Synthesis, Characterization, and Reactivity toward MeI of Carbonyl Rh(I) Complexes Containing a PNO Hydrazonic Ligand

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The reaction of the potentially tridentate hydrazonic ligand 2-(diphenylphosphino)-benzaldehyde benzoylhydrazone (HL, **1**) with $Rh_2(CO)_4Cl_2$ in diethyl ether led to the isolation of Rh(HL)(CO)Cl (**2**), where the neutral ligand was PN bidentate. Addition of Et_3N or NaOMe caused the deprotonation of the ligand, with the consequent formation of the three-coordinated carbonyl Rh(I) complex Rh(L)(CO) (**3**), which was X-ray characterized. The **2** → **3** conversion was reversible, as it was found that **2** could be regenerated by bubbling a stoichiometric amount of HCl into an ethereal solution of **3**. On treating a solution of **2** with silver triflate, the cationic carbonyl complex $[Rh(HL)(CO)](CF_3SO_3)$ (**4**) was obtained, where the neutral ligand showed a tridentate PNO behavior. All the complexes were allowed to react with MeI at room temperature. Complex **2** led to two different acetyl stereoisomers Rh(HL)(MeCO)ClI (**5**), where the neutral ligand coordinated in a PNO fashion. Complex **3** led to different products depending on the reaction solvent; thus the pentacoordinated acetyl complex Rh(L)(MeCO)I (**8**) and the solvated octahedral acetyl complex [Rh(L)(MeCO)(THF)I]-(THF) (**9**) were isolated in CH_2Cl_2 and in THF, respectively; the X-ray structure of **9** is reported. On carrying out the reaction in Et_2O, the immediate precipitation of the hexacoordinated methylcarbonyl complex Rh(L)(CO)(Me)I (**7**) was observed, which rapidly rearranged into **8** after dissolution in CH_2Cl_2 or $CHCl_3$. Finally, the reaction between **4** and MeI formed the cationic PNO coordinated acetyl complex $[Rh(HL)(MeCO)I](CF_3SO_3)$ (**10**). All the oxidative addition reactions were monitored by liquid IR spectroscopy.

Introduction

The potentially tridentate PNO ligand 2-(diphenylphosphino)benzaldehyde benzoylhydrazone (HL, **1**), along with other similar acyl hydrazonic ligands, has been recently employed by us in the synthesis of Pd(II) complexes. HL always behaved as a tridentate anionic ligand, leading to complexes of the type Pd(L)X (X = OAc, Cl, I), where the deprotonated ligand coordinated the metal by means of the three P, N, and O donor atoms.[1] These complexes were used as catalysts in the chemoselective homogeneous hydrogenation of terminal alkynes; the mechanistic study of the reaction supported the heterolytic cleavage of the molecular hydrogen, occurring with protonation of the hydrazonic nitrogen and formation of a Pd(II) hydride.[2] In the proposed catalytic cycle, the hemilability of the ligand—PNO or PN coordination—was a fundamental requirement for the substrate coordination and then for the catalytic activity.

In light of the lack of data concerning the use of tridentate ligands in organometallic chemistry and catalysis,[3] and with the aim of extending the knowledge on the coordinating capability of HL toward other *soft* metal ions, here we report on the synthesis and characterization of some carbonyl Rh(I) complexes containing HL as ligand. To our best knowledge, the only examples of rhodium complexes with a tridentate PNO acylhydrazone ligand are those recently reported by Shaw.[4]

In view of the enormous importance of the oxidative addition step in many metal-catalyzed reactions,[5] the reactivity of the isolated carbonyl Rh(I) complexes toward methyl iodide was investigated. Furthermore, the X-ray crystal structures of a carbonyl Rh(I) complex and of an acetyl Rh(III) complex are reported.

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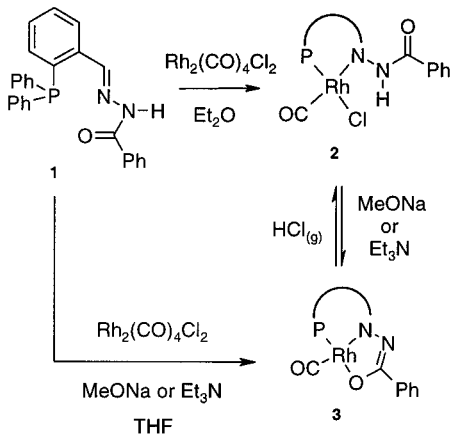
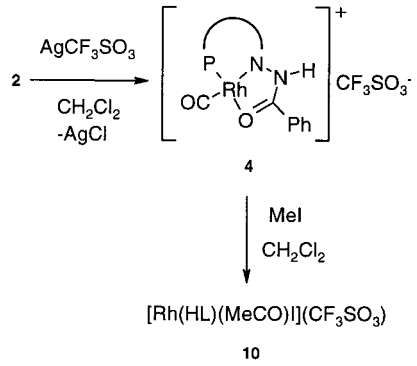
Scheme 1



Scheme 2



Results and Discussion

Synthesis of the Carbonyl Rh(I) Complexes. Reaction of 1 mol of $Rh_2(CO)_4Cl_2$ with 2 mol of HL in diethyl ether led to the fast precipitation of Rh(HL)(CO)Cl (**2**), in which the neutral ligand coordinates the metal by means of the phosphorus and the iminic nitrogen atoms (Scheme 1).

The ^{31}P NMR spectrum showed a doublet centered at 49.9 ppm with a $J_{Rh-P} = 163$ Hz, typical values for a phosphine coordinated to Rh(I) and cis to a carbonyl group.[6] The square-planar geometry is completed by a chlorine ligand trans to the phosphorus atom. The adopted stereochemistry is fully consistent with the donating properties of the groups around the metal; that is, the π-accepting ligands (P and CO) are positioned trans to the mainly σ-donor ones (Cl and N), thus reaching the most thermodynamically stable arrangement. The hydrazonic proton was not visible in the ^1H NMR spectrum, but its presence was confirmed by a weak stretching band at 3205 cm^{-1} in the IR spectrum. The remarkable high chemical shift observed for the iminic proton (10.02 ppm) is attributable to the flexibility of the ligand, which may allow the electron-withdrawing oxygen atom to point to the iminic proton. Such an interaction, as intramolecular hydrogen bonding, has already been evidenced by us in the crystalline structures of a methyl and an acetyl Pd(II) complex containing the ligand 2-pyridylcarboxaldehyde benzoylhydrazone.[7] The IR stretching of the C═O bond in **2** was well visible with a strong band at 1683 cm^{-1}, while an intense IR band at 2005 cm^{-1} demonstrated the presence of a C≡O bonded to Rh(I). Deprotonation of the ligand by a base such as MeONa or Et_3N led to the isolation of Rh(L)(CO) (**3**), in which the deprotonated ligand coordinates rhodium in a tridentate PNO fashion (Scheme 1). Its ^{31}P NMR spectrum showed a doublet centered at 49.6 ppm with a $J_{Rh-P} = 160$ Hz, while its ^1H NMR spectrum strongly resembled those of the Pd(L)X complexes.[1,2] In the IR spectrum neither the ν(NH) nor the ν(C═O) bands were present, while an intense signal at 1982 cm^{-1} indicated the presence of a coordinated C≡O ligand. In **3** the electronic density on the metal is higher than in **2**, owing to the anionic tridentate character of the ligand; this causes a higher metal−CO back-donation and the consequent lowering of the carbonyl stretching frequency (1982 cm^{-1} for **3** and 2005 cm^{-1} for **2**). By slow evaporation of a toluene solution of **3**, crystals suitable for X-ray analysis confirmed the proposed structure of the complex (vide infra). Interestingly, the **2** → **3** conversion is reversible, as we found out that by bubbling a stoichiometric amount of gaseous HCl in an ethereal solution of **3**, the fast re-formation of **2** was observed (Scheme 1). The reaction may proceed either by direct protonation of the hydrazonic nitrogen of the ligand and attack of the Cl^- anion to rhodium (as already hypothesized by us for the molecular hydrogen activation catalyzed by palladium(II) complexes) or by a two-step path: oxidative addition of HCl on rhodium followed by hydrogen shift to the ligand.

To force the protonated ligand to coordinate the metal in a tridentate fashion, a reaction of **2** with silver triflate was carried out in dichloromethane. Fast formation of silver chloride was observed, and [Rh(HL)(CO)](CF_3SO_3) (**4**) was isolated (Scheme 2).

In this complex the phosphorus atom originates a doublet at 50.8 ppm with a $J_{Rh-P} = 162$ Hz, while the hydrazonic proton gives rise to a singlet at 13.60 ppm in the ^1H NMR spectrum. In the IR spectrum, a weak band at 3200 cm^{-1} was attributed to the ν(NH), while a strong signal split in two bands at 1603−1555 cm^{-1} was ascribed to the coordinated C═O amide group of the ligand,[8] where the signal at lower frequencies might contain the contribution of the C═N stretching. The metal valence is satisfied by an uncoordinated triflate anion, originating a strong IR band with two maxima at 1299 and 1241 cm^{-1}, respectively.[9]

Complexes **2** and **3** are stable in the solid state, whereas in solution only complex **3** is stable for weeks under a nitrogen atmosphere. Complex **4** is poorly stable even in the solid state, and in order to prevent the formation of metallic rhodium, it must be stored at low temperature in an inert atmosphere.

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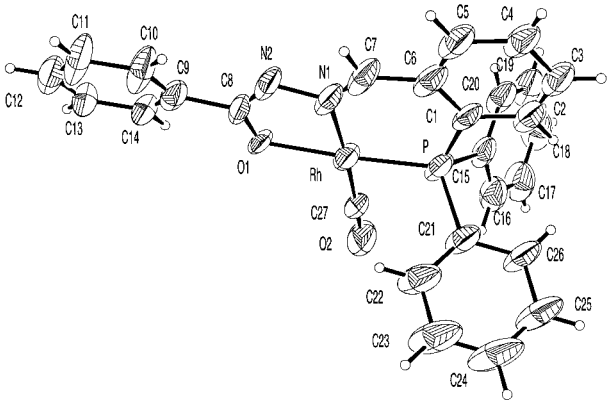


Figure 1. View of the structure of the complex Rh(L)(CO) (**3**). Thermal ellipsoids are drawn at the 30% probability level. The toluene solvation molecule is omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Rh−P	2.184(5)	N1−N2	1.40(2)
Rh−O1	2.05(1)	N1−C7	1.23(4)
Rh−N1	2.02(1)	N2−C8	1.32(4)
Rh−C27	1.77(2)	C27−O2	1.18(2)
O1−C8	1.23(2)		
P−Rh−O1	173.1(3)	Rh−O1−C8	111(1)
P−Rh−N1	95.7(4)	Rh−N1−N2	114.6(9)
P−Rh−C27	87.5(7)	Rh−N1−C7	129(2)
O1−Rh−N1	77.5(5)	N2−N1−C7	116(2)
O1−Rh−C27	99.3(7)	N1−N2−C8	109(2)
N1−Rh−C27	176.2(9)	Rh−C27−O2	178(2)

Complexes **2**, **3**, and **4** are examples of the high versatility of HL, which can adopt a tridentate PNO coordination both in the neutral (**4**) and in the anionic (**3**) form, as well as a bidentate PN coordination when it is protonated (**2**).

The crystal structure of compound **3** is shown in Figure 1, along with the numbering scheme. The Rh(I) atom is surrounded by the PNO chelating system of L^- and by a CO ligand, in a square-planar fashion.

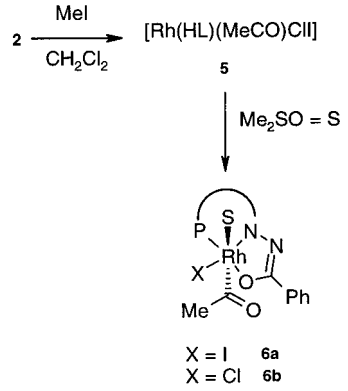
Table 1 reports the most relevant bonding parameters for **3**.

The bond angles O1−Rh−N1 (77.5(5)°) and P−Rh−N1 (95.7(4)°) are strained due to the geometric constraints imposed by the five-membered O1−C8−N1−N2−Rh and six-membered N1−C7−C6−C1−P−Rh chelation rings, respectively. The Rh−C27 bond (1.77(2) Å) to the carbonyl ligand shows a remarkable shortening compared with the average (1.824(2) Å) observed for the 419 crystal structures containing a tetracoordinated rhodium bonded to a CO molecule. Accordingly, the C27−O2 bond (1.18(2) Å) is weaker than the average (1.141(1) Å) found in the above collection of 419 compounds present in the Cambridge Structural Database. This is in agreement with spectroscopic data and indicates a high degree of back-donation exerted by the metal on the CO molecule, confirming that the deprotonated ligand is able to transfer electron density on the metal through N1 and O1. In fact, the Rh−O1 bond (2.05(1) Å) is among the shortest ever observed for all known 56 square-planar rhodium complexes containing the trans O−Rh−P system, where the Rh−O distances range from 2.03 to 2.25 Å and where bonds shorter than 2.05 Å occur only in the presence of an acetylacetonate ligand. The geometry of the five-membered chelation ring formed by the negatively charged hydrazonic system compares well with the one observed in μ-*N*,*N*′-dibenzoylhydrazidobis(dicarbonylrhodium),[10] where the double negative charge of the ligand is shared by two symmetry equivalent Rh(I) atoms (Rh−N = 2.07, N−N = 1.40, N−C = 1.31, C−O = 1.25, Rh−O = 2.03 Å, N−Rh−O = 78°).

The ligand core, defined by atoms C1−C14, O1, N1, N2, P is planar within 0.4 Å, and the largest deviations are due to the terminal C9−C14 phenyl, which is rotated by 18° around the C8−C9 bond with respect to the average ligand plane.

The unit cell contains also a toluene molecule disordered around an inversion center.

Scheme 3



Oxidative Addition Reactions with MeI. To investigate the reactivity of the carbonyl Rh(I) complexes **2**−**4** toward oxidative addition, solutions of **2**, **3**, and **4** were allowed to react with an excess of MeI at room temperature.

The reaction involving **2** was carried out in dichloromethane and led to the precipitation of a yellow powder. The NMR data of the filtered product Rh(HL)(MeCO)ClI (**5** in Scheme 3), recorded in deuterated methanol, showed unequivocally the presence of two different acetyl isomers, as pointed out by two doublets in the ^{31}P NMR spectrum (58.4 ppm, J_{Rh-P} = 150 Hz and 54.0 ppm, J_{Rh-P} = 152 Hz, respectively) and by two singlets in the ^{1}H NMR spectrum (2.87 and 2.62 ppm, respectively); only an intense band at 1689 cm^{-1} was detected in the acetyl stretching region of the IR spectrum. The sharpness of the NMR lines ruled out any fluxional behavior. On the basis of the NMR integrals, a 2:1 ratio was established between the two isomers, with the more deshielded NMR lines belonging to the most abundant one; the ratio did not change maintaining the solution at room temperature for several hours. No NMR signal for a hydrazonic proton was found, but its presence was confirmed by a weak IR band centered at 3132 cm^{-1}. The coordination of the carbonyl oxygen of the ligand gave rise to an intense bifurcated band at 1600−1558 cm^{-1}, as previously observed in **4**. The stability in solution of the coordinating Rh−O bond (supported by the sharpness of the NMR lines) excludes the possibility of having coordinating isomers, and then the two different detected species can be geometrical or rotational isomers; the presence of two acetyl resonances in the ^{1}H NMR spectrum is in favor

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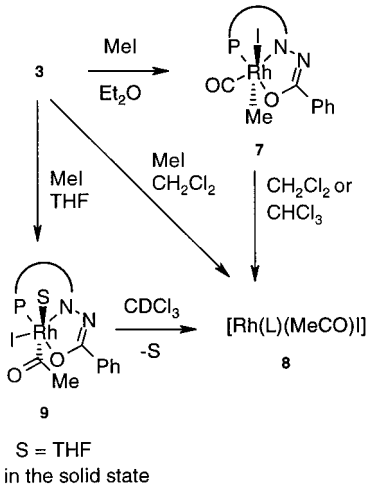
Scheme 4



of the former type of isomerism.[11] On considering that the apical disposition of the acetyl ligand seems to be the most likely for acetyl rhodium(III) complexes,[12] we assume that in the most abundant isomer of **5** this ligand occupies an apical position. Complex **5** dissolved in deuterated Me_2SO generated only one set of NMR signals, with the acetyl group giving rise to a singlet at 2.47 ppm in the ^1H NMR spectrum and the phosphorus atom originating a doublet at 50.3 ppm ($J_{Rh-P} = 149$ Hz) in the ^{31}P NMR spectrum. In the CI-MS spectrum of the Me_2SO solution two peaks corresponding to the two acetyl complexes Rh(L)(MeCO)I (**6a**, $m/z = 679$, relative intensity = 67) and Rh(L)(MeCO)Cl (**6b**, $m/z = 587$, relative intensity = 55) were visible, pointing out the solvent-induced de-hydrohalogenation of **5**, which is a known effect for complexes containing neutral acyl hydrazonic ligands.[13] Probably a Me_2SO molecule completes the octahedral geometry, as shown in Scheme 3. No attempts were made to separate **6a** and **6b**.

When complex **3** and MeI were allowed to react in dichloromethane, the coordinatively unsaturated acetyl complex Rh(L)(MeCO)I (**8** in Scheme 4) was isolated.

The MeCO moiety originates a singlet at 2.95 ppm in the ^1H NMR spectrum and a strong IR stretching band at 1727 cm^{-1} (both in KBr and in CH_2Cl_2). In the ^{31}P NMR spectrum was present a doublet centered at 49.4 ppm with a $J_{Rh-P} = 144$ Hz. On carrying out the reaction in THF, complex [Rh(L)(MeCO)(THF)I](THF) (**9** in Scheme 4) was isolated; its spectroscopic patterns were similar to those of **8**, but the acetyl stretching band was centered at 1690 cm^{-1} (1727 cm^{-1} in CH_2Cl_2), and, in the ^1H NMR spectrum recorded in $CDCl_3$, were also present the two characteristic multiplets of an uncoordinated THF molecule. From a refrigerated THF/hexane mixture, crystals of **9** suitable for X-ray analysis were collected (vide infra). The structure showed an octahedral coordination, where the three donors of the anionic ligand and an iodine atom completed the square plane, while a THF molecule and an acetyl group occupied the apical positions.

The reaction between **3** and MeI was repeated in diethyl ether. When the alkyl halide was added, the immediate precipitation of Rh(L)(Me)(CO)I (**7**) was observed, for which the stereochemistry depicted in Scheme 4 is assumed. In its IR spectrum the presence of the C≡O ligand was pointed out by an intense band at 2075 cm^{-1}, while the remaining part of the spectrum was identical to that of **3**. In deuterated chloroform the methyl group attached to rhodium was visible as a triplet at 0.90 ppm, with a $J_{Rh-H} = J_{P-H} = 2.2$ Hz; on standing the solution at room temperature, such a signal disappeared in favor of a singlet at 2.95 ppm. Moreover, the ^{31}P NMR spectrum of **7** recorded in $CDCl_3$ at room temperature showed only the doublet already seen for **8**, while at 233 K a doublet centered at 45.9 ppm with a $J_{Rh-P} = 115$ Hz was detected, which are values similar to those found for a strictly related carbonyliodomethyl Rh(III) complex.[4] These data agree with the role of intermediate species **7** in the formation of **8** (Scheme 4).

The addition of an excess of MeI to a dichloromethane solution of **4** led to the formation of [Rh(HL)(MeCO)I]-(CF_3SO_3) (**10** in Scheme 2) as a unique acyl species, in which the neutral ligand coordinates the metal in a tridentate PNO fashion. The presence of the NH bond was clear both in the IR spectrum (weak band at 3191 cm^{-1}) and in the ^1H NMR spectrum (broad singlet at 13.90 ppm). The involvement of the C═O group of the ligand in the coordination was pointed out by a bifurcated IR band at 1604−1557 cm^{-1}, while the singlet at 3.03 ppm in the ^1H NMR spectrum was attributed to the acetyl group bonded to rhodium. The stretching of the acetyl ligand was found at 1702 cm^{-1}; in the ^{31}P NMR spectrum there was a doublet centered at 54.5 ppm with a $J_{Rh-P} = 148$ Hz.

In the solid state, complexes **5**, **7**, and **8** are stable for weeks; complex **9** partially transforms into **8** after some days at room temperature by losing THF, whereas complex **10** decomposes after a few days. In solution complexes **5**, **8**, and **9** are stable for days under nitrogen, whereas complex **10** decomposes rapidly. Complex **8** remains stable also in refluxing CH_2Cl_2 without observing any decarbonylation process as described for other pentacoordinated acetyl Rh(III) complexes.[14]

The reactions between **2**, **3**, and **4** with MeI at room temperature were monitored by liquid IR (CH_2Cl_2), by using solutions having comparable complex concentrations.

In the reaction with complex **2** after 30 min from the MeI addition, the stretching band of the starting complex was still present (2015 cm^{-1}) together with a band at 2084 cm^{-1}, and no signal for an acetyl group was visible. With the progress of the reaction an intense band at 1727 cm^{-1} appeared, and in the carbonyl region was noted the presence of an additional weak band at 2101 cm^{-1}; within 5 h the signals at 2015, 2084, and 2101 cm^{-1} vanished in favor of the acetyl stretching band.

In the reaction with complex **3** the C≡O stretching of the starting complex (1975 cm^{-1}) disappeared im-

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(12) See X-ray structure of **9** in this paper and: (a) Egglestone, D. L.; Baird, M. C.; Lock, C. J.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576. (b) Pinillos, M. T.; Elduque, A.; Martìn, E.; Navarro, N.; Oro, L. A.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1995**, *11*, 3105. (c) Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A. *J. Am. Chem. Soc.* **1999**, *121*, 11233.

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mediately after the addition of MeI, and simultaneously a band at 2080 cm^{-1} appeared, very similar to that found in the solid IR of **7** (2075 cm^{-1}); this progressively diminished in favor of the acetyl band at 1727 cm^{-1}, and the reaction was completed within 15 h.

In the reaction with complex **4** the band at 2084 cm^{-1} was never detected, and only a band at 2101 cm^{-1} appeared within 2 h, together with an acetyl signal at 1738 cm^{-1}; the C≡O stretching of the starting complex (2018 cm^{-1}) vanished within 9 h, while the band at 2101 cm^{-1} disappeared within 15 h.

The above-reported data are in agreement with the initial formation of a hexacoordinated methylcarbonyl Rh(III) intermediate, having a ν(C≡O) at 2080 cm^{-1} for **2**, 2084 cm^{-1} for **3**, and 2101 cm^{-1} for **4**, characteristic values for a Rh(III)−C≡O bond.[15] The faster oxidative addition observed for **3** is attributable to the anionic tridentate character of the ligand, which makes rhodium more nucleophile.[16] The band at 2101 cm^{-1} was observed both in **4** and in **2**; this suggests that also in the latter case a cationic methylcarbonyl intermediate might be involved, but currently it is hard to say if it derives from a rearrangement of the neutral methylcarbonyl species initially formed or from a parallel reaction pathway.

The subsequent step is then the migratory insertion of the methyl into the Rh−C≡O bond, with the consequent formation of the acetyl species. It is worth noticing that for complexes **5** and **9** the ν(MeCO) found in solution are shifted to higher frequencies as compared with those found in the solid state, and moreover they are very similar to the ν(MeCO) found for the pentacoordinated acetyl complex **8**; this finding suggests that in solution coordinatively unsaturated species would predominate over hexacoordinated ones. If for **9** the lability of the coordinated THF molecule has already been evidenced by NMR spectroscopy, for **5** it remains difficult to visualize a dissociative equilibrium, unless hypothesizing the breaking of a Rh−halogen bond.

The lower ν(MeCO) frequencies found in the hexacoordinated complexes suggest that in these cases the carbene structure $Rh^{+} = C(O^{-})(Me)$ may contribute in a description of the electronic structure of the Rh−acetyl moiety.[17]

The molecular structure of **9** is shown in Figure 2, along with the atomic numbering.

Table 2 reports the most significant bonding parameters.

The coordination geometry of Rh(III) is an irregular octahedron, consisting of an equatorial plane containing the tridentate PNO ligand and a iodine atom trans to the L^{-} N atom. The apical positions are occupied by the acyl group and by a THF molecule. The coordination mode of L^{-} is the same as in **3**, and the bite angles of the five-membered and six-membered chelation rings (80.7(4)° and 94.7(4)°, respectively) are similar to those previously observed for **3**. The six-membered chelation ring has a certain envelope character, with the P atom deviating by 0.5 Å from the average plane defined by the remaining five atoms. Besides the constraints imposed by the chelation, the distortion from regular octahedral geometry derives from the steric hindrance of the iodine and triphenylphosphine groups, associated with the relative lability of the coordinated THF molecule (Rh−O3 = 2.451(4) Å). The largest deviations from regularity involve the bending of the apical ligands toward the L^{-} side (C27−Rh−O3 = 169.9(2)°) and the bending of the THF molecule away from P and I (O1−Rh−O3 = 78.6(1)°, N1−Rh−O3 = 84.3(2)°). The ligand core is planar within 0.3 Å.

The most relevant difference in L^{-} coordination between square-planar Rh(I) and octahedral Rh(III) is found for the Rh−P bond, which is remarkably longer in **9**, in accordance with the trend observed by examining four- and six-coordinated complexes of rhodium(triphenylphosphine) contained in the Cambridge Structural Database. In both cases, however, the Rh−P bond with L^{-} is among the shortest observed for the corresponding coordination geometry. The acyl ligand is oriented in a staggered geometry with respect to the equatorial coordination bonds, as shown by the torsion angle N1−Rh−C27−O2 = 60°. The acyl oxygen points toward the P atom (O2···P = 3.127 Å), while the methyl makes an intramolecular short contact with O1 (C28···O1 = 2.981(9) Å).

The crystal packing is completed by a solvation molecule of THF.

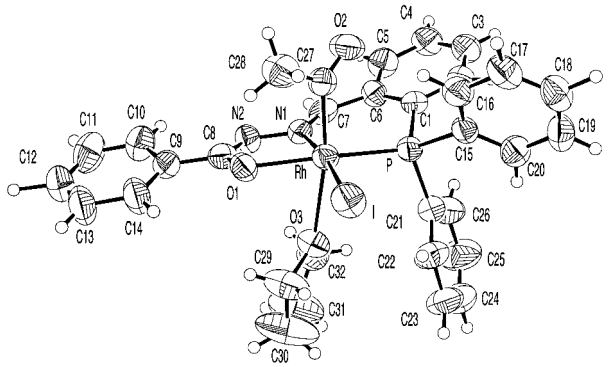

Figure 2. View of the structure of the complex [Rh(L)(MeCO)(THF)I](THF) (**9**). Thermal ellipsoids are drawn at the 50% probability level. The THF solvation molecule is omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 9

Rh−C27	1.986(6)	O1−C8	1.296(7)
Rh−N1	2.007(4)	O2−C27	1.175(7)
Rh−O1	2.070(4)	N1−C7	1.277(7)
Rh−P	2.236(1)	N1−N2	1.393(6)
Rh−O3	2.451(4)	N2−C8	1.320(7)
Rh−I	2.665(1)	C27−C28	1.503(8)
C27−Rh−N1	89.4(2)	O1−Rh−I	93.3(1)
C27−Rh−O1	92.4(2)	P−Rh−I	94.30(4)
N1−Rh−O1	78.9(2)	O3−Rh−I	91.8(1)
C27−Rh−P	92.5(2)	C8−O1−Rh	109.3(3)
N1−Rh−P	93.2(1)	C7−N1−N2	114.3(5)
O1−Rh−P	170.7(1)	C7−N1−Rh	131.2(4)
C27−Rh−O3	169.9(2)	N2−N1−Rh	114.4(3)
N1−Rh−O3	86.3(2)	C8−N2−N1	111.7(4)
O1−Rh−O3	78.6(1)	O1−C8−N2	125.2(5)
P−Rh−O3	95.7(1)	O2−C27−C28	121.3(5)
C27−Rh−I	93.4(2)	O2−C27−Rh	123.7(5)
N1−Rh−I	171.9(1)	C28−C27−Rh	114.8(4)

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Experimental Section

General Comments. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. Solvents were dried prior to use and stored under nitrogen. Elemental analysis (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 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 NMR spectra were recorded on a Bruker CPX 200 FT using H_3PO_4 85% as external standard. All spectra were collected at 298 K, unless otherwise reported. MS spectra (CI, methane) were recorded on a Finnigan SSQ 710 spectrometer, collecting negative ions; in brackets are reported the relative intensities. 2-(Diphenylphosphino)benzaldehyde benzoylhydrazone was synthesized as previously reported.[2] $Rh_2(CO)_4Cl_2$, AgTfO, and MeI were purchased by Aldrich.

Rh(HL)(CO)Cl, 2. $Rh_2(CO)_4Cl_2$ (50 mg, 0.13 mmol) was dissolved in 15 mL of diethyl ether. When solid HL (105 mg, 0.26 mmol) was added, the solution turned orange and after 1 h of stirring at room temperature the precipitation of an orange solid was observed. The solid was filtered and washed with diethyl ether and then dried in a vacuum. Yield: 111 mg (75%). Anal. Calcd for $C_{27}H_{21}ClN_2O_2PRh$: C, 56.42; H, 3.68; N 4.87. Found: C, 56.34; H, 3.71; N, 4.91. ^{31}P NMR ($CDCl_3$): δ 49.9 (d, J_{Rh-P} = 163 Hz). ^1H NMR ($CDCl_3$): δ 10.02 (s, 1H, HC=N), 8.44 (d, $2H_o$, Ph(C=O), ^1J = 7.4 Hz), 7.84−7.32 (m, 17H, Ph). IR (KBr): ν/cm^{-1} (NH) 3205_w, (C=O) 1683_s, (C≡O) 2005_{vs} (2015_s cm^{-1} in CH_2Cl_2). CI-MS: *m/z* 538 {[Rh(L)(CO)]$^-$, 100}.

Rh(L)(CO), 3. Method a: $Rh_2(CO)_4Cl_2$ (35 mg, 0.09 mmol) was dissolved in 15 mL of THF, and solid HL (74 mg, 0.18 mmol) was added. The orange solution was stirred for 30 min at room temperature, and then Et_3N (0.04 mL, 0.27 mmol) or MeONa (15 mg, 0.27 mmol) was added, stirring again for 2 h. The solution was filtered in order to remove the salts formed, and the resulting clear solution was treated with diethyl ether, causing the immediate precipitation of a yellow solid, which was filtered, washed with diethyl ether, and dried in a vacuum. Yield: 68.5 mg (60%). Method b: **2** (30 mg, 0.05 mmol) was dissolved in 5 mL of dichloromethane, and MeONa (8 mg, 0.16 mmol) was added, stirring at room temperature for 3 h. The mixture was filtered, and the resulting clear solution was treated with diethyl ether in order to precipitate the product, which was collected, washed with diethyl ether, and dried in a vacuum. Crystals suitable for X-ray analysis were obtained from a refrigerated toluene solution. Yield: 18 mg (55%) Anal. Calcd for $C_{27}H_{20}N_2O_2PRh{\cdot}C_7H_8$: C, 64.77; H, 4.48; N, 4.44. Found: C, 64.71; H, 4.45; N, 4.50. ^{31}P NMR ($CDCl_3$): δ 49.6 (d, J_{Rh-P} = 160 Hz). ^1H NMR ($CDCl_3$): δ 8.51 (s, 1H, HC=N), 8.18 (d, $2H_o$, Ph(C=O), ^1J = 6.6 Hz), 7.63−7.14 (m, 17H, Ph). IR (KBr): ν/cm^{-1} (C≡O) 1982_{vs} (1975_s cm^{-1} in CH_2Cl_2). CI-MS: *m/z* 538 {[Rh(L)(CO)]$^-$, 100}.

[Rh(HL)(CO)](CF$_3$SO$_3$), 4. 2 (50 mg, 0.09 mmol) was dissolved in 25 mL of dichloromethane, and solid $AgCF_3SO_3$ (45 mg, 0.17 mmol) was added, stirring the resulting mixture for 2.5 h at room temperature. After removal of the inorganic salts by filtration over a glass filter, the product was precipitated as an orange solid by addition of *n*-hexane, filtered, washed with *n*-hexane, and dried in a vacuum. Yield: 71 mg (95%). Anal. Calcd for $C_{28}H_{21}F_3N_2O_5PSRh{\cdot}CH_2Cl_2$: C, 41.98; H, 2.94; N, 3.26; S, 3.76. Found: C, 42.05; H, 2.85; N, 3.50; S, 3.70. ^{31}P NMR ($CDCl_3$): δ 50.8 (d, J_{Rh-P} = 162 Hz). ^1H NMR ($CDCl_3$): δ 13.60 (s, 1H, NH), 9.35 (s, 1H, HC=N), 8.22 (d, $2H_o$, Ph(C=O), ^1J = 7.5 Hz), 8.11−7.44 (m, 17H, Ph). IR (KBr): ν/cm^{-1} (NH) 3200_w, (C≡O) 2015_{vs} (2018_s cm^{-1} in CH_2Cl_2), (C=O) 1603_s, (SO) 1299_s-1241_s. CI-MS: *m/z* 538 {[Rh(L)(CO)]$^-$, 100}.

Rh(HL)(MeCO)ClI, 5. 2 (50 mg, 0.09 mmol) was dissolved in 10 mL of dichloromethane, and MeI (0.22 mL, 3.48 mmol) was added to the solution, which was stirred at room temperature for 5 h. The yellow solid was filtered, washed with dichloromethane, and dried in a vacuum. Yield: 47 mg (68%). Anal. Calcd for $C_{28}H_{24}ClIN_2O_2PRh{\cdot}CH_2Cl_2$: C, 43.45; H, 3.27; N, 3.49. Found: C, 43.50; H, 3.41; N, 3.37. Data for isomer I: ^{31}P NMR (CD_3OD): δ 58.4 (d, J_{Rh-P} = 150 Hz). ^1H NMR (CD_3OD): δ 8.84 (br, 1H, HC=N), 8.18 (d, $2H_o$, Ph(C=O), ^1J = 6.6 Hz), 7.63−7.14 (m, Ph), 2.87 (s, 3H, MeCO). Data for isomer II: ^{31}P NMR (CD_3OD): δ 54.0 (d, J_{Rh-P} = 152 Hz). ^1H NMR (CD_3OD): δ 8.87 (br, 1H, HC=N), 2.62 (s, 3H, MeCO). The integration of the aromatic region of the spectrum is incorrect owing to the presence of both isomers. IR (KBr): ν/cm^{-1} (NH) 3132_w, (MeCO) 1689_s (1727_s cm^{-1} in CH_2Cl_2). CI-MS: *m/z* 636 {[Rh(L)I]$^-$, 16}, 537 {[Rh(L)(CO)]$^-$, 100}.

Rh(L)(MeCO)X [X = Cl (6b) or I (6a)]. The characterization was done only in solution. On dissolving **5** (10 mg, 0.01 mmol) in 0.5 mL of Me_2SO-d_6, the following NMR spectrum were recorded. ^{31}P NMR: δ 50.3 (d, J_{Rh-P} = 149 Hz). ^1H NMR: δ 8.74 (s, 1H, HC=N), 8.14 (d, $2H_o$, Ph(C=O), ^1J = 7.5 Hz), 8.06 (tbr, 1H, Ph), 7.83 (t, 1H, Ph, ^1J = 7.4 Hz), 7.67 (t, 1H, Ph, ^1J = 7.5 Hz), 7.54−7.31 (m, 14H, Ph), 2.48 (s, 3H, MeCO). CI-MS: *m/z* 679 {[Rh(L)(MeCO)I]$^-$, 67}, 637 {[Rh(L)I]$^-$, 67}, 587 {[Rh(L)(MeCO)Cl]$^-$, 55}, 544 {[Rh(L)Cl]$^-$, 59}, 537 {[Rh(L)(CO)]$^-$, 100}.

Rh(L)(CO)(Me)I, 7. 3 (50 mg, 0.08 mmol) was dissolved in 5 mL of diethyl ether, and MeI (0.20 mL, 3.17 mmol) was added, obtaining a clear solution, which was stirred at room temperature for 5 h. The yellow solid was filtered, washed with diethyl ether, and dried in a vacuum. Yield: 24 mg (45%). Anal. Calcd for $C_{28}H_{23}IN_2O_2PRh$: C, 49.43; H, 3.41; N, 4.12. Found: C, 49.48; H, 3.38; N, 4.08. ^{31}P NMR ($CDCl_3$, 233 K): δ 45.9 (d, J_{Rh-P} = 115 Hz). ^1H NMR ($CDCl_3$): δ 8.65 (br, 1H, HC=N), 8.17 (d, $2H_o$, Ph(C=O), ^1J = 8.0 Hz), 0.90 (t, 3H, Rh−Me, $^2J_{Rh-H}$ = 2.2 Hz, $^3J_{P-H}$ = 2.2 Hz). The signals of the aromatic region cannot be correctly assigned owing to the rapid conversion of **7** into **8**. IR (KBr): ν/cm^{-1} (C≡O) 2075_s (2080_s cm^{-1} in CH_2Cl_2). CI-MS: *m/z* 679 {[Rh(L)(CO)(Me)I − 1]$^-$, 60}, 636 {[Rh(L)I − 1]$^-$, 100}.

Rh(L)(MeCO)I, 8. 3 (50 mg, 0.08 mmol) was dissolved in 10 mL of dichloromethane, and MeI (0.20 mL, 3.17 mmol) was added stirring for 15 h. The final bright yellow solution was concentrated and treated with 20 mL of *n*-hexane, causing the precipitation of a yellow solid, which was filtered, washed with *n*-hexane, and dried in a vacuum. Yield: 32.4 mg (60%). Anal. Calcd for $C_{28}H_{23}IN_2O_2PRh{\cdot}1/2CH_2Cl_2$: C, 47.36; H, 3.35; N, 3.88. Found: C, 47.39; H, 3.32; N, 3.91. ^{31}P NMR ($CDCl_3$): δ 49.4 (d, J_{Rh-P} = 162 Hz). ^1H NMR ($CDCl_3$): δ 8.64 (s, 1H, HC=N), 8.33 (d, $2H_o$, Ph(C=O), ^1J = 8.3 Hz), 7.23−7.72 (m, 17H, Ph), 2.95 (s, 3H, MeCO). IR (KBr): ν/cm^{-1} (MeCO) 1727_s (equivalent in CH_2Cl_2). CI-MS: *m/z* 680 {[Rh(L)(MeCO)I]$^-$, 4}, 636 {[Rh(L)I]$^-$, 21}, 537 {[Rh(L)(CO)]$^-$, 100}.

[Rh(L)(MeCO)(THF)I]·(THF), 9. The procedure is identical to that reported for **8**, but the solvent was THF. A yellow solid was isolated. Crystals suitable for X-ray analysis were obtained by crystallization from THF/*n*-hexane (1:1.5, v/v). Yield: 41 mg (68%). The partial loss of THF from the product prevented a correct elemental analysis. The ^{31}P NMR spectrum recorded in $CDCl_3$ was equivalent to that of **8**, as well as the ^1H NMR spectrum recorded in the same solvent, except for the presence, in the latter, of two multiplets belonging to the protons of an uncoordinated molecule of THF, centered at 3.74 (4H, α-CH_2) and 1.84 (4H, β-CH_2) ppm, respectively. IR (KBr): ν/cm^{-1} (MeCO) 1690_s, (1727_s in CH_2Cl_2). CI-MS: The signals are the same as those observed for **8**.

[Rh(HL)(MeCO)I](CF$_3$SO$_3$), 10. 4 (50 mg, 0.07 mmol) was dissolved in 15 mL of dichloromethane, and MeI (0.18 mL, 2.90 mmol) was added, stirring the resulting solution for 15 h at room temperature. After concentration of the solution and addition of *n*-hexane, an orange solid was filtered, washed with *n*-hexane, and dried in a vacuum. Yield: 40 mg (67%). The instability of the solid product prevented the carrying out of

Table 3. Crystal Data and Structure Refinement

	3	**9**
empirical formula	$C_{30.5}H_{23.5}N_2O_2PRh$	$C_{36}H_{39}IN_2O_4PRh$
fw	583.95	824.54
temperature	293(2) K	293(2) K
wavelength	0.71069 Å	0.71069 Å
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
unit cell dimens	$a = 14.051(5)$ Å	$a = 9.746(4)$ Å
	$b = 10.477(4)$ Å	$b = 9.576(4)$ Å
	$c = 9.667(4)$ Å	$c = 37.366(9)$ Å
	$\alpha = 106.75°$	
	$\beta = 98.44°$	$\beta = 92.98(2)°$
	$\gamma = 102.95°$	
volume	1294(1) Å^3	3483(2) Å^3
Z	2	4
calcd density	1.518 Mg/m^3	1.435 Mg/m^3
abs coeff	0.754 mm^{-1}	1.453 mm^{-1}
$F(000)$	602	1496
cryst size	0.6 × 0.4 × 0.3 mm	0.5 × 0.5 × 0.3 mm
θ range	3.05 to 22.05°	3.05 to 30.07°
no. of reflns collected/unique	3158/3158	10 314/10 182
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3158/208/268	10 182/0/463
goodness-of-fit on F^2	0.927	0.896
final R indices [$I>2\sigma(I)$]	R1[a] = 0.0798, wR2[b] = 0.2283	R1[a] = 0.0491, wR2[b] = 0.1523
R indices (all data)	R1[a] = 0.1615, wR2[b] = 0.2648	R1[a] = 0.1147, wR2[b] = 0.1893

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

the elemental analysis. ^{31}P NMR ($CDCl_3$): δ 54.5 (d, J_{Rh-P} = 148 Hz). ^{1}H NMR ($CDCl_3$): δ 13.9 (br, 1H, NH), 9.5 (s, 1H, HC═N), 8.36 (d, 2H$_o$, Ph(C═O), ^1J = 7.3 Hz), 8.23−7.43 (m, 17H, Ph), 3.03 (s, 3H, MeCO). IR (KBr): ν/cm^{-1} (NH) 3191$_w$, (MeCO) 1702$_s$ (1739$_s$ in CH_2Cl_2), (SO) 1285$_s$−1241$_s$. CI-MS: m/z 637 {[Rh(L)I]$^-$, 6}, 538 {[Rh(L)(CO)]$^-$, 100}.

Conversion of 3 into 2. A 14 mg sample of KCl (0.19 mmol) was placed in a three-neck round-bottom flask equipped with a dropping funnel containing 5 mL of concentrated H_2SO_4 (96%). The flask was connected to the nitrogen line and to an additional flask, wherein 40 mg (0.06 mmol) of **3** had been dissolved in 20 mL of iced Et_2O. H_2SO_4 was slowly dropped onto the solid KCl, and the evolved HCl was carried by nitrogen flux through a trap of H_2SO_4 (96%) and then bubbled into the solution containing the metal complex. The reported Rh/KCl molar ratio was chosen in order to have a Rh/HCl molar ratio close to 1:1, 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 reached the reactant solution. KCl was completely converted within 2 h, during which time the solution initially changed color from light red to orange, and then it released the final product; filtering, washing with diethyl ether, and drying in a vacuum yielded 31 mg of **2** as orange solid (85% yield).

Structure Determinations. Single crystals suitable for X-ray diffractometric analysis were obtained for **3** (dark red prisms) and **9** (yellow prisms). Diffraction data for both compounds were measured at room temperature on a Siemens AED diffractometer using Mo Kα (λ = 0.71073 Å) radiation, graphite monochromator, $\theta/2\theta$ scan. In both cases the intensity of one standard reflection was monitored every 100 measurements: only for **9** was a significant decay observed, and data were rescaled accordingly. The intensity data were processed with a peak-profile procedure and corrected for Lorentz and polarization effects. Table 3 reports a summary of relevant parameters concerning data collection and structure refinement for both compounds. In both cases the phase problem was solved by direct methods, using SIR97,[18] which allowed the retrieval of all non-hydrogen atoms. Neutral atomic scattering factors were employed, those for non-hydrogen atoms being corrected for anomalous dispersion. Structures were successively refined by full-matrix least-squares on F^2 with SHELXL97.[19] For **9** data were corrected for absorption effects,[20] resulting in a significant improvement in the isotropic R-factor and in the quality of the difference Fourier map. In the last stages of refinement anisotropic displacement parameters were used for all non-hydrogen atoms. Phenyl groups in **3** were treated as rigid bodies. Hydrogen atoms were partly located on the Fourier difference map and refined with isotropic displacement parameters and partly introduced at calculated positions, riding on their carrier atoms. The final geometry was analyzed by the program PARST97,[21] and the drawings were made with ZORTEP.[22] All calculations were performed on a Digital Alpha 255 computer at the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. in Parma. Besides referring to original literature, data for comparison with other compounds were retrieved and analyzed by the software packages of the Cambridge Structural Database.[23] The full list of final atomic fractional coordinates, atomic displacement parameters, and bond distances and angles have been deposited as Supporting Information.

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Supporting Information Available: Tables of X-ray data for complexes **3** and **9**. ^{1}H NMR and MS-CI spectra of complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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