

## DIMETHYLFORMAMIDE CARBONYLATION OF PLATINUM GROUP METALS UNDER MILD HOMOGENEOUS CONDITIONS. REACTIONS OF CARBONYL-CONTAINING COMPLEXES

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### SUMMARY

If platinum metal halides are heated in dimethylformamide as a solvent, the resulting solutions are found to contain carbonyl halo species. Such carbonylated solutions ("carsols") provide extremely convenient starting material for synthesizing various carbonyl-containing complexes of the platinum group metals. The syntheses of  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ , *trans*- $\text{RhL}_2(\text{CO})\text{Cl}$ ,  $\text{RhL}'(\text{CO})_2$ ,  $\text{RhL}'\text{L}''$ ,  $\text{RhL}'\text{PPh}_3(\text{CO})$ ,  $[\text{Pt}(\text{CO})\text{Cl}_3]^-$ ,  $(\text{CO})\text{Cl}_2\text{Pt}(\text{Bipy})\text{PtCl}_2(\text{CO})$ ,  $[\text{Pt}(\text{Bipy})(\text{CO})\text{Cl}]^+ [\text{Pt}(\text{CO})\text{Cl}_3]^-$  are briefly described in this paper, and some reactions of  $\text{RhOxPPh}_3(\text{CO})$  are considered.

In 1965 Rusina and Vlček<sup>1</sup> unexpectedly obtained the rhodium(I) carbonyl complex, *trans*- $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ , by heating rhodium trichloride in dimethylformamide\* in the presence of triphenylphosphine. This reaction is similar to the carbonylation of platinum metals by alcohols, formic acid etc., but proceeds much more vigorously. The ease of rhodium carbonylation in DMF medium suggests that such reactions may be used as a basis for other carbonyl synthesis.

Heating platinum metal halides in DMF as a solvent at  $\sim 150^\circ$  results in the formation of solutions containing carbonyl halo complexes. Such carbonylated solutions (for convenience these are referred to below as "carsols") provide convenient starting materials for the synthesis of various carbonyl-containing complexes. The only exception is palladium, whose halides when heated in DMF are rapidly reduced to the metal. The heating of  $\text{PdCl}_2$  or  $\text{Na}_2(\text{PdCl}_4)$  in DMF in the presence of allyl chloride produces  $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ , and the addition of  $\text{PPh}_3$  makes it possible to obtain  $\pi\text{-C}_3\text{H}_5\text{PdPPh}_3\text{Cl}$  in one step. In this case no palladium metal is formed, and it is conceivable that in the course of these reactions the intermediate formation of palladium carbonyl complexes occurs.

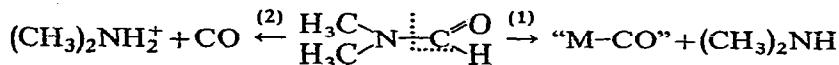
\* Abbreviations used: DMF, dimethylformamide; DMA, dimethylamine; Ph, phenyl; single charged radicals (L') of: Acac, acetylacetonate, Ox, 8-hydroxyquinoline, Mcq, 8-mercaptoquinoline, Dth, dithizone and Tsa, thiosalicylic acid; Bipy, 2,2'-bipyridine; Phea, *o*-phenanthroline; Py, pyridine; TCNE, tetracyanoethylene; TNB, 1,3,5-trinitrobenzene; HMB, hexamethylbenzene.

Evaporation in argon of Rh-carsol ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in DMF after a 20 min heating) in the presence of tetraalkylammonium halide yields the corresponding salt of the dicarbonyl anion  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ . The addition of triphenylphosphine and triphenylstibine to Rh-carsol results in the release of CO (1 mol/Rh) and the formation of *trans*- $\text{RhL}_2(\text{CO})\text{Cl}$ , where  $\text{L} = \text{PPh}_3, \text{SbPh}_3$ . The interaction between Rh-carsol and bidentate singly-charged ligands [ $\text{L}' = \text{Acac}, \text{Ox}, \text{Mcq}, \text{Dth}, \text{Ths}$  etc. (in the  $\text{H}^+$ - and  $\text{Na}^+$ -forms)] leads to the formation of *cis*-dicarbonyl derivatives of the type  $\text{RhL}'(\text{CO})_2$ . A great number of these derivatives show dichroism and metal glitter which are characteristic properties of column structures with metal-metal bonds. An alternative method of synthesizing these compounds has been previously described<sup>2</sup>. The treatment of these complexes with  $\text{PPh}_3$  (1 mol) leads to the evolution of CO (1 mol/Rh) and the formation of monocarbonyl derivatives  $\text{RhL}'\text{PPh}_3(\text{CO})$ . Subsequent addition of ligands  $\text{L}'$  and neutral bidentate ligands ( $\text{L}'' = \text{Bipy}, o\text{-Phen}$ ) to Rh-carsol allows the formation of bicyclic compounds of the type  $\text{RhL}'\text{L}''$  in one stage process without the isolation of intermediate products.

If Pt-carsol ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in DMF after a 20 min heating) is evaporated in the presence of tetraalkylammonium chlorides salts of the monocarbonyl anion  $[\text{Pt}(\text{CO})\text{Cl}_3]^-$  are obtained. The treatment of Pt-carsol with  $\text{PPh}_3$  causes the evolution of CO from the solution and the formation of *cis*- $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ . The interaction between Pt-carsol and Bipy does not result in CO evolution and yields a bridged binuclear complex of the type  $(\text{CO})\text{Cl}_2\text{Pt}(\text{Bipy})\text{PtCl}_2(\text{CO})$  with  $\nu(\text{CO})$  2127, 2118 ( $\text{sh}$ )  $\text{cm}^{-1}$ .

If hydrochloric acid is added to Pt-carsol previous to its treatment with Bipy a salt with  $\nu(\text{CO})$  2139 (cation) and 2106  $\text{cm}^{-1}$  (anion) and identical to the product previously described<sup>3</sup> as  $[\text{Pt}(\text{Bipy})\text{COCl}]^+ [\text{Pt}(\text{CO})\text{Cl}_3]^-$  is formed instead of the bridged complex mentioned above.

The above data show that Rh-carsol contains mainly dicarbonyl derivatives of  $\text{Rh}^{\text{I}}$ . In Pt-carsol the principal constituents appear to be monocarbonyl derivatives of  $\text{Pt}^{\text{II}}$ . In Ir-carsol [ $\text{K}_2(\text{IrCl}_6)$  in DMF], from which *trans*- $\text{Ir}(\text{PPh}_3)_2\text{COCl}_3$  may be obtained by  $\text{PPh}_3$  treatment, iridium is present mainly as monocarbonyl derivatives of  $\text{Ir}^{\text{III}}$ , whilst the extent of reduction and carbonylation of ruthenium and osmium in carsols obtained from  $\text{RuOHCl}_3$  and  $\text{H}_2\text{OsCl}_6$  is as yet uncertain. The evaporation of Rh-carsol in the air leads to the complete decarbonylation and oxidation of Rh and to the formation of the anionic complex (HDMA)  $[\text{Rh}(\text{DMA})_2\text{Cl}_4]$ . The dimethylamine in this complex apparently arises as a result of DMF-decarbonylation by the metal [reaction (1)]. Evaporation in the presence of HCl produces dimethylammonium hexachlororhodate (HDMA)<sub>3</sub> ( $\text{RhCl}_6$ ), and the same salt is gradually crystallized from  $\text{RhCl}_3$  solutions in DMF plus HCl at room temperature. In this case the HDMA<sup>+</sup> cation is the product of DMF acid decarbonylation [reaction (2)]:



The reverse process to reaction (1) has been described for dicobalt octacarbonyl<sup>4</sup>, and we have found<sup>5</sup> that DMF is formed as a result of interaction between DMA and  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ; in this latter case the reaction product is probably best described as  $[\text{Rh}(\text{DMA})_2\text{DMFCl}]$ , *i.e.* it contains a coordinated DMF molecule [ $\nu(\text{CO})$  1590  $\text{cm}^{-1}$ ]. It is not improbable that the process " $\text{Rh} + \text{DMF} \rightleftharpoons \text{Rh}-$

CO" + DMA passes the same transition state irrespective of the direction of the reaction.

It is not possible to discuss here the most important chemical aspects of carbonyl rhodium(I) planar complexes. In this paper we have been confined ourselves to mentioning only a few facts, which are of the greatest interest to the topics immediately under discussion. Thus differences in the reactions of Rh-carsol with an excess of oxyquinoline or mercaptoquinoline<sup>6</sup> are apparently connected with the *trans*-effect mentioned by Chernyaev. The reaction with excess Ox (N,O-ligand), always leads to the formation of a complex containing one bidentate ligand irrespective of the reaction conditions. No replacement of carbonyl groups has been observed in this particular reaction, and in this respect Ox is similar to Acac (O,O-ligand). The action of excessive Mcq (N,S-ligand) leads to the replacement of both carbonyl groups and to the formation of the bicyclic complex [RhMcq(HMcq)]. This difference may either be due to one of the following factors or to their combined effect:

(a) Carbonyl groups in Rh(Mcq)(CO)<sub>2</sub> are more readily replaced than in RhOx(CO)<sub>2</sub>, irrespective of the nature of the replacing agent.

(b) Mcq has a stronger tendency to cause the replacement of carbonyl groups in RhL'(CO)<sub>2</sub> irrespective of the nature of ligand (L') contained in this complex.

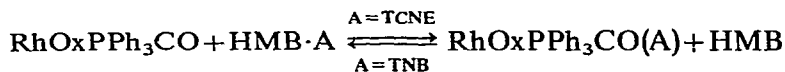
These factors may be observed independently in the reaction of RhMcq(CO)<sub>2</sub> + Ox and RhOx(CO)<sub>2</sub> + Mcq. In both cases the release of CO and formation of the same mixed complex RhMcq(HOx) or RhOx(HMcq) was observed, and suggests that the difference in the behaviour of Ox and Mcq is caused by the combined action of both of the above factors. The labilizing effect of sulphur-containing ligands in comparison with the effect of oxygen-containing ones is one of the characteristic features of the *trans*-effect.

One of the most interesting features of planar rhodium(I) complexes is their unsaturation which gives rise to a tendency for these complexes to indulge in addition reactions. Thus, we have isolated a series of complexes containing pentacoordinated rhodium(I), e.g. RhAcacPy<sub>3</sub>, RhMcq(PPh<sub>3</sub>)<sub>3</sub>, RhOx(PPh<sub>3</sub>)<sub>3</sub>, RhOx(PPh<sub>3</sub>)CO(SO<sub>2</sub>), and complexes with *n* = 2, 3 in the series Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>(Bipy)<sub>*n*</sub>, where *n* = 1, 2, 3.

The interaction of RhOxPPh<sub>3</sub>CO with tetracyanoethylene and with 1,3,5-trinitrobenzene results in the formation of adducts of 1/1 composition, the addition of TCNE being accompanied by a sharp increase in the  $\nu(\text{CO})$  frequency (from 1950 cm<sup>-1</sup> in the initial complex spectrum to 2075 cm<sup>-1</sup>). A similar effect was observed during the formation of RhAcac(CO)<sub>2</sub>TCNE, RhOx(CO)<sub>2</sub>TCNE, RhAcacPPh<sub>3</sub>-COTCNE. This effect has been discussed for a number of other complexes<sup>7</sup>.

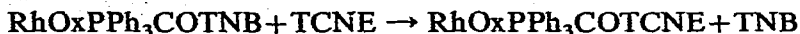
The addition of the weaker  $\pi$ -acceptor TNB leads to hardly any change in the  $\nu(\text{CO})$  frequency value (1966 cm<sup>-1</sup>).

The ability of RhOxPPh<sub>3</sub>CO to play the role of an analogue and a competitor with organic  $\pi$ -donors is exhibited by exchange reactions of the following type:



The direction of these reactions indicates that the rhodium complex is superior to HMB in its ability for gaining TCNE but is inferior to HMB with respect to TNB addition. The greater stability of the [RhOxPPh<sub>3</sub>CO] + TCNE adduct is in agreement with the differences in the values of the  $\nu(\text{CO})$  frequency noted above and is

supported by the direct replacement reaction:



Since free and coordinated  $\text{O}_x$  appears to be capable of forming adducts with  $\text{TNB}^8$ , it is essential that the structure of the product of the TNB addition to  $\text{RhO}_x\text{PPh}_3\text{CO}$  should be clarified, *i.e.*, whether this addition complex has the structure  $\text{O}_x\text{-Rh-TNB}$  or  $\text{Rh-O}_x\text{-TNB}$ .

Reaction of  $\text{RhO}_x\text{PPh}_3\text{CO}$  with molecular chlorine yields the octahedral complex  $\text{Rh}^{\text{III}}\text{L}'\text{PPh}_3(\text{CO})\text{Cl}_2$  with  $\nu(\text{CO})$   $2115\text{ cm}^{-1}$ , where  $\text{L}'$  is hexachloro-8-hydroxyquinoline, being the result of the complete replacement of the hydrogen atoms in the ligand by chlorine. This result is surprising, for it is well-known that 5,7-dichloro-8-hydroxyquinoline is formed as a result of the chlorination of unchelated 8-hydroxyquinoline.

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