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Reactivity of Rh(I) and Rh(III) complexes containing a PNO hydrazonic ligand toward HCl

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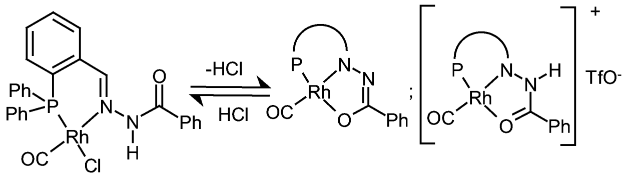
Received 7th January 2002, Accepted 31st January 2002
First published as an Advance Article on the web 20th March 2002

The tridentate hydrazonic ligand 2-(diphenylphosphino)benzaldehyde benzoylhydrazone (HPNO) reacts with $Rh_2(CO)_4Cl_2$ in toluene or THF leading to the formation of the chloro Rh(III) complex [$RhCl_3$(HPNO)] (**5**) and of the carbonyl Rh(I) complex [Rh(PNO)(CO)] (**3**); the reaction occurs with evolution of CO and H_2. The same products are obtained on refluxing a THF or a toluene solution of the chloro-carbonyl Rh(I) complex [RhCl(HPN)(CO)] (**2**). Furthermore, complex **5** also forms on bubbling gaseous HCl into a solution of **3**, but in this case its formation is preceded by the precipitation of another species that is tentatively identified as the hydride-carbonyl Rh(III) complex [$RhCl_2H$(HPN)(CO)] (**4**). Pure **5** is synthesized by reacting equimolar amounts of HPNO and hydrated $RhCl_3$ in THF at room temperature. Once dissolved in dmso, complex **5** transforms into complex [$RhCl_2$(PNO)(dmso)]·dmso (**6**) by elimination of a HCl molecule; complex **6** has been structurally characterized. On bubbling an excess of HCl into a solution of the acetyl Rh(III) complex [RhI(MeCO)(PNO)] (**7**), complex **5** and acetaldehyde are produced. Conversely, on using a stoichiometric amount of HCl, the reaction brings to the acetyl complex [$RhCl_{1.6}I_{0.4}$(MeCO)(HPNO)]·CH_2Cl_2 (**8**), which has been characterized by X-ray crystallography.

Introduction

As part of our ongoing research program on the coordinating capability of potentially tridentate ligands towards d^8 metal ions,[1] we have recently described the different coordination modes adopted by the PNO ligand, 2-(diphenylphosphino)-benzaldehyde benzoylhydrazone, in a series of carbonyl rhodium(I) complexes.[2] Depending on the experimental conditions, the ligand can coordinate the metal maintaining its protic character (HPN or HPNO coordination modes) or it can lose the hydrazonic proton and act as an anionic PNO chelator. The three different types of complexes arising from the three different coordination modes are depicted in Scheme 1. Complex **2** has been obtained by reacting the HPNO ligand and $Rh_2(CO)_4Cl_2$ in diethyl ether at room temperature; under these conditions **2** precipitates just after having mixed the reagents. Later on, we repeated the same reaction in different solvents like THF and toluene, observing again the fast precipitation of a solid; but surprisingly, once characterized, the resultant product was found to be a completely different species from that isolated in diethyl ether.



HPN PNO HPNO

2 3

Scheme 1 Ligand HPNO and its coordination modes towards Rh(I).

The aim of this paper is to describe the new course that the reaction takes in THF and toluene and the nature of the corresponding products.

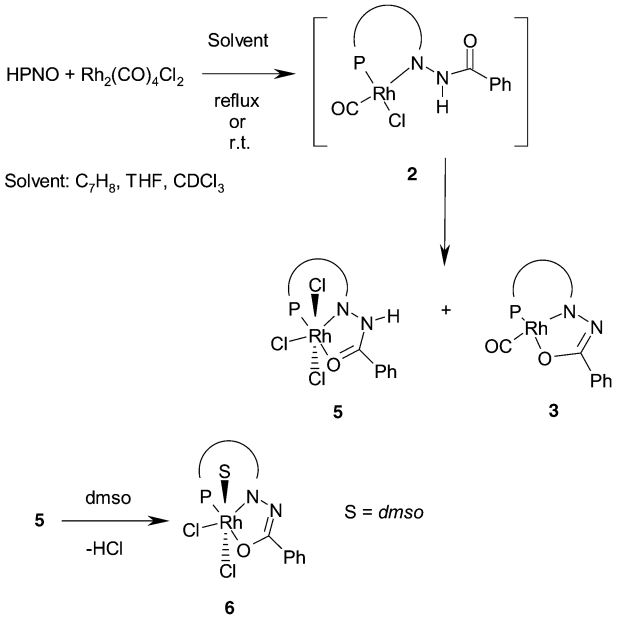
Results and discussion

Synthesis

When the potentially tridentate ligand HPNO is reacted with $Rh_2(CO)_4Cl_2$ in diethyl ether, the complex [RhCl(HPN)(CO)] (**2**) quickly precipitates as an orange solid.[2] In this complex, the hydrazone shows a neutral HPN bidentate behaviour, with exclusion of the C=O group by the coordination sphere (Scheme 1).

When the same reaction is repeated in THF at room temperature, initially the solution becomes orange, probably because of the formation of **2**, but within one hour of stirring a floccular yellow solid precipitates. The same outcome is observed on repeating the reaction under reflux (THF or toluene as solvent), but in this case the precipitation of the yellow solid is much faster. Interestingly, the same yellow product quickly precipitates on refluxing a toluene or THF solution of **2**, or on standing a deuterated chloroform solution of **2** at room temperature for one day. The IR spectrum of the filtered solid shows the characteristic signals of a N–H bond and of a coordinated amide C=O group at 3180w cm^{-1} and 1600s–1558vs cm^{-1}, respectively; moreover, no signal is detected for a CO group bound to rhodium. The elemental analysis of the filtered solid agrees with the unexpected formula [$RhCl_3$(HPNO)] (**5** in Scheme 2); the ligand is neutral and PNO coordinated, and the coordination octahedron is completed by three chlorine atoms. For all the abovementioned reactions, as a consequence of the refrigeration of the mother liquor at −18 °C, crystals of the carbonyl Rh(I) complex **3**[2] (Scheme 1)

DOI: 10.1039/b201174n



Scheme 2 Formation of complexes **5** and **6**. (The dmso lattice solvent of complex **6** has been omitted for clarity.)

are obtained. On the basis of the weighted amounts a rough **3** : **5** = 2 : 1 molar ratio can be established.

Complex **5** is obtained as unique product by reacting equimolar amounts of HPNO and $RhCl_3 \cdot 3H_2O$ in THF at room temperature, as confirmed by the IR spectrum of the yellow solid which forms within 3 hours of stirring.

The low solubility of **5** forced us to record its NMR spectra in d_6-dmso: in this solvent the ^1H NMR spectrum does not show any N–H signal; the ^{31}P NMR spectrum shows a doublet centred at 38.8 ppm with a J_{Rh-P} = 116 Hz, a classic value for a Rh(III) complex.[3]

By slow evaporation of a dmso solution of **5**, crystals suitable for X-ray analysis were collected; the crystalline structure reveals the following complex: $[RhCl_2(PNO)(dmso)] \cdot dmso$ (**6** in Scheme 2); the metal centre is coordinated by the three donors of the ligand, by two chlorine atoms and, in an apical position, by a dmso molecule bound to rhodium through the S atom (see Crystallographic section).

Thus, in dmso complex **5** loses a HCl molecule to give complex **6**; the dmso induced deprotonation of a hydrazone bound to a metal ion has already been observed by us in some palladium(II) complexes.[1] In complex **6** the anionic character of the ligand is confirmed by the IR spectrum of the crystals (disappearance of the N–H and of the C=O stretching bands), while the coordinated dmso molecule originates a band at about 1129 cm^{-1}, a characteristic value for dmso S-coordinated to a Rh(III) ion.[4]

A careful examination of the experimental findings concerning the **2** ⟶ **5** transformation, leads to the conclusion of eqn. (1) as the overall reaction scheme.

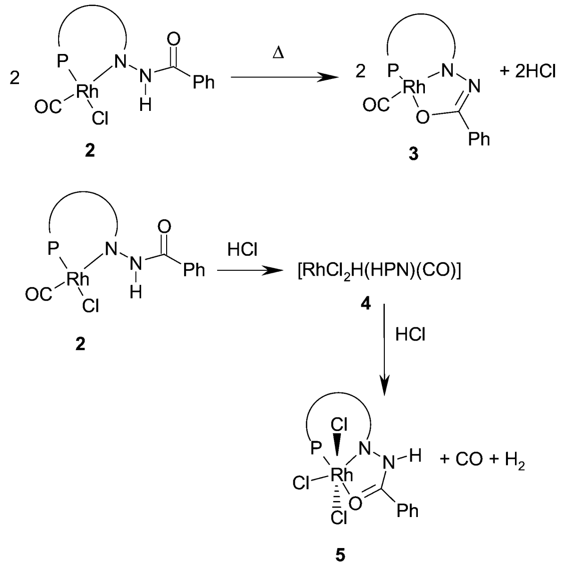
$$3(\mathbf{2}) \longrightarrow 2(\mathbf{3}) + (\mathbf{5}) + CO + H_2 \qquad (1)$$

It is clear that the formation of **5** requires the presence, in the reaction system, of HCl. This has been confirmed by bubbling gaseous HCl into a toluene solution of **3**: the chloride complex **5** is still recovered, although its formation is preceded by the precipitation of a complex mixture of different products.

The reaction has been spectroscopically monitored (both by IR and ^1H NMR techniques), but owing to the high reaction speed and the low solubility of the products, only limited useful information has been obtained: in the IR spectrum, besides some characteristic signals for **5**, two strong bands at 2093 cm^{-1} and 2070 cm^{-1} and a medium band at 2009 cm^{-1} are visible. The first two are characteristic values for C≡O groups coordinated to a Rh(III) ion,[5] while the band at 2009 cm^{-1} can be tentatively attributed to a Rh–H stretching band,[6] so that the hypothesis of the formation of a hydrido-carbonyl intermediate can be advanced; the two carbonyl stretching bands could be attributed to two different isomeric arrangements around the metal centre. Repeated attempts aimed at isolating the hydride intermediate in a pure form have always led to the formation of complex mixtures.

Two points must be clarified in order to justify eqn. (1): (i) where does HCl originate, and (ii) does the reaction proceed with the elimination of CO and H_2 or through the elimination of formaldehyde.

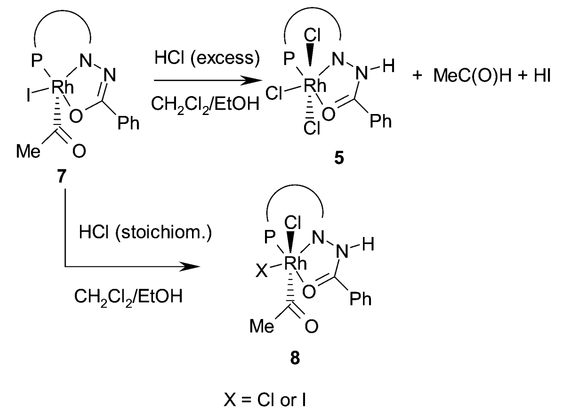
As regards HCl, this can only originate from complex **2**. Then the first step must be the detachment of a HCl molecule from **2** with the consequent formation of a molecule of **3** (Scheme 3); the HCl elimination might be assisted by an intramolecular hydrogen bond of the type Rh–Cl · · · H–N, whose existence has been proved in a chloro-methyl Pd(II) complex containing the same hydrazinic moiety.[1] The so formed hydrochloric acid can now follow two different pathways: (i) to react again with complex **3** and restore complex **2** (Scheme 1) or (ii) oxidatively add on a second molecule of **2**, giving rise to a hydrido-carbonyl Rh(III) intermediate (**4** in Scheme 3). The final step requires the intervention of an additional molecule of HCl, which must derive from a second **2** ⟶ **3** transformation; this accounts for the **3** : **5** = 2 : 1 molar ratio found experimentally.



Scheme 3 Proposed reaction scheme for the formation of **5** starting from **2**.

As regards the nature of the volatiles, the simple elimination of CO and H_2 is more likely than formaldehyde elimination.[7] This in fact would imply the insertion of a hydride into the Rh–CO bond (see complex **4** in Scheme 3), with consequent formation of a formyl intermediate complex, a thermodynamically disfavoured step.[8] Repeated attempts aimed at detecting formaldehyde as the acetal of ethyl alcohol were all unsuccessful (see Experimental). Moreover, the elimination of CO has been established by the following experiments: (a) gas chromatographic analysis of the volatiles evolved from a toluene solution of **2** heated at 85 °C for three hours; and (b) formation of palladium black when the same volatiles have been bubbled into a water solution of K_2PdCl_4. On the basis of these findings it must be concluded that the formation of **5** proceeds through the elimination of CO and H_2, as depicted in Scheme 3.

In light of the aforementioned results, it is not surprising that complex **5** can be obtained also by bubbling gaseous HCl into a CH_2Cl_2/EtOH mixture of the penta-coordinated acetyl Rh(III) complex [RhI(MeCO)(PNO)] (**7** in Scheme 4), whose synthesis



Scheme 4 Reactivity of complex **7** toward HCl. (The dichloromethane molecule of complex **8** has been omitted for clarity.)

and characterization have previously been reported.[2] The reaction leads to the fast precipitation of **5** and to the elimination of acetaldehyde (detected as an acetal of ethyl alcohol, see Experimental).

In contrast, when a stoichiometric amount of gaseous HCl is slowly bubbled into a solution of **7**, the precipitation of **5** is much slower and well shaped crystals of the acetyl Rh(III) complex $[RhCl_{1.6}I_{0.4}(MeCO)(HPNO)]\cdot CH_2Cl_2$ (**8**) are recovered after refrigeration of the mother liquor (Scheme 4). The X-ray analysis shows a neutral tridentate PNO behaviour of the ligand, with the acetyl ligand and a chlorine atom mutually *trans* on the apices of the octahedron.

The protonated nature of the hydrazone is confirmed by a weak IR band at 3205 cm^{-1}; the acetyl ligand gives rise to a singlet at 2.47 ppm in the ^{1}H NMR spectrum and to a stretching band centred at 1694 cm^{-1} in the IR spectrum. Unfortunately, the few collected crystals have not allowed a ^{31}P NMR spectrum to be recorded; no other characterizable product has been isolated from the reaction mixture. Thus, it appears that the reaction between **7** and HCl proceeds with the initial protonation of the hydrazonic nitrogen of the ligand and formation of a coordinative Rh–Cl bond; the intervention of a second HCl molecule starts to substitute the iodide ligand rather than the acetyl one and only in the presence of a large excess of HCl does the elimination of acetaldehyde take place, probably *via* a hydroxy carbene intermediate of the type Rh=C(OH)Me.[8]

Structures of the complexes 6 and 8

Figs. 1 and 2 show the crystal structures and numbering schemes of complexes **6** and **8**, respectively; Tables 1 and 2 report the most relevant bond parameters.

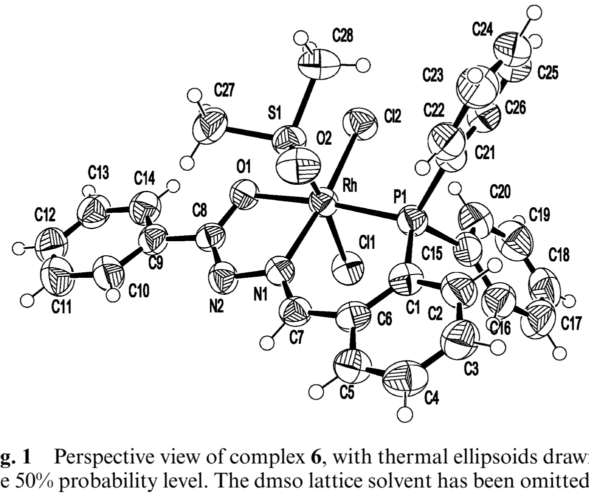


Fig. 1 Perspective view of complex **6**, with thermal ellipsoids drawn at the 50% probability level. The dmso lattice solvent has been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **6**, with s.u.'s in parentheses

Rh–N1	1.998(5)	O1–C8	1.316(7)
Rh–O1	2.081(4)	N1–N2	1.392(6)
Rh–P	2.263(2)	N1–C7	1.267(7)
Rh–S1	2.291(2)	N2–C8	1.306(7)
Rh–Cl1	2.368(2)	C1–C6	1.398(8)
Rh–Cl2	2.357(2)	C6–C7	1.477(8)
P–C1	1.814(6)	C8–C9	1.480(8)
P–C21	1.828(6)		
P–C15	1.837(7)		
N1–Rh–O1	80.2(2)	C1–P–C15	105.3(3)
N1–Rh–P	95.6(1)	C21–P–C15	103.8(3)
O1–Rh–P	174.5(1)	C1–P–Rh	110.8(2)
N1–Rh–S1	88.8(1)	C21–P–Rh	116.2(2)
O1–Rh–S1	90.4(1)	C15–P–Rh	114.8(2)
P–Rh–S1	93.07(6)	C8–O1–Rh	107.7(3)
N1–Rh–Cl2	171.1(1)	C8–N2–N1	113.5(5)
O1–Rh–Cl2	91.0(1)	C7–N1–N2	115.2(5)
P–Rh–Cl2	93.15(7)	C7–N1–Rh	131.4(4)
S1–Rh–Cl2	92.64(6)	N2–N1–Rh	113.4(4)
N1–Rh–Cl1	84.7(1)	C2–C1–C6	117.8(6)
O1–Rh–Cl1	86.7(1)	C6–C7–N1	129.5(5)
P–Rh–Cl1	89.41(5)	N2–C8–O1	125.2(5)
S1–Rh–Cl1	173.28(6)	N2–C8–C9	117.9(5)
Cl1–Rh–Cl2	93.46(6)	O1–C8–C9	116.9(5)
C1–P–C21	105.0(3)		

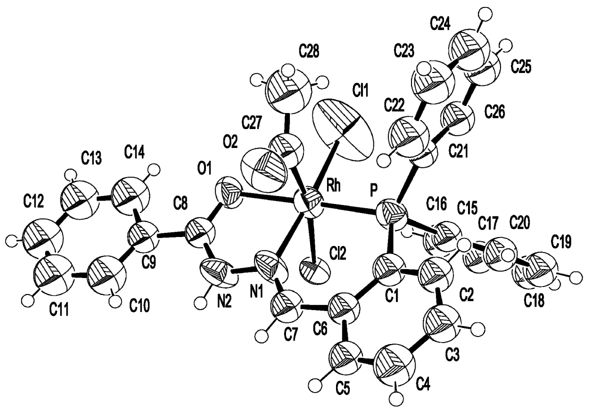


Fig. 2 Perspective view of complex **8**, with thermal ellipsoids drawn at the 50% probability level. The dichloromethane molecule has been omitted for clarity.

The coordination around Rh(III) in complex **8** can be described as a distorted octahedral geometry. The equatorial plane contains the chelating PNO ligand in its protonated form and it is completed by a halogen atom *trans* to the N atom of the ligand. Structure refinement showed that some molecules contain a chlorine, while the remaining molecules keep the iodine present in the original compound. The ratio Cl/I has been refined as approximately 60 : 40. The apical positions are filled by a chlorine and an acyl group. Although a detailed geometric discussion is not allowed due to the limited quality of the data, some general considerations can be evidenced by structural determination. Ligand coordination causes the formation of one five-membered and one six-membered chelating ring and their bite angles (80.7(5) and 94.7(4)° respectively) are similar to those already observed in our previous work.[2] The distortion from regular octahedron is principally due to chelation constraints, but it is also evident in the bending of the apical ligands (C27–Rh–Cl2 = 168.2(4)°) probably due to repulsion between Cl2 and phosphorus-bound phenyl rings, as shown by the particularly stretched P–Rh–Cl2 angle (101.4(1)°) and by the short intramolecular distance Cl2 ··· C16 = 3.280(1) Å. The apical Rh–Cl2 distance is apparently significantly longer than the equatorial Rh–Cl1 bond. As stated in the Experimental section, the value of the abnormal apical Rh–Cl2

Table 2 Selected bond lengths (Å) and angles (°) for **8**, with s.u.'s in parentheses

Rh–N1	1.99(1)	O1–C8	1.33(1)
Rh–C27	2.06(2)	O2–C27	1.17(1)
Rh–O1	2.129(7)	N1–C7	1.29(1)
Rh–P	2.233(4)	N1–N2	1.38(1)
Rh–Cl1	2.44(2)	N2–C8	1.27(1)
Rh–I1	2.569(6)	C1–C6	1.40(1)
Rh–Cl2	2.648(3)	C6–C7	1.49(2)
P–C15	1.77(1)	C8–C9	1.52(2)
P–C21	1.80(1)	C27–C28	1.40(2)
P–C1	1.83(1)		
N1–Rh–C27	91.4(5)	C15–P–C1	103.3(7)
N1–Rh–O1	80.7(5)	C21–P–C1	102.8(7)
C27–Rh–O1	87.6(4)	C15–P–Rh	119.3(6)
N1–Rh–P	94.7(4)	C21–P–Rh	116.3(4)
C27–Rh–P	88.6(4)	C1–P–Rh	112.1(6)
O1–Rh–P	173.9(3)	C8–O1–Rh	105.9(9)
N1–Rh–Cl1	170.5(6)	C7–N1–N2	114(1)
C27–Rh–Cl1	94.3(7)	C7–N1–Rh	135(1)
O1–Rh–Cl1	92.0(6)	N2–N1–Rh	110(9)
P–Rh–Cl1	93.0(5)	C8–N2–N1	119(1)
N1–Rh–Cl2	81.6(3)	C2–C1–C6	117(1)
C27–Rh–Cl2	168.2(4)	N1–C7–C6	123(1)
O1–Rh–Cl2	81.9(2)	N2–C8–O1	123(1)
P–Rh–Cl2	101.4(1)	O2–C27–C28	125(2)
Cl1–Rh–Cl2	91.5(5)	O2–C27–Rh	114(1)
C15–P–C21	100.9(7)	C28–C27–Rh	121(1)

bond length could partly be an artefact deriving from a possible residual Cl/I substitutional disorder involving also the apical position, but the above described hindrance of phenyl rings around the apical coordination site points out that there exists a steric reason for the observed elongation.

The six-membered ring shows a slight deviation from planarity with phosphorus lying 0.22 Å away from the mean plane, the ligand core is planar within 0.3 Å. The distances among the donor atoms of the ligand and the metal are all in the typical range observed in similar structures.

The acyl group is in an eclipsed geometry with respect to the equatorial coordination bonds as shown by the torsion angle N1–Rh–C27–O2 = 6°. The crystal packing is characterized by hydrogen bonded centrosymmetric dimers based on N–H ··· Cl interactions (N2 ··· Cl2i = 3.177(1) Å, N2–H ··· Cl2i = 162.75(3)° i = $-x$, $-y$, $-z$). The crystal packing is completed by one CH_2Cl_2 molecule.

For complex **6** the coordination geometry is similar to the one described for **8**, with a dmso molecule substituted for the acyl group of **8** and with no partial replacement of the equatorial chlorine. The distances around rhodium reflect the charged nature of the ligand by a shortening of the equatorial Rh–O and Rh–Cl bonds, while the Rh–P bond is slightly elongated with respect to **8**. The relevant strengthening of the apical Rh–Cl bond in comparison to the value observed for **8** derives from the different *trans* influence of dmso with respect to the acyl group. As regards the ligand geometry, deprotonation on N2 apparently does not affect significantly the bond distances within the ligand backbone. The octahedral geometry is slightly less distorted: the distortion due to the constraints imposed by the ligand rigidity is the same, but the S1–Rh–Cl1 angle is wider (173.28(6)°) than the corresponding angle in **8**.

Crystal packing is principally due to weak van der Waals interactions, and it is completed by two dmso molecules. One of the solvent molecules is disordered between two alternative positions.

Conclusions

We have shown that the chloro-carbonyl rhodium(I) complex [RhCl(HPN)(CO)] (**2**) easily leads to the formation of the chloro rhodium(III) complex [$RhCl_3$(HPNO)] (**5**). This remarkable conversion is triggered by the release of a HCl molecule from the starting rhodium(I) complex, with formation of the carbonyl rhodium(I) complex [Rh(PNO)(CO)] (**3**). The released HCl molecule reacts with a second molecule of **2**, leading to the probable formation of the hydride-carbonyl intermediate [$RhCl_2H$(HPN)(CO)] (**4**). The final step considers a reaction between a second molecule of HCl, coming from another molecule of **2**, and complex **4**, with formation of **5** and elimination of CO and H_2.

The reaction of the penta-coordinated acetyl rhodium(III) complex [RhI(MeCO)(PNO)] (**7**) with an excess of HCl leads again to the formation of **5** and to the evolution of acetaldehyde; conversely, the use of a stoichiometric amount of HCl blocks, at least partially, the reaction to the stage of the iodo-chloro-acetyl complex [$RhCl_{1.6}I_{0.4}$(MeCO)(HPNO)]·CH_2Cl_2 (**8**), which probably plays the role of intermediate in the **7** ⟶ **5** transformation.

Experimental

General methods

All reactions were performed under an atmosphere of dry nitrogen employing standard Schlenk techniques. Solvents were dried prior to use and stored under nitrogen. Elemental analyses (C, H, N and S) were performed by using a Carlo Erba Model EA 1108 apparatus. Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range using KBr disks. ^{1}H NMR spectra were obtained on a Bruker 300 FT spectrophotometer using $SiMe_4$ as internal standard, while ^{31}P NMR spectra were recorded on a Bruker CPX 200 FT using 85% H_3PO_4 as external standard. MS spectra (CI, methane) were recorded on a Finnigan SSQ 710 spectrometer, collecting positive ions; relative intensities are reported in parentheses. The GC-MS analyses were made by using an HP-5890 series 2 (Hewlett-Packard) gas chromatograph, equipped with a MSD HP-5971A detector and a split–split ness injector. The gas chromatographic CO detection was made using a Carlo Erba Model Fractovap C, equipped with a ATC/f detector, and a column packed with 5 Å molecular sieves. Gaseous HCl was purchased from Aldrich, as well as hydrated $RhCl_3$. The syntheses and the characterizations of HPNO,[9] **2**, **3** and **7** have already been reported.[2]

[$RhCl_3$(HPNO)] (5)

Method 1. HPNO (0.100 g, 0.24 mmol) was dissolved in THF (30 cm^3) and an equimolar amount of hydrated $RhCl_3$ (51.0 mg) was added, the mixture was then stirred for 3 h at room temperature. A flocculent yellow solid was filtered off, washed with THF and diethyl ether and then dried *in vacuo* for several hours (0.106 g, 70%).

Method 2. HPNO (0.105 g, 0.26 mmol) and $Rh_2(CO)_4Cl_2$ (0.050 g, 0.13 mmol) were placed in refluxing toluene or THF (15 cm^3). The immediate formation of a flocculent yellow solid was observed. The mixture was refluxed for two hours and then **5** was filtered off, washed with the solvent and dried *in vacuo* (0.045 g, 28%). The remaining solution was concentrated *in vacuo* and refrigerated at −20 °C for a week, obtaining crystals of **3** (0.085 g, 62%). Similar yields were obtained on carrying out the reactions at room temperature for one day.

Method 3. **2** (0.030 g, 0.05 mmol) was refluxed in toluene or THF (10 cm^3); after 2 h a flocculent yellow solid was filtered off and worked up as reported above (0.010 g, 31%). The remaining solution was concentrated *in vacuo* and refrigerated at −20 °C for a week, obtaining crystals of **3** (0.008 g, 29%). (Found: C, 50.44; H, 3.62; N, 4.49%. $C_{26}H_{21}Cl_3N_2OPRh$ requires C, 50.56; H, 3.43; N, 4.53%). ν_{max}/cm^{-1} (NH) 3180w, (C=O + C=N) 1600s–1558vs; *m*/*z* 545 (M − HCl − Cl, 100%).

Table 3 Crystal data and structure refinement for **8** and **6**

	8	**6**
Empirical formula	$C_{29}H_{26}Cl_{3.6}I_{0.4}N_2O_2PRh$	$C_{32}H_{38}Cl_2N_2O_4PRhS_3$
Formula weight	746.81	815.6
Wavelength/Å	0.71069	1.54178
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a/Å	18.172(5)	13.939(5)
b/Å	22.005(5)	12.862(5)
c/Å	14.952(5)	20.133(5)
β/°	—	92.10(5)
Volume/Å^3	5979(3)	3607(2)
Z	8	4
Calculated density/Mg m^{-3}	1.659	1.502
Absorption coefficient/mm^{-1}	1.390	7.544
F(000)	2979	1672
Crystal size/mm^3	0.6 × 0.4 × 0.3	0.4 × 0.4 × 0.3
θ range/°	3–22	3–70
Reflections collected/unique	7186/3671	6996/6806
Data/restraints/parameters	3671/12/363	6806/96/444
Goodness-of-fit on F^2	0.578	0.934
Final R indices [$I > 2\sigma(I)$]	$R1^a = 0.0422$, $wR2^b = 0.0738$	$R1^a = 0.0606$, $wR2^b = 0.1728$
R indices (all data)	$R1^a = 0.2232$, $wR2^b = 0.0967$	$R1^a = 0.0871$, $wR2^b = 0.1973$

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CO detection

Method 1. 2 (0.080 g, 0.14 mmol) was placed in a 50 cm^3 capacity Schlenk tube and dissolved in toluene (7 cm^3). The reactor was closed with a rubber stopper and thermostatted at 85 °C with stirring. After 3 h, 1 cm^3 of the vapour phase was withdrawn by syringe and analysed by GC.

Method 2. 2 (0.100 g, 0.17 mmol) was placed in a 50 cm^3 capacity two necked round bottom flask, equipped with a magnetic stirrer bar and connected with a gas nitrogen line; the reaction vessel was connected to a Schlenk tube containing K_2PdCl_4 (0.018 g) dissolved in water (3 cm^3). The solution containing the rhodium complex was heated at 85 °C for 3 hours, and the evolved gases were bubbled, by a gentle nitrogen flux, into the palladium containing solution; within two hours palladium black release was observed.

H_2CO detection

The methodology and amount of **2** were equivalent to those described for the CO detection in Method 1, but in this case the evolved gases were bubbled into a dry ethanol solution previously acidified with gaseous HCl. After neutralization of the solution with sodium carbonate, this was analysed by GC-MS.

[$RhCl_2$(PNO)(Me_2SO)]·(Me_2SO) (6)

5 (0.010 g, 0.02 mmol) was dissolved in Me_2SO-d$_6$ (0.5 cm^3) obtaining a yellow solution. The following NMR data were found: δ_P (Me_2SO-d$_6$) 38.8 (d, J_{Rh-P} = 116 Hz); δ_H (Me_2SO-d$_6$) 8.76 (s, 1H, HC=N), 8.16 (d, 2H, Ph(C=O), ^1J = 7.5 Hz), 8.05 (t, 1H, Ph), 7.90 (t, 1H, Ph), 7.74 (t, 1H, Ph), 7.69–7.32 (m, 14H, Ph). By slow evaporation of the solvent crystals suitable for X-ray analysis were collected. (Found: C, 49.00; H, 4.35; N, 3.89; S, 8.71%. $C_{30}H_{32}Cl_2N_2O_3PRhS_2$ requires C, 48.86; H, 4.37; N, 3.80; S, 8.69%). ν_{max}/cm^{-1} (S=O) 1129s; *m*/*z* 580 (M − 2Me$_2$SO, 14%), 545 (M − 2Me$_2$SO − Cl, 100%).

Reaction of 3 with HCl

3 (0.050 g, 0.08 mmol) was dissolved in toluene (8 cm^3) and gaseous HCl was bubbled through a glass capillary into the solution. Immediately a pale yellow solid precipitated (mixture of **2**, **4** and **5**), which was filtered off, repeatedly washed with toluene and then with water and finally dried *in vacuo* (43 mg). By slow evaporation of the remaining solution **5** was filtered off, washed with toluene and dried *in vacuo* (0.015 g, 31%).

[$RhCl_{1.6}I_{0.4}$(MeCO)(HPNO)]·CH_2Cl_2 (8)

KCl (0.013 g, 0.18 mmol) was placed in a three necked round bottom flask equipped with a dropping funnel containing 5 cm^3 of concentrated H_2SO_4 (96%). The flask was connected with a gas nitrogen line and with a second flask wherein **7** (0.040 g, 0.06 mmol) had been dissolved in a CH_2Cl_2–EtOH mixture (6 cm^3, 1 : 1). H_2SO_4 was slowly dropped onto the solid KCl and the evolved HCl was carried by the nitrogen flux through a trap of H_2SO_4 (96%) and then bubbled through a glass capillary into the metal complex solution. The reported Rh/KCl molar ratio was chosen in order to have a Rh/HCl molar ratio close to 1 : 3, because a preliminary titration of an aqueous solution of HCl obtained with the aforementioned method (NaOH 0.1 M, methyl orange), demonstrated that only one third of the HCl thus formed reaches the reactant solution. KCl was completely converted within 4 h during which time the solution bleached from deep orange to light orange. After addition of 30 ml of diethyl ether a yellow–orange solid precipitated, which was filtered off, washed with diethyl ether and dried *in vacuo*. By IR spectroscopy it was identified as a mixture of **5** and **8**. From the mother liquor a few crystals suitable for X-ray analysis were collected by slow evaporation of the solvent. (Found: C, 45.02; H, 3.25; N, 3.72%. $C_{29}H_{26}Cl_{3.6}I_{0.4}N_2O_2PRh$ requires C, 45.09; H, 3.24; N, 3.76%). The low amount of isolated product did not allow the ^{31}P NMR spectrum to be recorded. δ_H (Me_2SO-d$_6$) 8.73 (s, 1H, HC=N), 8.14 (dbr, 2H, Ph(C=O)), 8.05–7.30 (m, 17H, Ph), 2.47 (s, 3H, MeCO). ν_{max}/cm^{-1} (NH) 3205w, (MeCO) 1694s.

Reaction of 7 with an excess of HCl

A cylinder of gaseous HCl was connected to the reaction vessel *via* a hosepipe with a glass capillary at one end which was immersed into an ice cold CH_2Cl_2–EtOH mixture containing **7** (0.040 g, 0.06 mmol). As soon as HCl reached the solution a yellow solid precipitated, which was filtered off, washed with water and characterized by IR spectroscopy as a mixture of **5** and undefined products. A portion of the resulting solution was neutralized with sodium carbonate and then analyzed by GC-MS. From the mother solution, refrigerated at −18 °C, pure **5** was filtered off, washed and dried *in vacuo* (0.025 g, 69%).

Structure determinations

Air stable crystals suitable for structural determination by single crystal X-ray diffraction were obtained for compounds **6** and **8**. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer employing Cu-Kα radiation for **6** and on a Siemens AED diffractometer with Mo-Kα radiation for **8**. Relevant details of the X-ray experimental conditions, data collection and refinement are given in Table 3. Data were corrected for Lorentz and polarization effects. No decay was observed. In both cases the phase problem was solved by direct methods with SIR97[10] and refinement was carried out by full-matrix least-squares on all F^2 with SHELXL97.[11] All non-hydrogen atoms were refined anisotropically. The quality of structural results for **8** is heavily affected by the poor diffracting power of the tiny crystals (resulting in the paucity of observed reflections and in the relatively low resolution of the collected data) and by a Cl/I substitutional disorder involving the metal coordination sphere, which affects the fine definition of coordination geometry. For compound **6** the Hope[12] absorption correction was applied after the last isotropic refinement, as implemented in SHELXL97, and then the absorption parameters were held fixed in the successive refinement cycles. Hydrogen atoms were introduced in calculated positions and constrained to ride on their parent atoms. The disordered solvent molecule (Me_2SO) in compound **6** was refined applying both geometrical and thermal restraints.

Calculations were performed on a Digital Alpha 255 workstation at the 'Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.' in Parma. Extensive use was made of the Cambridge Structural Database.[13]

CCDC reference numbers 174285 and 174286.

See http://www.rsc.org/suppdata/dt/b2/b201174n/ for crystallographic data in CIF or other electronic format.

Acknowledgements

The authors are thankful to the Centro Interfacoltà di Misure "Giuseppe Casnati" of the University of Parma for technical support. Prof. P. Moggi of the Dipartimento di Chimica Organica ed Industriale of the University of Parma is thanked for the gas chromatographic CO detection. The C.N.R. (Rome) and M.U.R.S.T. (Ministero dell'Università e della Ricerca Scientifica, ex 40%) are gratefully acknowledged for financial support.

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