N, 7·5; Pd, 28·6%).

Reaction between $(C_6H_4Me{\cdot}NC)_2Pd$ *and Tri*-p-*chlorophenyl Phosphite*.—The complex (0·36 g., 1 mmole) and the ester (1·5 g., 4 mmoles) in benzene solution (3 ml.) were refluxed on a water-bath, until the dark solution become orange-yellow (about 10 min.). Benzene was then distilled off in a vacuum, and the dry residue washed twice with 5 ml. of cold absolute alcohol and crystallised from the same boiling solvent. p-*Tolyl*iso*nitrilotris*(*tri*-p-*chlorophenyl phosphite*) was thus obtained in white needles, m. p. 105° (sharp), which slowly blackened on exposure to air (Found: C, 51·0; N, 1·0; Cl, 22·3; P, 6·3; Pd, 7·4. $C_{62}H_{43}O_9NCl_9P_3Pd$ requires C, 50·8; N, 1·0; Cl, 21·9; P, 6·4; Pd, 7·3%).

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