

New Starting Materials in Platinum(II) Chemistry

THREE USEFUL PLATINUM NITRILE COMPLEXES

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Some years after Moissan had first isolated fluorine in 1886, Sir William Ramsay sent him a sample of argon to check its reaction with the fluorine (1). There was no reaction, so it was thought that the Noble Gases could not react with anything. If Ramsay had sent a sample of another gas as starting material, xenon, for example, then the chemistry of the Noble Gases might not have been delayed for sixty years until the pioneering work by Bartlett (2). This little historical example illustrates a well known fact amongst synthetic chemists, that a preparation is easier to achieve if the starting materials cover a broad spectrum.

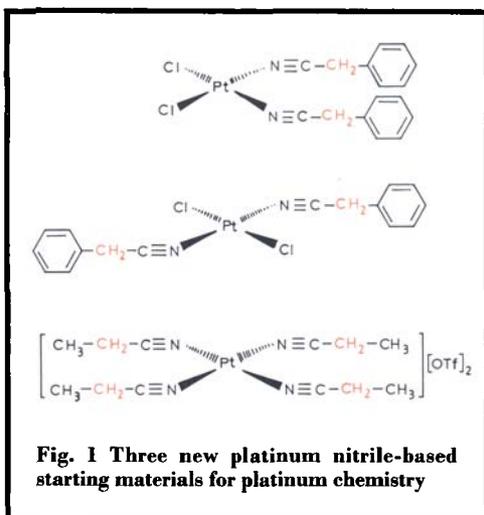
The increasing use of non-aqueous solvents in the synthetic co-ordination chemistry of platinum makes the choice of starting materials for synthesis involving ligand substitution particularly important. Ideally, starting materials must be isomerically pure, freely soluble in non-aqueous solvents, readily available and contain ligands which are relatively weak donors and, are therefore easily replaced. Solvento-complexes (that is, complexes whose ligands are more commonly encountered as solvents) in general and organonitrile compounds in particular satisfy these requirements.

In synthetic chemistry, $[\text{PtCl}_2(\text{MeCN})_2]$ and $[\text{PtCl}_2(\text{PhCN})_2]$ are widely used as synthons for the preparation of other platinum compounds (3). However, the disadvantage of both compounds, prepared by conventional methods, is their isomeric impurity. Indeed, *cis*- $[\text{PtCl}_2(\text{MeCN})_2]$, produced from $\text{K}_2[\text{PtCl}_4]$ and acetonitrile in water, contains about 16 per cent of the *trans*-isomer (4). Similarly, the interaction of PtCl_2 and PhCN results in the formation of an isomeric mixture of *cis*- and *trans*-

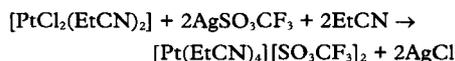
$[\text{PtCl}_2(\text{PhCN})_2]$ (5–7). When syntheses require either *cis*- or *trans*- $[\text{PtCl}_2(\text{PhCN})_2]$ as the starting material, the isomers must first be separated by chromatography (6). An additional drawback of *cis*- and *trans*- $[\text{PtCl}_2(\text{MeCN})_2]$ is the low solubility of both in water and also in the most commonly used organic solvents.

Recently, we prepared the platinum nitrile compounds *cis*- and *trans*- $[\text{PtCl}_2(\text{PhCH}_2\text{CN})_2]$ which have certain advantages over their acetonitrile and benzonitrile analogs (8). The *cis*-isomer is formed by interaction of the clathrate $\text{Pt}_6\text{Cl}_{12} \cdot 0.1\text{C}_2\text{H}_5\text{Cl} \cdot 5.7\text{H}_2\text{O}$ (which is easily obtained (8) and is a very reactive form of “ PtCl_2 ” (9)) with commercially available PhCH_2CN . The *cis*- $[\text{PtCl}_2(\text{PhCH}_2\text{CN})_2]$ complex is isomerised to *trans*- $[\text{PtCl}_2(\text{PhCH}_2\text{CN})_2]$ in almost quantitative yield on heating in the solid phase or on heating in kerosene under nitrogen (10). The process of isomerisation can be routinely monitored by thin-layer chromatography or quantitatively by ^1H NMR spectroscopy. Both isomerically pure *cis*- and *trans*- $[\text{PtCl}_2(\text{PhCH}_2\text{CN})_2]$ complexes are readily soluble in a number of organic solvents – for instance, dichloromethane, acetone, nitromethane and *N,N*-dimethylformamide – and can be used for homogeneous liquid phase syntheses.

Examples of homoleptic solvento-complexes of platinum(II) containing weak donor ligands (11) are scarce and are restricted to $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Pt}(\text{Me}_2\text{SO})_2(\text{Me}_2\text{SO})_2]^{2+}$ and $[\text{Pt}(\text{MeCN})_4]^{2+}$ (12). The latter complex, $[\text{Pt}(\text{MeCN})_4]^{2+}$, is readily available but is very unstable towards hydrolysis, which can limit its potential synthetic applications. However, we have discovered that this disadvantage can be overcome by the use



of EtCN rather than MeCN as a ligand and solvent for the synthesis (13):



The useful properties of the compound $[\text{Pt}(\text{EtCN})_4][\text{SO}_3\text{CF}_3]_2$, in addition to its relative insensitivity to atmospheric moisture and

to hydrolysis in general, include excellent solubility in commonly used organic solvents, fairly high thermal stability (melting point of 175°C, with decomposition) and good leaving properties of the co-ordinated propanenitrile.

The English say: "There's nothing new under the sun", while the Russians say: "Everything new is the well-forgotten old"; indeed, these "new" compounds which we have prepared are very close structural analogs of "old" platinum(II) nitriles (14). However, these derivatives, made by the simple introduction of a CH₂ group, see Figure 1, have led to desirable properties which are absent in the analog acetonitrile and benzonitrile compounds.

We hope that the useful properties of these platinum nitrile complexes, combined with a facile synthesis will extend the range of reactions possible in synthetic platinum chemistry.

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