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# ASPECTS OF THE CHEMISTRY OF RHODIUM(III) COMPLEXES WITH 2,2'-BIPYRIDINE UNDER REDUCING CONDITIONS

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## SUMMARY

The reduction of rhodium(III)/2,2'-bipyridine (1/2) solutions with sodium borohydride in methanolic media is considered to proceed via labile hydrido-intermediates, one of which may be trapped by the addition of triphenylphosphine. Addition of organic halides, RX, to the medium results in the formation of new complexes $[Rh(Bipy)_2(R)X](ClO_4)$. The same compounds are formed when sodium amalgam replaces sodium borohydride and they are considered to arise from oxidative addition of RX to a mono(2,2'-bipyridine)rhodium(I) species.

The reaction of bis(2,2'-bipyridine)rhodium(III) complexes with alkaline ethanol in the presence of an excess of triphenylphosphine affords the known $HRh(PPh_3)_4$. Mass spectroscopic evidence for some contamination with $Ph_3PO$ is found even for specimens prepared under argon. The reaction of $HRh(PPh_3)_4$ with dilute mineral acids is briefly considered.

## INTRODUCTION

The recent synthesis[1] of some bis(2,2'-bipyridine) complexes of cobalt(III) containing cobalt to carbon $\sigma$-bonds prompts us to report some experiments we have been performing with related rhodium complexes. It has been known for some years that treatment of a rhodium(III) complex of 2,2'-bipyridine with reducing agents such as sodium borohydride or sodium amalgam affords intensely coloured solutions thought to contain rhodium(I) species[2]. The major species present in solution was believed to be the bis(2,2'-bipyridine)rhodium(I) cation which, in accordance with then accepted views, was considered to possess *trans* stereochemistry[2]. Despite the fact that numerous recent papers[3] have established, *ad nauseam*, the impossibility of this stereochemistry for a bis(2,2'-bipyridine) complex, the recent crystal structure determination[4,5] of the nitrate monohydrate of the isoelectronic $[Pd(Bipy)_2]^{2+}$ ion establishes the description "distorted planar" to be preferable to "tetrahedral". The known lability of the bis(1,10-phenanthroline)palladium(II) ion[6] might reasonably be parallelled by the rhodium(I)–2,2'-bipyridine analogue. We therefore set out to demonstrate the possibility of an oxidative addition reaction to some coordinately unsaturated rhodium(I)–2,2'-bipyridine compounds hoping to establish the existence of such species on a firmer footing.

## RESULTS AND DISCUSSION

In Table 1 we gather data for some new rhodium(III) compounds of the type $[Rh(Bipy)_2RX](ClO_4)$ where RX is an organic halide. We found that these compounds were relatively easy to prepare when using RI or RBr but, with the exception of benzyl chloride, we were unable to observe reactions with organic chlorides. We did not observe products of the type $[Rh(Bipy)_2R_2]^+$, hence the reaction with rhodium does not follow the same path as with cobalt[1].

TABLE 1

| *Complex* | *Analysis found (calcd.) (%)* | | | $\Lambda_M{}^a$ *in* $CH_3NO_2$ |
|---|---|---|---|---|
| | *C* | *H* | *N* | |
| $[Rh(Bipy)_2(Ph)I](ClO_4)$ | 42.3 | 3.2 | | 84 |
| | (43.4) | (2.9) | (7.8) | |
| $[Rh(Bipy)_2(PhCH_2)Cl](ClO_4)$ | 50.6 | 3.7 | 8.8 | 59 |
| | (50.5) | (3.6) | (8.7) | |
| $[Rh(Bipy)_2(CH_3)I](ClO_4)$ | 37.8 | 2.9 | 8.0 | 123 |
| | (38.4) | (3.0) | (8.5) | |
| $[Rh(Bipy)_2(C_2H_5)I](ClO_4)$ | 37.8 | 3.0 | 8.0 | 105 |
| | (39.3) | (3.1) | (8.3) | |
| $[Rh(Bipy)_2(PhCH_2)Br](ClO_4)$ | 48.2 | 3.8 | 8.0 | 69 |
| | (47.3) | (3.4) | (8.1) | |
| $[Rh(Bipy)(PPh_3)_2(H_2)](ClO_4)$ | 62.4 | 3.4 | 4.5 | 78 |
| | (62.4) | (3.1) | (4.6) | |
| $[RhC_{36}H_{30}N_3O_7P_2]^b$ | 55.1 | 3.9 | 5.4 | ~0 |
| | (55.3) | (3.8) | (5.4) | |
| $[Rh(PPh_3)_4H]$ | 74.7[c] | 5.4[c] | | ~0[d] |
| | (74.9) | (5.3) | | |
| | 72.9[e] | 5.0[e] | | |

[a] Molar conductivity of a $10^{-3}$ *M* solution. [b] Green product from reaction of $HRh(PPh_3)_4$ with dilute $HNO_3$. [c] Synthesis of $HRh(PPh_3)_4$ from $[Rh(Bipy)_2Cl_2]Cl \cdot 2\ H_2O$ under argon. [d] Decomposed. [e] Synthesis of $HRh(PPh_3)_4$ from $[Rh(Bipy)_2Cl_2]Cl \cdot 2\ H_2O$ under air.

The most convenient synthetic route was to use a methanolic solution of sodium borohydride as the reducing medium. When bis(2,2′-bipyridine) complexes of rhodium(III) were reduced in this manner in the presence of triphenylphosphine, addition of perchlorate ions afforded a white material shown to be $[Rh(Bipy)(PPh_3)_2H_2](ClO_4)$. The $^1H$ NMR spectrum showed a quartet centred on $\tau$ 25.7 (1/3/3/1). This probably arises from a pair of overlapping triplets (1/2/1) and implies that $J(Rh\text{–}H) \approx J(P\text{–}H) \approx 15$ Hz. This spectrum, and the value of $J(P\text{–}H)$[7], suggest that the phosphine ligands are located *cis* to equivalent hydrogen atoms. The split band (2120, 2050 $cm^{-1}$) for $\nu(RhH)$ in the IR spectrum suggests the cation to be *cis*-dihydrido-*trans*-bis(triphenylphosphine)rhodium(III). The same compound, less well-characterised, and prepared by a different route, was recently reported by Mestroni *et al.*[8]. The isolation of this compound is significant in this context for two reasons: it establishes the possible existence of mono(2,2′-bipyridine)rhodium species under our experimental conditions, also it indicates that hydrido-complexes may be involved.

To our knowledge the only previous indication that mono(2,2'-bipyridine) species may occur in this system has come from two kinetic studies[2,9]. Gillard and Wilkinson[10] have shown that borohydride ions may function as a source of hydride ions in reaction with dichlorobis(ethylenediamine)rhodium(III) complexes and that substitution reactions may occur to afford mono- or dihydrido-complexes. Similarly Kulasingam[11] has been able to synthesise a hydrido-species by reaction of dichlorobis(di-2-pyridylamine)rhodium(III) salts with sodium borohydride. Although this complex is not well characterised, and is probably polymeric, the stoichiometry establishes that one molecule of bidentate base is lost. We have been able to reproduce Kulasingam's observations but have failed to prepare $[Rh(Dipyam)(PPh_3)_2H_2]ClO_4$ (Dipyam = di-2-pyridylamine) due to the insolubility of Kulasingam's compound ["$Rh(Dipyam)H_2 \cdot ClO_4$"]. There are thus precedents in the literature to suggest that the following reaction sequence may occur:

$$\begin{tikzcd}
Rh(Bipy)_2Cl_2^+ \arrow[r, "BH_4^-"] & \underset{(I)}{Rh(Bipy)_2H_2^+} \arrow[r, "-Bipy"] & \underset{(II)}{Rh(Bipy)H_2^+} \arrow[r, "-H_2"] \arrow[d, "PPh_3"] & \underset{(III)}{Rh(Bipy)^+} \\
 & & {[Rh(Bipy)(PPh_3)_2H_2]^+} &
\end{tikzcd} \tag{1}$$

Depending upon the ligand selected, stages corresponding to (I) (En), (II) (Dipyam) or (III) (Bipy) in eqn. (1) may represent the completion of the reaction. The role of triphenylphosphine is to trap and stabilise the labile intermediate (II). The organic halide, RX, may react with (II) or (III). We therefore carried out experiments using sodium amalgam as the reducing agent since this is not expected to afford hydrido-intermediates and we found that we were unable to prepare $[Rh(Bipy)(PPh_3)_2H_2]^+$ by addition of triphenylphosphine to the reaction, but that we did achieve oxidative addition of RX. Thus we favour the following mechanism for the reaction of RX using borohydride as the reducing agent for rhodium:

$$\begin{tikzcd}
Rh^{III}(Bipy)H_2^+ \arrow[r, shift left] & Rh^{I}(Bipy)^+ + H_2 \arrow[l, shift left] \arrow[r, shift left, "Bipy"] \arrow[d, "RX"] & Rh(Bipy)_2^+ \arrow[l, shift left, "Bipy"] \\
 & Rh^{III}(Bipy)RX^+ \arrow[r, "Bipy"] & {[Rh^{III}(Bipy)_2RX]^+}
\end{tikzcd} \tag{2}$$

We therefore believe that the compounds in Table 1 arise from the oxidative addition of organic halides to a coordinately unsaturated rhodium(I) complex.

It is known that alkaline ethanol may reduce rhodium(III) in the presence of 2,2'-bipyridine[12] and also that the rate equation for the reduction of the same system with molecular hydrogen contains a hydroxide dependent term[9]. Robinson[13] has recently used ethanolic KOH to effect clean and rapid syntheses of a number of rhodium and iridium phosphine complexes. We have been studying the behaviour of some rhodium complexes in alcoholic KOH in the presence of an excess of triphenylphosphine. We find that, in air, the reaction of $[Rh(Bipy)_2Cl_2]Cl$ and of $[Rh(Dipyam)_2Cl_2]Cl$ under these conditions affords identical orange yellow products which are hydrides [$\nu$(RhH) 2140 $cm^{-1}$]. The same reaction performed in an atmosphere of argon gives pure yellow compounds with identical infrared spectra to those of the orange yellow compounds. The analytical figures for carbon fluctuated over several percent, being higher for the products from the experiments performed under argon. The orange-yellow material resembled a specimen of hydridotetrakis(triphenylphosphine)rhodium(I) prepared by Robinson's method using borohydride as reductant[14]; the yellow compound was identical with a specimen of $HRh(PPh_3)_4$ prepared by Robinson's more recent method[13].

The mass spectra of compounds from various preparations were measured but we observed only the fragmentation pattern of the phosphine ligands and no parent ion peak. However in addition to the expected fragmentation pattern of $PPh_3$[15], we also observed peaks at *m/e* 278 and 277 which accurate mass determination proved to be the $P^+$ and $(P-1)^+$ ions of triphenylphosphine oxide. The expected fragmentation pattern of the oxide was also seen[15]. Not surprisingly the presence of $Ph_3PO$ was more apparent for those specimens of $HRh(PPh_3)_4$ prepared in air, however some evidence for the $277^+$ peak was seen in the mass spectrum of *all specimens* even when scrupulous care had been taken to use freshly purified reagents and to exclude oxygen. We have prepared other triphenylphosphine complexes of rhodium following literature methods, *e.g.* $(PPh_3)RhCl$[16] and $HRh(PPh_3)_4$[14], and found mass spectral evidence for $Ph_3PO$ in each case.

Closer examination of the IR spectra of our preparation of $HRh(PPh_3)_4$ revealed that, in those cases where the mass spectrum showed the largest $277^+$ peaks, there was enhanced intensity for a band at 1122 $cm^{-1}$. This band is not reported for free triphenylphosphine but corresponds to the *q*-mode of the phenyl ring for the oxide[17]. Coordination may lower $\nu(P{=}O)$, which occurs at 1193 $cm^{-1}$ in free $Ph_3PO$, as far as the *q*-mode[17], hence the band we observe at 1122 $cm^{-1}$ may be composite. Thus it appears that minor contamination of triphenylphosphine complexes of rhodium with triphenylphosphine oxide is even more common than is often appreciated.

We have briefly examined the reaction of yellow hydridotetrakis(triphenylphosphine)rhodium(I) with dilute mineral acids. Thus, reaction with dilute hydrochloric acid affords pure chlorotris(triphenylphosphine)rhodium(I), which gives no mass spectral evidence for the presence of $Ph_3PO$. Reaction of $HRh(PPh_3)_4$ with dilute nitric acid affords, reproducibly, a green complex which is a non-electrolyte and which gives an infrared spectrum consistent with the presence of nitrosyl [$\nu$(NO) 1646, 1635 (sh) and 1593 (?) $cm^{-1}$] and nitrato [1539 (?), 1512, 1271, 985, 827, 790 $cm^{-1}$] ligands. Analysis suggests the empirical formula $RhC_{36}H_{30}N_3O_7P_2$, thus the complex appears to be the nitrato analogue of $RhCl_2(NO)(PPh_3)_2$ for which $\nu$(NO) 1630 $cm^{-1}$ [18]. However mass spectroscopic examination shows only the fragmentation pattern for triphenylphosphine oxide there being, in particular, no $P^+$ peak (*m/e* 262) for $Ph_3P$. Thus the alternative formulation of $Rh(Ph_3PO)_2(NO)_2(NO_3)$ must be considered, and on present evidence, preferred. An intense band at 1098 $cm^{-1}$ may be assigned as $\nu(P{=}O)$ and another IR band at 1539 $cm^{-1}$ may be $\nu$(NO) rather than a nitrate mode. We have noted that the reaction of $HRh(PPh_3)_4$ with dilute perchloric acid is complex and yields, ultimately, a product containing only coordinated triphenylphosphine oxide. We are attempting to investigate the reaction mechanistically in the hope that we shall be able to clarify a number of points raised here.

## EXPERIMENTAL

Infrared spectra were recorded on nujol mulls in caesium iodide supports between 4000 and 250 $cm^{-1}$ with a Perkin–Elmer 457 instrument. The spectra of new bis(2,2'-bipyridine)rhodium(III) complexes were recorded between 400 and 200 cm$^{-1}$ with a Perkin–Elmer 225 instrument. Each new compound gave a spectrum consistent with the presence of *cis*-bis(2,2'-bipyridine) ligands[19]. $^1$H NMR spectra at 100 MHz were recorded for nitromethane solutions of [Rh(Bipy)$(PPh_3)_2H_2$]$ClO_4$ using TMS as an internal reference, with a Perkin–Elmer R.14 instrument. Mass spectra were recorded at 70 eV with an AEI MS9 mass spectrometer. Conductivity measurements were made for $10^{-3}$ *M* solutions of complex in pure nitromethane with a Henelec bridge.

*Preparations*

Synthesis of [Rh$^{III}$(Bipy)$_2$RX]$ClO_4$ where RX is an organic halide—the initial stage of each preparation was the same and is given here. The working up of each compound was different in detail and is given separately.

Rhodium trichloride trihydrate (0.26 g, 1 mmole) was dissolved in nitrogen-saturated methanol (100 ml). Excess organic halide was added to the solution followed by 2,2'-bipyridine (0.312 g, 2 mmole) in nitrogen saturated methanol (20 ml). [Alternatively pure Rh(Bipy)$_2$Cl$_2\cdot$Cl$\cdot$2 $H_2O$ could be used as the source of rhodium and bipyridine]. Sodium borohydride was slowly added to the solution which was maintained under an atmosphere of nitrogen until the colour changed through red-violet to brown, the resulting solution was then refluxed for 2 h and cooled.

*Iodophenylbis(2,2'-bipyridine)rhodium(III) perchlorate.* An excess of sodium perchlorate was added to the brown solution and excess solvent was removed on a rotatory evaporator. The solid residue was washed well with water to remove soluble components and with ether to remove iodobenzene. The remaining material was recrystallised from a water/methanol mixture to afford yellow crystals of the product.

*Chlorobenzylbis(2,2'-bipyridine)rhodium(III) perchlorate.* A procedure similar to that above was followed. The crude material was recrystallised from an acetone/water mixture to give brown-yellow crystals of complex.

*Iodomethylbis(2,2'-bipyridine)rhodium(III) perchlorate.* Solid material remaining after the reflux period was removed by filtration. Excess sodium perchlorate was added to the dark brown filtrate which was then treated as above. The crude product was recrystallised from a methanol/water mixture to afford orange-yellow crystals of the complex. The repeat of this preparation in which methyl iodide was added after the reduction of the rhodium with sodium borohydride gave an identical product.

*Iodoethylbis(2,2'-bipyridine)rhodium(III) perchlorate.* The method was identical with that of the reaction with iodomethane. The crude material was recrystallised from methanol/water to give orange-brown crystals of complex.

*Bromobenzylbis(2,2'-bipyridine)rhodium(III) perchlorate.* The filtrate was treated with excess sodium perchlorate and worked up as for the other compounds. The crude compound was recrystallised from methanol/water to afford brownish-yellow crystals of the pure complex.

In a separate experiment Rh(Bipy)$_2$Cl$_2\cdot$Cl$\cdot$2 $H_2O$ (0.24 g) was dissolved in nitrogen-saturated methanol and reduced, under an atmosphere of nitrogen, with freshly prepared sodium amalgam until the solution assumed a reddish purple colour. The amalgam was removed from the reaction medium and an excess of benzylbromide was added to the remaining solution. The colour changed to orange-brown. The solution was filtered and treated with excess sodium perchlorate and worked up as described for the products from the borohydride reductions. Recrystallisation of the final product from methanol/water gave a complex identical to that prepared by the borohydride route.

*Dihydridobis(triphenylphosphine) bis(2,2'-bipyridine) rhodium(III) perchlorate.* Pure $Rh(Bipy)_2Cl_2 \cdot Cl \cdot 2\ H_2O$ (0.24 g) was dissolved in nitrogen saturated methanol (50 ml) under a nitrogen atmosphere. An excess of sodium borohydride was added and, when the colour of the solution became reddish-violet a ten-fold molar excess of triphenylphosphine was rapidly introduced. The solution was vigorously stirred and the colour changed to pink-brown at which stage it was set aside for 1 h. The solution was filtered and addition of sodium perchlorate to the filtrate afforded white crystals of the product. A duplicate experiment which was identical except for the replacement of sodium borohydride by sodium amalgam gave no hydrido complex.

*The reaction of rhodium(III) compounds with triphenylphosphine in alkaline ethanol.* The conditions we employed were essentially those reported recently by Robinson and his co-workers[13]. We find that the rhodium may be introduced as the trichloride, as $Rh(Bipy)_2X_2 \cdot X$ (X = Cl, Br) or as dichlorobis(di-2-pyridylamine)rhodium(III) chloride and that, under our conditions, the product was, in each case, "$HRh(PPh_3)_4$". We used a ten-fold excess of phosphine and found that under air orange-yellow products were obtained [$\nu$(RhH) 2140 cm$^{-1}$]. These correspond in description to specimens of $HRh(PPh_3)_4$ given by Robinson's earlier[14] method using borohydride as reducing agent. Performing the experiments under an atmosphere of nitrogen or argon affords yellow products in good yield [$\nu$(RhH) 2140 cm$^{-1}$] which correspond in description to products obtained more recently by Robinson[13]. All products, including those made by Robinson's method, give mass spectroscopic evidence of contamination with triphenylphosphine oxide. Deliberate use of triphenylphosphine oxide, instead of the phosphine, in alkaline ethanol with $Rh(Bipy)_2Cl_2 \cdot Cl$ gives a reddish-violet solution ($\lambda_m$ 557 nm) identical to that reported[2] for "$Rh(Bipy)_2^+$", however the stability to air oxidation seems superior in the presence of $Ph_3PO$. The triphenylphosphine used in our synthetic work showed no mass spectroscopic evidence of contamination with the oxide.

*Reaction of $HRh(PPh_3)_4$ with dilute mineral acids.* (*a*) Dilute $HNO_3$: Hydridotetrakis(triphenylphosphine)rhodium(I) (0.1 g) was suspended in dilute nitric acid (4 *M*) and refluxed for 2 h. The resulting green solid was filtered and washed with water and dried *in vacuo* over $P_4O_{10}$.

(*b*). Dilute hydrochloric acid: The reaction was carried out as above using dilute hydrochloric acid (4 *M*) and afforded pure chlorotris(triphenylphosphine)-rhodium(I)[16] for which no mass spectroscopic evidence of contamination with triphenylphosphine oxide was found.

Analytical data and other criteria of purity are gathered into the table.

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## REFERENCES

1 G. Mestroni, A. Camus and E. Mestroni, *J. Organometal. Chem.*, 24 (1970) 775.

2 B. Martin, W. R. McWhinnie and G. M. Waind, *J. Inorg. Nucl. Chem.*, 23 (1961) 207.
3 E. D. McKenzie, *Coord. Chem. Rev.*, 6 (1971) 187.
4 A. J. Carty and P. C. Chieh, *J. Chem. Soc., Chem. Commun.*, (1972) 158.
5 M. Hinamoto, S. Ooi and H. Kuroya, *J. Chem. Soc., Chem. Commun.*, (1972) 356.
6 S. E. Livingstone and B. Wheelahan, *Aust. J. Chem.*, 17 (1964) 219.
7 K. C. Dewhurst, W. Kein and C. A. Reilly, *Inorg. Chem.*, 7 (1968) 546.
8 C. Cocevar, G. Mestroni and A. Camus, *J. Organometal. Chem.*, 35 (1972) 389.
9 J. D. Miller and F. D. Oliver, personal communication (paper submitted to *J. Chem. Soc., Dalton Trans*, 1972).
10 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1963) 3594.
11 G. C. Kulasingam, Ph.D. Thesis, University of London (1967); see also W. R. McWhinnie, *Coord. Chem. Rev.*, 5 (1970) 293.
12 G. C. Kulasingam, W. R. McWhinnie and J. D. Miller, *J. Chem. Soc. A*, (1969) 521.
13 N. Ahmad, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans*, (1972) 843.
14 J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, (1970) 2947.
15 D. H. Williams, R. S. Ward and R. G. Cooks, *J. Amer. Chem. Soc.*, 90 (1968) 966.
16 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A*, (1966) 1711.
17 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, 24 (1968) 845.
18 S. D. Robinson and M. F. Uttley, *J. Chem. Soc. A*, (1971) 1254.
19 I. I. Bhayat and W. R. McWhinnie, *Spectrochim. Acta, Part A*, 28A (1972) 743.