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Carbonyl rhodium(I) complexes containing a hydrazonic tridentate HNN′O ligand. Synthesis, X-ray structure and reactivity toward methyl iodide

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Abstract

The ligand (2-pyridinecarboxaldehyde) benzoylhydrazone (**HNN′O**) has been reacted with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in diethyl ether, isolating the carbonyl complex $[Rh(\kappa^2\text{-}HNN')(CO)Cl]$ (**1**), where the neutral ligand coordinates the metal through the nitrogen atoms, the amidic oxygen been excluded by the coordination sphere. Repeated attempts aimed to force the ligand to an anionic tridentate coordination, both by prior deprotonation of the free ligand or deprotonation of **1**, have resulted in extensive deposition of metallic rhodium. The reaction between **HNN′O** and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in basic media and in the presence of PPh_3, has led to the isolation of the complex $[Rh(\kappa^2\text{-}N'O)(PPh_3)(CO)]\cdot 1/2CH_2Cl_2$ (**2**), where the anionic ligand is N′O bidentate. Compound **1** has been reacted with an excess of MeI in CH_2Cl_2 or THF, isolating $[Rh(\kappa^2\text{-}HNN')(CH_3CO)ClI]$ (**4**) and $[Rh(\kappa^2\text{-}HNN')(CH_3CO)(THF)ClI]$ (**5**), respectively. Although the oxidative addition step is practically instantaneous in both cases, the migratory insertion step results faster in THF, as established by liquid film IR spectroscopy. Compound **2** has been reacted with MeI in THF isolating the complex $[Rh(\kappa^2\text{-}N'O)(PPh_3)(CO)(Me)I]$ (**6**), which, however, does not transform into the corresponding acyl complex. The crystal structure of complex $\mathbf{2}\cdot 1/4CH_2Cl_2$ has been solved.

Keywords: Rhodium; Insertion; Tridentate ligands; Hydrazones; N ligands

1. Introduction

The use of tridentate ligands in organometallic chemistry and catalysis has received increased attention in the last years [1]. However, the use of protic tridentate ligands in the synthesis of d^8 metal ion complexes does not count a great number of examples [2]. One of the more interesting chemical aspects of this type of ligands, lies in the fact that they can adopt different coordination modes, i.e., mono-, bi- or tridentate, thus giving rise to different structures and steric encumbrances around the metal centre. The hemilability of the bi- and tridentate ligands, due to a donor atom which can reversibly bind a metal, is often invoked as responsible of the observed catalytic activities of the corresponding complexes [2a,3]. Moreover, when the ligand carries an acidic proton, an additional feature is represented by the possibility of varying the electron density on the metal nucleus, depending on the protic or anionic nature of the ligand itself, and this can significantly affect the reactivity of the complexes. As a part of our ongoing interest towards the reactivity of d^8 metal ion complexes containing protic tridentate hydrazonic ligands [4], we have recently shown as the neutral or anionic nature of the HPNO ligand 2-(diphenylphosphino)benzaldehyde benzoylhydrazone strongly influences the reactivity of some carbonyl rhodium(I) complexes toward MeI [5]. Previously, we had found that the reactivity with CO of some methyl Pd(II) complexes containing different

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HNN′O ligands, was strongly dependent on the anionic or neutral nature of these [6]. In this paper, we show the preparation of carbonyl Rh(I) complexes containing this latter type of ligand and their reactivity in the oxidative addition of MeI, highlighting how the coordination mode and the electronic properties of **HNN′O** rule the reaction course and the nature of the final products.

2. Experimental

2.1. General

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 analysis (C, H, N) were performed by using a Carlo Erba Mod. EA 1108 apparatus. Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range by using KBr disks or a NaCl cell. ^1H NMR spectra were obtained on a Bruker 300 FT spectrometer using $SiMe_4$ as internal standard, while $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CPX 200 FT using H_3PO_4 85% as external standard. All spectra were collected at 300 K, unless otherwise reported. The ligand HNN′O was synthesised as previously described [6]. $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and MeI were purchased by Aldrich, while 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene (MTBD) was purchased by Fluka.

2.2. Preparation of the Rh(I) complexes

2.2.1. [Rh(κ²-HNN′)(CO)Cl] (1)

$[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (0.043 g, 0.111 mmol) was dissolved in diethyl ether (20 ml) and **HNN′O** (0.050 g, 0.222 mmol) was added at room temperature (r.t.). The resulting purple solution was stirred at r.t. for 3 h, during which time a deep purple solid was released; consequently the solution became almost uncoloured. The solid was filtered off and dried under vacuum. Yield: 0.076 g (84%). *Anal*. Calc. for $C_{14}H_{11}ClN_3O_2Rh\cdot H_2O$: C, 40.91; H, 2.79; N, 10.09. Found: C, 41.05; H, 3.20; N, 10.26%. ^1H NMR ($CDCl_3$): $\delta = 11.73$ (s, 1H, N–H), 9.91 (s, 1H, C(H)=N), 8.68 (dbr, 1H, H_1), 7.94 (d, 2H, Ph *o*-C(O), $^3J_{H,H} = 7.3$ Hz), 7.63–7.48 (m, 5H, H_3–H_4–Ph), 7.26 (t, 1H, H_2, $^3J_{H,H} = 6.3$ Hz). IR (KBr, *ν*, cm^{-1}): 3220m (N–H), 1974vs (C≡O) (1994 in CH_2Cl_2), 1675s (C=O).

2.2.2. [trans-(PPh₃)₂(CO)Cl]

Compound **1** (0.050 g, 0.122 mmol) was dissolved in dichloromethane (20 ml). PPh_3 (0.032g, 0.122 mmol) was added, obtaining the instantaneous colour change from purple to yellow. Within 2 min a yellow solid precipitated and the resulting mixture was stirred at r.t. for 10 min. The solid was filtered off, washed with diethyl ether and dried in vacuum. Yield: 0.066 g (79%). The characterization was in agreement with the literature data [13].

2.2.3. [Rh(κ²-N′O)(PPh₃)(CO)]·1/2CH₂Cl₂ (2)

HNN′O (0.050 g, 0.222 mmol) was dissolved in dichloromethane (25 ml). To the obtained solution were subsequently added MTBD (0.034 g, 0.04 ml, 0.222 mmol), PPh_3 (0.080 g, 0.222 mmol) and $[Rh(\mu\text{-}Cl)_2(CO)_4]$ (0.060 g, 0.111 mmol). The resulting blood-red solution was stirred at r.t. for 2 h during which time it turned to deep orange. The solvent was partially removed under vacuum and n-hexane was added. Refrigeration at −18 °C led to a deep orange powder. Yield: 0.129 g (84%). *Anal*. Calc. for $C_{32}H_{25}N_3O_2PRh\cdot 1/2CH_2Cl_2$: C, 59.15; H, 3.97; N, 6.37. Found: C, 59.42; H, 4.03; N, 6.47%. ^{31}P NMR ($CDCl_3$): $\delta = 29$ (d, $^1J_{Rh,P} = 127$ Hz). ^1H NMR ($CDCl_3$, 253 K): $\delta = 9.38$ (d, 1H, H_4, $^3J_{H,H} = 8.0$ Hz), 8.74 (d, 1H, H_1, $^3J_{H,H} = 4.4$ Hz), 8.24 (d, 1H, C(H)=N, $^3J_{Rh,H} = 3.3$ Hz), 7.92 (t, 1H, H_3, $^3J_{H,H} = 7.6$ Hz), 7.89 (d, 2H, Ph *o*-C(O), $^3J_{H,H} = 7.4$ Hz), 7.72–7.26 (m, 19H, H_2 and Ph), 5.31 (s, 1H, CH_2Cl_2). IR (KBr, *ν*, cm^{-1}): 1975vs (C≡O). Red crystals of $\mathbf{2}\cdot 1/4CH_2Cl_2$ suitable for X-ray analysis were collected after repeated recrystallization of **2** in a CH_2Cl_2/n-hexane mixture at −18 °C.

2.3. Preparation of the Rh(III) complexes

2.3.1. General method

The carbonyl Rh(I) complex (0.050 g) (0.122 mmol for **1**, in 5 ml of CH_2Cl_2 or THF, 0.076 mmol for **2**, in 5 ml of THF) was treated with a fortyfold excess (0.32 ml for **1**, 0.20 ml for **2**) of MeI at r.t. The reactions were monitored by liquid film IR until no changes were observed. The final products were isolated by partial removal of the solvent under reduced pressure and addition of n-hexane, followed by drying under vacuum for several hours. The reported yields refer to the products recovered as solids.

2.3.2. [Rh(κ²-HNN′)(MeCO)ClI] (4)

The reaction was carried out in dichloromethane. Green solid. Yield: 0.068 g (45%). *Anal*. Calc. for $C_{15}H_{14}ClIN_3O_2Rh$: C, 33.77; H, 2.64; N, 7.88. Found: C, 33.93; H, 2.70; N, 7.76%. ^1H NMR ($CDCl_3$): $\delta =$ 11.80 (s, 1H, N–H), 9.99 (d, 1H, C(H)=N, $^3J_{Rh,H} = 2.7$ Hz), 9.47 (d, 1H, H_1, $^3J_{H,H} = 5.4$ Hz), 8.03 (t, 1H, H_3, $^3J_{H,H} = 7.3$ Hz), 7.97 (d, 2H, Ph *o*-C(O), $^3J_{H,H} = 7.5$ Hz), 7.84 (d, 1H, H_4, $^3J_{H,H} = 7.7$ Hz), 7.54 (m, 2H, H_2+ Ph *p*-C(O)), 7.42 (t, 2H, Ph *m*-C(O), $^3J_{H,H} = 7.6$ Hz), 2.82 (s, 3H, MeC(O)–Rh). IR (KBr, *ν*, cm^{-1}): 3215w (N–H), 1713vs (MeCO+C=O).

2.3.3. [Rh(κ²-HNN′)(MeCO)(THF)ClI] (5)

The reaction was carried out in THF. Brown solid. Yield: 0.029 g (40%). Irreproducible amounts of THF prevented a correct elemental analysis. ^{1}H NMR ($CDCl_3$): the spectrum is identical to that found for **4**, with the exception of two multiplets corresponding to uncoordinated THF (3.74 and 1.84 ppm). IR (KBr, ν, cm^{-1}): 3217w (N–H), 1702vs (MeCO+C=O).

2.3.4. [Rh(κ²-N′O)(PPh₃)(CO)(Me)I] (6)

The reaction was carried out in dichloromethane. Orange solid. Yield: 0.025 g (41%). *Anal*. Calc. for $C_{33}H_{28}IN_3O_2PRh\cdot 1/2CH_2Cl_2$: C, 50.17; H, 3.65; N, 5.24. Found: C, 50.16; H, 3.55; N, 5.25%. ^{31}P NMR ([D_6] DMSO): $\delta = 30.3_d$, $^1J_{Rh,P} = 134$ Hz. ^{1}H NMR (CD_2Cl_2): $\delta = 9.32$ (d, 1H, H_4, $^3J_{H,H} = 8.1$ Hz), 8.73 (m, 1H, CH=N), 8.18 (d, 1H, H_1, $^3J_{H,H} = 5.4$ Hz), 8.15 (d, 2H, Ph *o*-C(O), $^3J_{H,H} = 9.5$ Hz), 7.99–7.92 (m, aromatics), 7.58–7.36 (m, aromatics), 1.34 (t, 3H, $^2J_{Rh,H} = 2$ Hz, Me–Rh). IR (KBr, ν, cm^{-1}): 2066s (C≡O).

2.4. Crystal structure determination of 2·1/4CH₂Cl₂

Single crystals of $[Rh(\kappa^2\text{-}N'O)(PPh_3)(CO)]\cdot 1/4CH_2Cl_2$ suitable for X-ray structure analysis were obtained from dichloromethane/n-hexane. X-ray diffraction data were collected on a Bruker–Siemens SMART AXS 1000 equipped with CCD detector, using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data collection details are: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 30 s, oscillation $\Delta\omega = 0.300°$. Crystal decay resulted negligible. Data were processed by the SAINT package [7] and corrected for absorption effects by the SADABS [8] procedure ($T_{max} = 1.000$, $T_{min} = 0.662$). Data reduction was performed up to $d = 0.85$ Å. The phase problem was solved by direct methods [9] and refined by full-matrix least-squares on all F^2 [10]. Anisotropic displacement parameters were refined for all non hydrogen atoms, while hydrogen atoms were introduced in idealized positions. A partially occupied (50%) CH_2Cl_2 molecule was found on a inversion position in the asymmetric unit. The final map was featureless, except for residual density around the partially occupied solvent site. Details of data collection and structure refinement are in Table 1. For the discussion use was made of the Cambridge Structural database facilities [11].

Table 1
Crystal data and structure refinement for compound **2**·1/4CH_2Cl_2

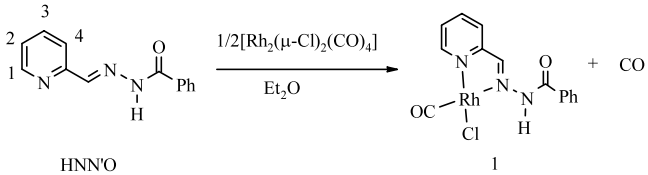
Empirical formula	$(C_{32}H_{25}N_3O_2PRh)\cdot 1/4CH_2Cl_2$
Formula weight	638.66
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	31.650(5)
b (Å)	8.8630(10)
c (Å)	25.725(4)
β (°)	124.688(2)
V (Å³)	5933.6(15)
Z	8
D_{calc} (Mg m^{-3})	1.430
Absorption coefficient (mm^{-1})	0.708
F(000)	2596
Crystal size (mm^3)	0.3 × 0.4 × 0.7
θ Range for data collection (°)	1.56–24.72
Index ranges	$-37 \le h \le 37$, $-10 \le k \le 10$, $-30 \le l \le 30$
Reflections collected	26561
Independent reflections	5070 [$R_{int} = 0.0413$]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5070/0/366
Goodness-of-fit on F^2	1.124
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0475$, $wR_2 = 0.1500$
R indices (all data)	$R_1 = 0.0570$, $wR_2 = 0.1620$
Largest Δ*F* maximum/minimum (e $Å^{-3}$)	1.728/−0.745

3. Results and discussion

3.1. Carbonyl Rh(I) complexes

When the ligand (2-pyridincarboxaldehyde) benzoylhydrazone, **HNN′O**, is reacted with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in diethyl ether at room temperature, the fast precipitation of the chloro-carbonyl Rh(I) complex [Rh(κ²-**HNN′**)(CO)Cl] (**1**) occurs in high yields. The ligand is neutral and NN′ coordinated, the carbonyl oxygen being excluded by the coordination. The square planar geometry is completed by a chlorine atom and a carbonyl group. The proposed structure of **1** is depicted in Scheme 1.

The neutral character of the ligand is well evidenced by the ^{1}H NMR signal of the hydrazonic proton, which resonates as a singlet at 11.73 ppm. A further confirmation of the protic nature of the ligand, derives from the IR stretching band of the N–H bond, which is a weak band centred at 3220 cm^{-1}. The uncoordinated C=O group originates an intense band centred at 1675 cm^{-1}. The high deshielding observed for the imine proton with respect to the free ligand (9.91 vs. 7.27 ppm), indicates that the metal-imine back donation is negligible. More important is the metal–C≡O back donation, as evidenced by the somewhat low ν(C≡O) values (1974



Scheme 1.

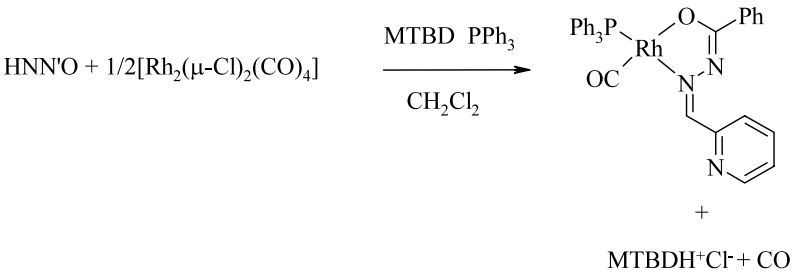
cm^{-1}). As usually observed for pyridyl–imine metal complexes, also in this case the NN′ bidentate coordination causes a change in the sequence of the pyridine ^1H NMR signals, with respect to the free ligand [6,12]. In the last in fact, the sequence is, from low fields to high ones, $H_1 > H_4 > H_3 > H_2$, whereas in **1** it becomes $H_1 > H_3 > H_4 > H_2$. This change is due to the rotation around the py–C(imine) bond imposed by the coordination, with consequent removal of the anisotropic effect that the C(H)=N bond exerts on the H_4 proton in the free ligand. Two possible isomers can be drawn for **1**, where the carbonyl ligand displays a *cis* or a *trans* disposition with respect to the C(H)=N bond. Based on the observation that the chemical shift of H_1 in the complex is similar to that observed in the free ligand (8.68 vs. 8.54 ppm), we assume that the arrangement around the metal centre is that shown in Scheme 1, i.e. the carbonyl ligand *trans* to the C(H)=N moiety. In the *cis* arrangement the chlorine ligand would be adjacent to the pyridine ring, and a stronger deshielding of the H_1 proton would be expected [12]. Furthermore, in the *trans* isomer an intramolecular Rh–Cl···H–N hydrogen bond becomes feasible, as structurally observed for a chloride–methyl Pd(II) complex containing the same ligand [6]. Complex **1** is fairly stable in the solid state (rhodium release occurs only after several months at room temperature), while in solution at room temperature it decomposes to metallic rhodium within 1 day. The same decomposition takes place after one week at 255 K. Repeated attempts aimed to isolate a carbonyl Rh(I) complex of the type [Rh(κ^3-NN′O)(CO)], i.e. containing the anionic ligand behaving as tridentate, were unsuccessful and resulted in extensive decomposition to metallic rhodium and uncharacterizable products.[1] It is interesting to note that the carbonyl rhodium(I) complex [Rh(κ^3-PNO)(CO)], i.e. containing an anionic tridentate ligand, has been isolated and structurally characterized [5]; evidently, the soft phosphorous atom is necessary to remove the excess of negative charge placed on the metal. Complex **1** has been reacted with an equimolar amount of PPh_3 in dichloromethane at room temperature. The reaction leads to the fast precipitation of [*trans*-Rh(PPh_3)$_2$(CO)Cl], as evidenced by the spectroscopic characterization of the product [13]. However, when a dichloromethane solution of **HNN′O** is reacted with [Rh$_2$(μ-Cl)$_2$(CO)$_4$] in the presence of PPh_3 and MTBD in a 1:0.5:1:1 molar ratio, the carbonyl phosphine Rh(I) complex [Rh(κ^2-N′O)(PPh_3)(CO)]·1/2CH_2Cl_2 (**2**) forms (Scheme 2).

From a refrigerated dichloromethane/n-hexane mixture, crystals suitable for X-ray analysis of **2**·1/4CH_2Cl_2 have been collected (see Section 2.4); the structure is depicted in Fig. 1. The ligand shows an anionic N′O character, coordinating the metal through the imine nitrogen and the oxygen atoms; the square planar geometry is completed by a CO molecule and a PPh_3 molecule, *trans* to the oxygen and to the nitrogen donors, respectively. The ligand adopts a *Z* configuration around the C=N bond, with the pyridine ring excluded by the coordination sphere. The anionic character of the ligand is indicated by the disappearance of the NH spectroscopic signals, while the presence of a Rh–O coordinating bond is clearly pointed out by the disappearance of the ν(C=O) band in the IR spectrum. Moreover, the carbonyl ligand originates a strong $\nu(C \equiv O)$ band at 1975 cm^{-1}, while the phosphine gives rise, in the ^{31}P NMR spectrum, to a doublet centred at 29 ppm, with a $J(Rh–P) = 127$ Hz, typical values for a phosphine *trans* to an imine nitrogen and *cis* to a CO group [14]. The ^1H NMR spectrum recorded at 300 K shows only broad signals which does not allow any interpretation. The spectrum at 253 K shows sharper signals: H_1 generates a doublet centred at 8.74 ppm ($J_{HH} = 4.4$ Hz), H_4 a doublet centred at 9.38 ppm ($J_{HH} = 8.0$ Hz), while the imine proton generates a doublet centred at 8.24 ppm ($J_{Rh–H} = 3.3$ Hz). The high chemical shift of H_4 can be ascribed to the vicinal imine moiety (see Section 2.4); the shielding found for the C(H)=N proton can be instead ascribed to the *trans* influence of the phosphine ligand (see Fig. 1). Complex **2** results stable both in the solid state and in solution.

3.2. Structure of complex 2·1/4CH_2Cl_2

The molecular structure of **2**·1/4CH_2Cl_2 is shown in Fig. 1, while a list of the most relevant bond distances and angles is in Table 2. The rhodium adopts a square planar geometry, with the deprotonated ligand behaving as a N′O bidentate donor via the imine nitrogen and the amide carbonyl. The CO ligand is placed in *cis* to the imine nitrogen N′, replacing the pyridinic N coordination site adopted by the HNN′ ligand in complex **1**. The phosphine ligand therefore occupies the coordination site *trans* to the N′ donor, and this geometry differentiates complex **2**·1/4CH_2Cl_2 from the analogue complex [Rh(κ^3-PNO)(CO)] (PNO = 2-(diphenylphosphino)benzaldehyde benzoylhydrazone) [5]. The only relevant difference between the two coordination modes concerns the Rh–P bond length, which in **2**·1/4CH_2Cl_2 is remarkably longer (2.264(1) Å) than in [Rh(κ^3-PNO)(CO)] (2.236(1) Å). This can be ascribed to the *trans* influence of the iminic N′ donor, which is larger than the one of the amidic O donor. The difference in the *trans* influence of N′ and O on the Rh–CO bond in the two compounds is not equally evident

[1] These reactions were conducted following two different procedures: method (a) a free ligand solution was treated with a stoichiometric amount of a base (MTBD, NaOMe or Et_3N) and subsequently with [Rh$_2$(μ-Cl)$_2$(CO)$_4$] at room temperature; method (b) a solution of **1** was treated with a stoichiometric amount of a base (MTBD, NaOMe or Et_3N) at room temperature.



Scheme 2.

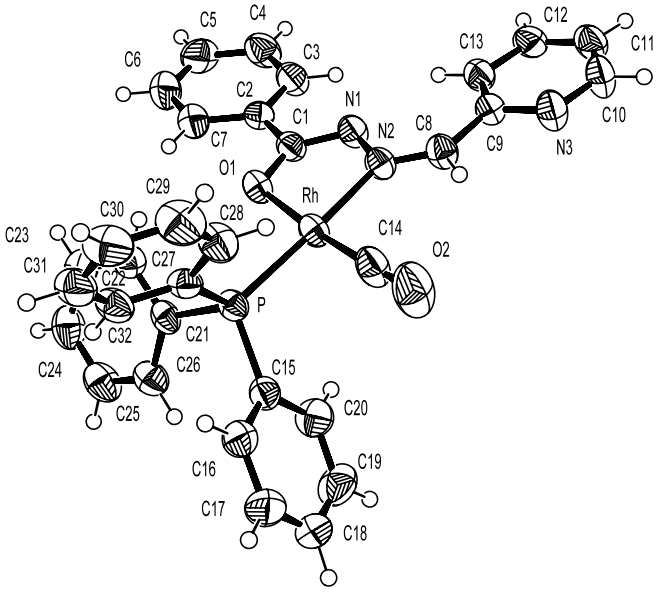


Fig. 1. Perspective view and labelling scheme of the molecular structure of compound **2**·1/4CH_2Cl_2, with thermal ellipsoids at the

Table 2
Relevant bond lengths (Å) and bond angles (°) for compound **2**·1/4CH_2Cl_2

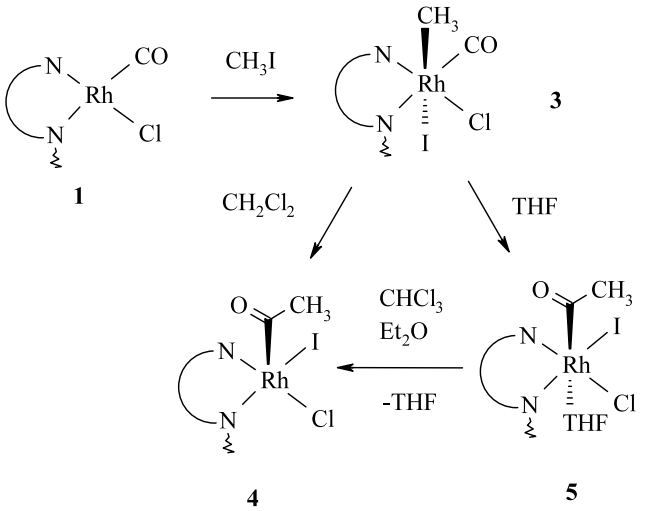
Bond lengths			
Rh–C14	1.803(6)	N2–C8	1.283(6)
Rh–O1	2.046(3)	O1–C1	1.290(5)
Rh–N2	2.085(4)	O2–C14	1.150(6)
Rh–P	2.264(1)	C1–C2	1.476(6)
N1–C1	1.318(6)	C8–C9	1.464(6)
N1–N2	1.396(5)	C9–N3	1.362(6)
Bond angles			
C14–Rh–O1	175.0(2)	C8–N2–N1	118.1(4)
C14–Rh–N2	97.7(2)	C8–N2–Rh	128.0(3)
O1–Rh–N2	77.3(1)	N1–N2–Rh	113.8(3)
C14–Rh–P	88.1(2)	C1–O1–Rh	112.2(3)
O1–Rh–P	96.88(9)	O1–C1–N1	125.3(4)
N2–Rh–P	173.6(1)	N2–C8–C9	131.0(4)
C1–N1–N2	111.2(4)	O2–C14–Rh	178.1(5)

(Rh–C = 1.77(2) in [Rh(κ^3-PNO)(CO)] and 1.803(6) Å in **2**), nevertheless the labilization of the Rh–CO bond when it is in *trans* to the iminic N′ may help in understanding the reason of the different reactivity of **1** and **2** toward the migratory insertion reaction.

The ligand N′O coordination defines a penta-atomic chelation ring, with geometry comparable to the one observed in the above mentioned PNO Rh(I) complex [5] (C–O = 1.23(2), N–N = 1.40(2), N–CH = 1.23(4), N–C(O) = 1.32(4) Å). The square coordination is distorted due to the nature of the ligands: the chelation bite angle is N2–Rh–O1 = 77.3(1)°, while the exocyclic P–Rh–O1 coordination angle (= 96.9(1)°) is widened. The phosphine donor is slightly displaced from the coordination plane (0.11 Å). The entire N′O ligand is planar within 0.22 Å, the largest deviations being due to the terminal phenyl ring. The terminal pyridinic ring is oriented away from the coordination centre, (N1–N2–C8–C9 = −1.2(8)°), while the N atom is facing the CO ligand, probably due to a favourable intramolecular interaction between C13–H and N1 (H13···N1 = 2.296(5) Å), accounting also for the chemical shift observed for H(C13) in the ^{1}H NMR spectrum.

3.3. Oxidative addition reactions

The carbonyl complexes **1** and **2** have been reacted with a forty fold excess of MeI at room temperature; the oxidative additions have been monitored by liquid film IR spectroscopy. The reaction with **1** has been at first performed in dichloromethane: the immediate disappearance of the ν(C≡O) band of the starting complex (1994 cm^{-1} in CH_2Cl_2) in favour of a new intense band centred at 2093 cm^{-1} has been observed. This is indicative of the formation of the carbonyl Rh(III) complex [Rh(κ^2-HNN′)(CO)(CH_3)ClI] (**3** in Scheme 3). Well visible are the bands of the ν(C=O) and ν(N–H) (1685 and 3247 cm^{-1}, respectively), which indicate that the coordination mode of the ligand does not vary during the oxidative addition. With time, the carbonyl band of **3** vanishes in favour of a band centred at 1705 cm^{-1}, indicating the formation of the pentacoordinated acetyl rhodium(III) complex [Rh(κ^2-HNN′)(CH_3CO)ClI] (**4**); the migratory insertion results complete within 24 h, although a weak residual band centred at 2072 cm^{-1} persists after 30 h of reaction. Once isolated complex **4** shows an intense IR stretching band at 1713 cm^{-1} and a singlet at 2.82 ppm in the ^{1}H NMR spectrum, which testify to the presence of an acetyl group bonded to rhodium; a weak band at 3215



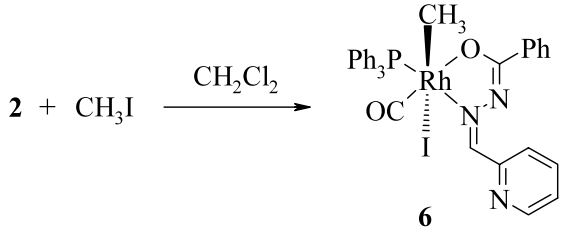
Scheme 3.

cm^{-1} and a singlet at 11.80 ppm confirm the protic nature of the ligand. The ν(C=O) band is obscured by the intense acetyl stretching signal. The strong deshielding of H_1 with respect to the free ligand (9.47 vs. 8.54 ppm), indicates the presence of an halogen adjacent to the pyridine, while the acetyl ligand probably occupies an apical position [15]. Complex **4** results stable under reflux in dichloromethane as well as under CO atmosphere. The residual band at 2072 cm^{-1} can be tentatively attributed to an isomer of **3**, in which the methyl and the carbonyl are mutually *trans*, i.e. an unfavourable disposition for the migratory insertion. The same reaction has been repeated in THF: again the disappearance of the carbonyl stretching band of **1** (1989 cm^{-1} in THF) is immediate after the addition of MeI, resulting in the appearance of an intense band centred at 2086 cm^{-1} (**3** in Scheme 3). The stretching bands of the C=O and N–H groups are still visible at 1689 and 3232 cm^{-1}, respectively. The band at 2086 cm^{-1} diminishes progressively with time, and it disappears completely within 3 h and a half, leaving an intense acetyl band centred at 1706 cm^{-1} (**5** in Scheme 3). As seen in the reaction conducted in dichloromethane, a residual weak band persists at 2071 cm^{-1} after 5 h of reaction. The different reaction rates observed with the two different solvents are not surprising, since it is known that coordinating solvents, like THF, may speed up the migratory insertion step of the reaction [16]. In the solid state **5** shows a $\nu(CH_3CO)$ band at 1702 cm^{-1}, while the ν(C=O) is obscured by the intense stretching band of the acetyl group. The differences observed in the IR stretching frequencies of the acetyl group for the complexes **4** and **5**, together with the fact that the ^1H NMR spectrum of **5** recorded in $CDCl_3$ is identical to that of **4**, with the only exception of two multiplets characteristic of uncoordinated THF, allow to propose the following formula for complex **5**: [Rh(κ^2-HNN′)(CH_3CO)(THF)ClI]. The coordinated THF molecule results easily displaceable: **4** can in fact be recovered from a chloroform solution of **5** by addition of an excess of diethyl ether, as depicted in Scheme 3.

As regards complex **2**, owing to the low solubility in THF, the oxidative addition of MeI has been performed only in dichloromethane. After the addition of MeI, besides the carbonyl stretching band of **2** (1974 cm^{-1}), a new intense band appears at 2058 cm^{-1}, to indicate the formation of a carbonyl Rh(III) species. After 30 min, the band at 1974 cm^{-1} disappears, and it remains an intense band centred at 2064 cm^{-1}. The situation does not change in the next 12 h. Thus, the oxidative addition of MeI to **2** blocks to the formation of the methyl carbonyl rhodium(III) complex [Rh(κ^2-N′O)(PPh_3)(CO)(CH_3)I] (**6**), and the migratory insertion does not take place, as depicted in Scheme 4. Once isolated as solid, complex **6** shows an intense ν(C≡O) band centred at 2066 cm^{-1}. In the ^1H NMR spectrum the methyl bonded to rhodium appears as a multiplet at 1.34 ppm, because of the coupling with the rhodium and phosphorous nuclei. The P atom originates, in the ^{31}P NMR spectrum, a doublet centred at 30.3 ppm, with a $J_{Rh-P} = 134$ Hz. The NMR data of **6** agree with those reported for *trans*-[Rh(ox)(CO)(PPh_3)(CH_3)(I)] (ox = 8-hydroxyquinolinato), whose X-ray structure shows the methyl and iodide ligands mutually *trans* [17]; the same strereochemistry is proposed for complex **6** (Scheme 4). A clear explanation of the not occurred migratory insertion is not easy at present. It should be considered that in **2**, because of the anionic character of the ligand, the metal nucleus has a higher electron density than in **1**; this makes stronger the Rh–Me bond and favours the metal–CO back donation, factors that are considered to disfavour the migratory insertion [5]. However, a steric effect of the phosphine cannot ruled out.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194780. Copies of this information may be obtained free of charge from The



Scheme 4.

Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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