Potentially Tridentate Hydrazonic Ligands in the Synthesis of Methyl and Acetyl Palladium(II) Complexes

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Potentially tridentate hydrazonic ligands of the type HNNO have been used in the synthesis of some methyl palladium(II) complexes. Depending on the applied experimental conditions two different kinds of complexes are obtained. Thus, the reactions between **HL1–HL5** and (COD)PdMeCl in diethyl ether led to the formation of bidentate methyl complexes of the type Pd(HNN)MeCl (**1–5**), where the ligands maintain a neutral character. However, in the presence of a base such as Et_3N or NaOMe, the ligands are deprotonated with the consequent formation of tridentate methyl complexes of the type Pd(NNO)Me (**7–10**). In solution, complexes **1–5** tend to lose the hydrazonic proton with elimination of methane and formation of a tridentate chloride complex Pd(NNO)Cl (**6**); this tendency can be correlated with the acidity of the free ligands, which has been determined. On bubbling carbon monoxide through solutions of **1–5**, the corresponding acetyl complexes Pd(HNN)[C(O)Me]Cl (**11–15**) are formed, in which both the *cis* and *trans* isomers are present. Their molar ratio is rationalised from the results of a molecular modelling study on the basis of electronic considerations. A remarkably different reactivity has been found in the carbonylation of the tridentate complexes **7–10**: they decompose rapidly and quantitatively to palladium black and an organic product corresponding to the ligand with an acetyl group bonded to the hydrazonic nitrogen. The X-ray structures of a methyl complex (**3**) and its corresponding acetyl (**13**) derivative have been determined.

Introduction

The use of potentially tridentate ligands in the synthesis of organometallic compounds has received much attention since tridentate metal complexes are expected to exhibit interesting catalytic properties, such as better stereoselective or chemoselective control of the reactions.[1] We have been interested in the study of the coordinating behaviour of tridentate hydrazonic ligands towards palladium(II) for some years,[2] and more recently our interest has been focused on the capability of the isolated complexes to activate a simple molecule like hydrogen.[3]

With the aim of studying the reactivity towards other simple molecules, we have investigated the insertion of CO into the Pd–C bond, this reaction being a key step in many palladium-mediated processes, such as the hydroxy- or alkoxycarbonylation of alkenes[4] and the copolymerisation of alkenes and CO.[5]

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In this field much work has been done with both symmetrical[6] and unsymmetrical bidentate ligands.[7] Recently complexes with rigid bidentate nitrogen ligands showed faster CO and alkene insertion than those with flexible bidentate nitrogen ligands.[8] Moreover, as opposed to complexes containing phosphorous ligands, the insertion of CO into the Pd–Me bond was not prevented by either the flexible or the rigid tridentate nitrogen ligands,[9] and kinetic studies have shown that the insertion rate of CO and strained alkenes increases with increasing rigidity of the ligand.[10]

Asymmetric tridentate ligands have been scarcely studied in the synthesis of methyl and acetyl palladium(II) complexes and, importantly, only neutral ligands have been employed.[11] Although mechanistic details have not been reported, the rupture of a coordinative bond seems to be a prerequisite for CO coordination and insertion. The breaking of a Pd–N or Pd–O coordinating bond has been proposed also by us as a key step in the homogeneous hydrogenation of terminal alkenes and alkynes catalysed by palladium(II) complexes with tridentate ligands.[3] In the present work, we have prepared methyl palladium(II) complexes with acylhydrazones, HNNO (Scheme 1), which can behave as either neutral bidentate, or as anionic tridentate ligands, placing the metal in diverse electronic and steric environments.

In relation to the experimental conditions, complexes with both coordination modes have been obtained, namely bidentate Pd(HNN)MeCl, and tridentate Pd(NNO)Me (see Scheme 2).

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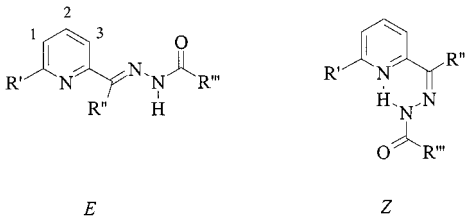
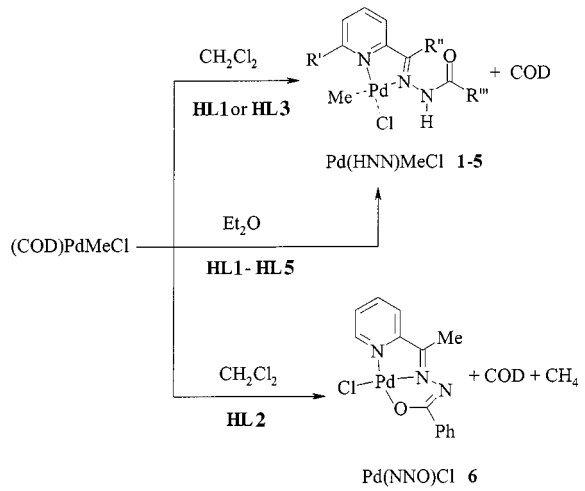


R'	R"	R"'	Ligand
H	Me	Me	**HL1**
H	Me	Ph	**HL2**
H	H	Ph	**HL3**
H	Et	Ph	**HL4**
Me	H	Ph	**HL5**

Scheme 1. The hydrazonic ligands **HL1–HL5**



Scheme 2. Synthesis of the complexes **1–6**

We now report on the synthesis and characterisation of these complexes, and on their reactivity towards CO insertion into the Pd–Me bond. The reactivity of the methyl complexes towards CO has also been investigated considering the coordination mode and steric hindrance of the ligand and, for the Pd(HNN)MeCl complexes, the acidity of the hydrazonic proton.

Results and Discussion

Synthesis and Characterisation of Ligands HL1–HL5

The acyl hydrazonic ligands **HL1–HL5** were obtained by condensation between a 2-pyridyl-carbonylic system and a hydrazide, in the presence of a catalytic amount of glacial acetic acid. All the ligands are colourless solids, readily soluble in common organic solvents. The N–H bond is visible in their IR spectra with a band at about 3200 cm^{-1}, whereas the C=O group gives rise to a strong band at about 1650 cm^{-1}. The hydrazonic chain is represented by two intense bands centred at about 1550 cm^{-1} and 1300 cm^{-1}, assigned to the AMIDE II and AMIDE III systems, respectively. With the exception of **HL5**, two different sets of signals are present in the ^{1}H-NMR spectrum of the ligands, showing the presence of both (*E*) and (*Z*) isomers (Scheme 1).[12]

Table 1. Selected ^{1}H-NMR ($CDCl_3$) data for ligands **HL1**–**HL5**

	δ[a] N–H	R′	H^1	H^2	H^3
HL1 (*E*)	8.89(s)	8.58(d)	7.26(t)	7.69(t)	8.07(d)
(*Z*)	9.04(s)	8.67(d)	7.32(t)	7.84(t)	7.51(d)
HL2 (*E*)	9.14(s)	8.59(d)	7.27(t)	7.70(t)	–[b]
(*Z*)	15.78(s)	8.71(d)	7.39(t)	7.91(t)	7.62(d)
HL3 (*E*)	11.15(s)	8.54(d)	7.33(t)	7.79(t)	8.13[b]
(*Z*)	15.48(s)	8.76(d)	7.41(t)	7.93(t)	8.02(d)
HL4 (*E*)	8.33(s)	8.59(d)	7.50(m)	7.68(t)	7.58(d)
(*Z*)	9.24(s)	8.75(d)	7.47(m)	7.93(t)	7.66(d)
HL5 (*E*)	9.67(s)	2.55(s)	7.13(d)	7.59(t)	7.88(d)

[a] For simplicity the coupling constants are not reported. – [b] Overlapping with other signals,

These can be distinguished from the signal of the hydrazonic proton (Table 1), which is more deshielded in the (*Z*) isomer, owing to the formation of an intramolecular hydrogen bond with the N_{py}.

Starting from the upper signal, the sequence shown by the pyridine protons of the (*E*) isomer is R′ > H^3 > H^2 > H^1, while in the (*Z*) isomer, and in the palladium complexes, the sequence becomes R′ > H^2 >H^3 >H^1. This indicates that the interaction between H^3 and the iminic nitrogen, present in the (*E*) form, is removed by rotation around the py–C(R′′)N bond upon hydrogen-bond formation or coordination to the metal.[8a] Taking into account these observations, an initial predominance of the (*E*) isomer was established, with an (*E*/*Z*) ratio of about 1:0.3 for ligands **HL1**–**HL4**. After 24 hours in chloroform solution at room temperature, **HL2** and **HL3**, containing R′′′ = Ph, showed a practically inverted ratio, whereas no change was observed for **HL1**, in agreement with the capacity of the phenyl group to support isomerisation around a C=N bond.[12a] For **HL5** the low deshielding of the hydrazonic proton and the sequence of the pyridinic signals are in favour of the *E* isomer and no changes were observed in a chloroform solution at room temperature after 24 hours.

Synthesis and Characterisation of the Bidentate Methyl Complexes Pd(HNN)MeCl (1–5)

Depending on the solvent, the ligands **HL1**–**HL5** showed a different reactivity towards (COD)PdMeCl. In dichloromethane, **HL1** and **HL3** gave the methyl complexes of formula Pd(HNN)MeCl (**1** and **3**), where the neutral ligand coordinates in a bidentate mode through the pyridinic and the iminic nitrogens, excluding the carbonyl oxygen from the coordination sphere (Scheme 2). The neutral character of the ligand is supported by both the IR and NMR spectra (presence of the N–H bond signals), whereas a strong IR band at about 1700 cm^{-1} indicates an uncoordinated C=O group. In the ^{1}H-NMR spectra of **1** and **3** (Table 2), the methyl group bonded to the metal gives rise to a singlet at 0.97 ppm and 1.01 ppm, respectively, which are typical values for a methyl group σ-bonded to palladium.[8a,c,9] The chemical shift of the R′ proton is useful in establishing the disposition of the methyl ligand with respect to the C=N

Table 2. Selected ^{1}H-NMR ($CDCl_3$) data for palladium complexes

	δ[a] N–H	R	H^1	H^2	H^3	Pd–Me
1 (*trans*)	9.53(s)	8.57(d)	7.56(t)	8.04(t)	7.78(d)	0.97(s)
2 (*trans*)	10.38(s)	8.59(d)	–[b]	8.08(td)	7.85(d)	0.98(s)
2 (*cis*)	9.78(s)	8.85(d)	7.43(t)	–[b]	–[b]	0.80(s)
3 (*trans*)[c]	11.15(s)	8.54(d)	7.64(d)	8.04(td)	7.73(d)	1.01(s)
4 (*trans*)	10.39(s)	8.64(d)	7.35(t)	8.08(t)	7.85(d)	1.01(s)
4 (*cis*)	10.66(s)	9.31(d)	7.37(t)	8.15(t)	7.66(d)	–[b]
5 (*cis*)	11.30(s)	2.75(s)	7.36(d)	7.83(t)	7.52(d)	1.18(s)
6	–	8.65(dd)	7.47(t)	7.91(td)	–[b]	–
7	–	8.53(d)	7.46(t)	7.99(t)	7.76(d)	0.69(s)
8[c]	–	8.38(d)	7.66(td)	8.03(td)	7.87(d)	0.24(s)
9	–	8.31(d)	7.34(td)	7.95(td)	7.68(d)	0.27(s)
10	–	2.93(s)	6.86(d)	7.37(m)[b]	7.15(d)	0.81(s)
11 (*trans*)	9.38(s)	8.50(d)	7.48(t)	8.04(t)	7.79(d)	2.59(s)
11 (*cis*)	10.80(s)	8.80(d)	7.48(t)	7.95(t)	7.82(d)	2.64(s)
12 (*trans*)	10.28(s)	8.57(d)	–[b]	–[b]	7.86(d)	2.62(s)
12 (*cis*)	11.66(s)	8.99(d)	–[b]	–[b]	7.86(d)	2.63(s)
13 (*trans*)	11.03(s)	8.54(d)	–[b]	8.08(td)	–[b]	2.67(s)
13 (*cis*)	12.40(s)	9.10(d)	–[b]	–[b]	–[b]	2.78(s)
14 (*trans*)	10.24(s)	8.60(d)	–[b]	–[b]	–[b]	2.62(s)
14 (*cis*)	11.44(s)	8.93(d)	–[b]	–[b]	–[b]	2.60(s)
15 (*trans*)	11.13(s)	2.76(s)	7.38(d)	7.83(t)	7.43(d)	2.70(s)

[a] For simplicity the coupling constants are not reported. – [b] Overlapping with other signals. – [c] Solvent: CD_2Cl_2.

bond. In fact when the alkyl group is *trans* to the C=N, R′ shows a resonance similar to that observed in the free ligand, while in a *cis* disposition, R′ resonates at higher ppm values as it is deshielded by the electron-withdrawing effect of the chlorine atom.[8a] On the basis of NMR spectroscopic data, a *trans* disposition was inferred for both **1** and **3**.

The assumed structures for **1** and **3** are confirmed by an X-ray analysis conducted on a single crystal of **3** obtained from a dichloromethane/diethyl ether mixture (1:1), as reported in the Crystallographic Section.

The reaction between **HL2** and (COD)PdMeCl in dichloromethane followed a different pathway (Scheme 2). No traces of the expected Pd(HNN)MeCl complex were observed, but only the formation of a tridentate chloride complex Pd(NNO)Cl (**6**). This reaction involves the deprotonation of the ligand with the consequent formation of methane. The loss of the hydrazonic proton forces the carbonylic oxygen to coordinate to the metal, as demonstrated by the disappearance of the stretching band of the C=O group in the IR spectrum.

The bidentate methyl complex **2** can be selectively obtained by addition of (COD)PdMeCl to an ethereal suspension of **HL2** (Scheme 2). The ^{1}H-NMR spectrum of **2** indicates the presence of both *cis* and *trans* isomers in a ratio of 0.07:1. The use of diethyl ether in the preparation of the Pd(HNN)MeCl complexes was extended to the synthesis of **1** and **3** with ligands **HL1** and **HL3**. The predominant *trans* configuration found in the Pd(HNN)MeCl complexes is probably due to steric factors, as previously reported.[8a,9b,13] In this way, the methyl ligand is kept far from the bulky hydrazonic chain. Furthermore, the *trans* configuration allows for the formation of a hydrogen bond between the chlorine atom and the hydrazonic proton, as shown by the molecular modelling study (see molecular modelling in the Crystallographic Section), and this may be considered as a further stabilising effect. This intramolecular interaction is clearly seen in the ^{1}H-NMR spectra of **2**, where the N–H signal of the *trans* isomer is more deshielded than that of the *cis* isomer (10.38 ppm for the *trans*, and 9.78 ppm for the *cis* isomer). As inferred from the molecular modelling study, the tendency to form the N–H···Cl hydrogen bond decreases with increasing bulkiness of R′′; with the aim of confirming this outcome, the reaction between **HL4** and (COD)PdMeCl in diethyl ether was carried out and, as expected, the resulting complex **4** showed a *cis*/*trans* ratio of 0.27:1, on the basis of the NMR integrals.

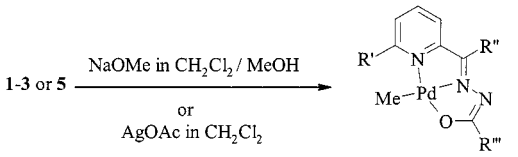
The different reactivity observed towards (COD)PdMeCl in dichloromethane for **HL2** relative to that of **HL1** and **HL3**, may be traced back to the different acidity of the hydrazonic proton, which was experimentally measured by spectrophotometric titration of the dissolved ligands with potassium hydroxide.[3b,e] These analyses established that **HL2** bears the most acidic proton and its acidity seems to be sufficient to cause the methane elimination in dichloromethane solution. On the other hand, when diethyl ether is used as solvent, complex **2** immediately precipitates, and deprotonation is prevented. On dissolution in deuteriochloroform, **2** appears to be rather unstable, and at room temperature its ^{1}H-NMR spectrum changes to that of the chloride complex **6** within a few hours. A similar behaviour was also found for complex **4**, whereas for complexes **1** and **3** only after several days was the transformation into the chloride complex complete (the full characterisation of the chloride complexes was not done, except for **6**).

One might suspect that the small amount of the *cis* isomer present in **2** and **4** could be responsible for their faster transformation into the chloride complexes, since the closeness of the methyl ligand to the hydrazonic proton should facilitate the methane formation. As this transformation happens in a quantitative way, an isomerisation around the metal centre would be required, whereby the methyl group shifts from a *trans* position to the more reactive *cis* one. In order to test this hypothesis, the reaction between the hindered ligand **HL5** and (COD)PdMeCl was carried out in diethyl ether. The presence of the methyl substituent on the aromatic ring forces the alkyl ligand to take a *cis* position,[8a,9b,14] so eventually favouring a faster methane elimination. Contrary to our expectations the stability of **5** in solution at room temperature was found to be higher than that of **2** under the same conditions; thus the acidity of the ligand must be considered decisive for the stability of complexes **1–5**. Furthermore, the ^{1}H-NMR spectra of **1–5** show very narrow resonance lines, indicating the absence of dynamic behaviour with respect to *cis*-*trans* isomerisation on the NMR time scale. Complexes **1–5** are stable in the solid state for months without releasing palladium black.

Synthesis and Characterisation of the Tridentate Methyl Complexes Pd(NNO)Me (7–10)

By adding an excess of a strong base like NaOMe to a solution of **1–3** or **5** at room temperature, or by stirring at

room temperature a dichloromethane solution of the same complexes in the dark overnight with a fivefold excess of silver acetate, the corresponding tridentate methyl complexes Pd(NNO)Me (**7–10** in Equation 1) were obtained as yellow-orange solids.

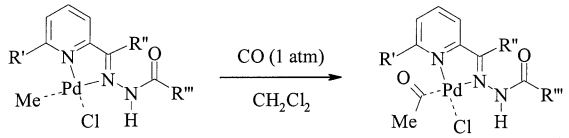


Pd(NNO)Me **7-10**

The addition of a base caused the deprotonation of the ligand and the consequent formation of a covalent Pd–O bond. Complexes **7–10** show a spectroscopic pattern similar to that of complex **6**, except for the presence of a Pd–Me resonance in the ^{1}H NMR spectra. This signal is generally more shielded than in the corresponding bidentate complexes (Table 2), owing to the increased electron density around the metal centre due to the higher chelating effect exerted by the tridentate ligands. A second significant difference with the ^{1}H-NMR spectrum of **6** is the stronger shielding of the R′ proton due to the absence of the electron-withdrawing effect of the chlorine atom; this proton, in fact, resonates at about 0.1–0.2 ppm lower (Table 2). To our knowledge these complexes represent the first example of methyl complexes where palladium is coordinated in a tridentate fashion by an anionic ligand; in fact the use of anionic chelating agents in this type of chemistry has so far been restricted to some bidentate systems.[15] Complexes **7–10** are stable for months in the solid state but only for some hours in solution, resulting in the formation of palladium black. The stability in solution of complex **10** is remarkably lower than that of complexes **7–9**, as expected from the encumbrance generated by the closeness of the alkyl ligand to the methyl substituent of the pyridine.

Carbonylation Reactions With Complexes Pd(HNN)MeCl

On bubbling CO for a few minutes through dichloromethane solutions of complexes **1** or **3–5** at room temperature, an insignificant amount of palladium black was formed. After filtration of the solution through celite and addition of an excess of *n*-hexane, the acetyl complexes Pd(HNN)[C(O)Me]Cl **11** and **13–15** were obtained in good yields (Equation 2).



1-5 Pd(HNN)(C(O)Me)Cl **11-15**

The CO insertion is clearly demonstrated in their ^{1}H-NMR spectra by the disappearance of the Pd–Me singlet in favour of a new singlet at about 3 ppm, a characteristic value for an acetyl group σ bonded to Pd.[8a,8c,9] The IR spectrum is not as helpful as usually reported in establishing the insertion as the stretching band of the carbonyl group of the ligand is partially overlapped by the same signal of the acetyl group bonded to palladium, and only a strengthening of the band at about 1700 cm^{-1} was observed. However, the persistence of the stretching band of the C=O group of the ligand, together with the IR and NMR signals of the N–H bond, indicates that the ligand behaviour in **11** and **13–15** is analogous to that in the methyl precursors. The ^{1}H NMR spectra of the four acetyl complexes show two sets of signals (Table 2), indicating the presence of the *cis* as well as the *trans* isomer.

Some difficulties have been found in the isolation of the acetyl complex of **2**. In fact by carrying out the reaction at room temperature in chloroform, dichloromethane or acetonitrile, the fast degradation of the complex to palladium black was observed. When the reaction was repeated in an NMR tube, the signals of the chloride complex **6** were found, together with other signals due to uncharacterised products. By bubbling CO into a dichloromethane solution of **2** at 0 °C, the decomposition was much slower, and two different acetyl isomers could be obtained, in good yields (**12**), where the ligand has the same chelating behaviour as observed in the other acetyl complexes. For **11–15** the separation of the two different isomers was not successful either by chromatographic techniques or by crystallisation. As already reported for the methyl complexes, no fluxional behaviour was found in their NMR spectra.

The amount of the *cis* isomer found in the acetyl complexes is much greater than that found in the methyl precursor. In fact, for complex **13** the *cis*/*trans* ratio is 0.41:1, but for **11**, **12** and **14** it becomes 1:0.57, 1:0.50, and 1:0.56, respectively. For complex **15** only the *cis* isomer was found which is in agreement with the encumbrance created in the coordination plane by a methyl R′ group. Usually an increase of the *cis*/*trans* ratio is observed from the methyl to the corresponding acetyl complexes,[8a,13] and this is generally justified by the tendency of the acetyl group to arrange itself perpendicularly to the coordination plane, thus reducing steric interactions. However the nature of the R′′ group also has a great deal of influence on the *cis*/*trans* ratio, as can be seen from the molecular modelling study (see Crystallographic Section). Thus whenever R′′ is an alkyl group (Me or Et) the *cis* isomer is the predominant one because of the formation of the N–H···O_{acetyl} hydrogen bond; this intramolecular interaction is also corroborated by the deshielding of the hydrazonic proton in the ^{1}H NMR spectra (Table 2).

An X-ray diffraction analysis carried out on a crystal of **13**, showed that only the *trans* isomer is present in the crystalline state but, interestingly, in the ^{1}H-NMR spectrum of the same crystals both isomers were present in the same *cis*/*trans* ratio seen for the powdery product.

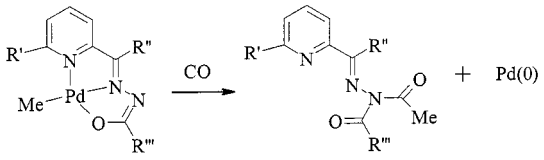
The fast formation of palladium black, observed when CO was bubbled into a solution of **2** at room temperature, can be related to the highly acidic character of the ligand, which is also responsible for the instability of **2** in solution.

The hydrazonic proton probably reacts with the acetyl ligand although, unfortunately, it was not possible to detect the presence of acetaldehyde by GC-MS or ^{1}H NMR analyses.

Owing to the high reaction rate, in no case could mechanistic information be obtained by monitoring the carbonylation reactions by ^{1}H NMR, even when conducting the reaction at –20 °C. At this temperature only the disappearance of the methyl resonance and the simultaneous appearance of the acetyl resonance was detected, without observing any signals attributable to an intermediate species. On the basis of literature data,[8a,16] we propose that the CO coordination occurs with the breaking of the Pd–py bond. The formation of both *cis* and *trans* isomers can be understood considering the possibility of rotation around the Pd–N_{iminic} bond after pyridine dissociation, a step which would involve a unidentate intermediate.

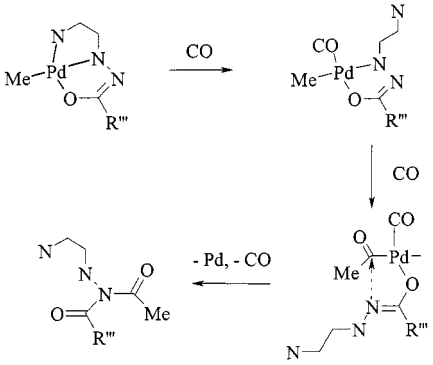
Carbonylation Reactions with Complexes Pd(NNO)Me

Contrary to what is usually reported in the literature for neutral tridentate ligands, the isolation of the tridentate acetyl palladium complexes of the type Pd(NNO)[C(O)Me] was unsuccessful owing to the fast formation of palladium black when CO was bubbled through a dichloromethane or THF solution of complexes **7–10** at 25, 0 or –40 °C. The formation of palladium black was accompanied by bleaching of the solutions. After removal of the metallic palladium, an MS analysis of the solution revealed the presence of a new organic species with a molecular weight corresponding to the acylated ligand. The spectroscopic data suggest that the acetyl group is bonded to the hydrazonic nitrogen, as depicted in Equation 3, giving rise to a bi(acyl) hydrazone derivative.



As a further confirmation, the same product i.e. 2-pyridylaldehyde *N*-acetylbenzoylhydrazone, was isolated by refluxing a mixture of **HL3** and acetylchloride in pyridine, following a known procedure.[17]

The course of the carbonylation reaction strongly resembles that of the palladium catalysed carbonylation of organic halides to form amides.[18] In this process an external nucleophile (usually a secondary amine in the presence of a base) directly attacks the acetyl group bonded to palladium or a pre-coordinated carbon monoxide molecule in a cationic intermediate.[19] Both pathways are followed by a reductive elimination step which leads to the formation of the amide and Pd^0. In our case, even if a plausible mechanism was not determined owing to the high reaction rate observed even at low temperatures, it is reasonable to suppose that the hydrazonic nitrogen acts as a nucleophile towards the acetyl group σ bonded to palladium, as depicted in Scheme 3; this attack is possible only if the formation of an oxygen-monodentate intermediate with a dangling ligand is supposed, the breaking of both Pd–N bonds being justified by the large excess of CO present in the reaction vessel.



Scheme 3. Proposed mechanism for the carbonylation with Pd(NNO)Me

In the attempt to isolate the tridentate acetyl complexes Pd(NNO)[C(O)Me] in the absence of CO, the corresponding bidentate acetyl complexes **11–15** were deprotonated by treatment with sodium methoxide in dichloromethane or THF. Rapid formation of palladium black was again observed and the ^{1}H-NMR spectra of the isolated product revealed the presence of the acylated ligand along with traces of the tridentate methyl complexes Pd(NNO)Me. This unexpected result can be rationalised by the presence of both *cis* and *trans* isomers in the solutions of **11–15**. In the case of the *cis* isomer it is plausible to suppose that, after deprotonation of the ligand, the hydrazonic nitrogen attacks the electrophilic acetyl group bonded to palladium, bringing about the formation of the acylated ligand, metallic palladium and NaCl. In the case of the *trans* isomer, the intramolecular nucleophilic attack is unlikely because of the distance of the acetyl group from the hydrazonic chain and, consequently, the deprotonation of the ligand may result only in the formation of the expected product Pd(NNO)-[C(O)Me]. This compound seems to lose CO rapidly, forming the corresponding tridentate methyl complex. A similar decarbonylation process undergone by the tridentate acetyl complexes has already been observed with tridentate ligands, both in solution and in the solid state.[9b,10,11b,11c]

Crystallographic Section

X-ray Crystal Structures of 13 and 3

In the neutral complex **13**, shown in Figure 1, the bidentate neutral ligand coordinates to the metal by the pyridinic and the iminic nitrogen atoms, while the carbonylic oxygen O1 does not participate in the chelation.

The square planar coordination around the palladium atom is completed by a chloride, *trans* to the pyridinic nitrogen, and by an acetyl group *trans* to the iminic nitrogen; the coordinated atoms are coplanar to the metal within 0.04 Å. A list of the most relevant bond lengths and angles is given in Table 3.

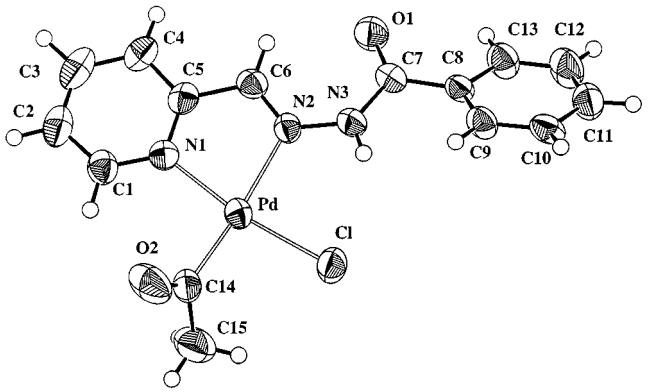


Figure 1. ORTEP view of **13**, with thermal ellipsoids at the 50% probability level

Table 3. Selected bond lengths [Å] and angles [°] with s.u.'s in parentheses for compound **13**

Bond Lengths		Bond Angles	
Pd–Cl	2.328(1)	C1–Pd–N1	1.70.52(1)
Pd–N1	2.090(3)	Cl–Pd–N2	92.8(1)
Pd–N2	2.166(3)	Cl–Pd–Cl4	92.4 (1)
Pd–C14	1.947(4)	N1–Pd–N2	77.8(1)
O1–C7	1.219(5)	N1–Pd–Cl4	97.0(2)
O2–C14	1.180(6)	N2–Pd–C14	174.8(2)
N1–C1	1.325(5)	Pd–N1–Cl	128.7(3)
N1–C5	1.357(6)	Pd–N1–C5	113.5(3)
N2–N3	1.366(4)	C1–N1–C5	117.7(4)
N2–C6	1.285(6)	Pd–N2–N3	121.7(2)
N3–C7	1.368(5)	Pd–N2–C6	115.2(3)
C1–C2	1.377(7)	N3–N2–C6	123.1(3)
C2–C3	1.373(9)	N2–N3–C7	129.1(3)
C3–C4	1.379(6)	N1–C1–C2	123.5(4)
C4–C5	1.391(7)	C1–C2–C3	118.9(5)
C5–C6	1.485(5)	C2–C3–C4	119.3(5)
C14–C15	1.492(7)	C2–C3–C4	119.3(5)
–	–	C3–C4–C5	118.6(4)
–	–	N1–C5–C4	122.1(4)
–	–	N1–C5–C6	118.0(4)
–	–	C4–C5–C6	119.9(4)
–	–	N2–C6–C5	115.4(4)
–	–	O1–C7–N3	122.2(4)
–	–	O1–C7–C8	123.3(4)
–	–	N3–C7–C8	114.4(3)
–	–	Pd–C14–O2	121.7(3)
–	–	Pd–C14–C15	117.1(3)
–	–	O2–C14–C15	121.2(4)

The entire ligand, with the exception of the terminal phenyl C8–C13, is coplanar within 0.22 Å, and the atoms which deviate most from this plane are the protonated hydrazonic N3 and the carbonyl O1, involved in the intramolecular hydrogen bonds N3–H···Cl [N3···Cl = 3.218(4) Å, H···Cl = 2.58(3)Å, N3–H···Cl = 145(3)°] and C6–H···O1 [C6···O1 = 2.806(5)Å, C6–H···O1 = 116(3)°]. The terminal phenyl C8–C13 makes a dihedral angle of 34° with the average molecular plane. The plane of the acetyl ligand is tilted by 63° with respect to the coordination plane. A search of the Cambridge Structural Database has shown that the corresponding values for acetyl groups coordinated to square-planar palladium or platinum atoms range from 68° to 90°. The bond Pd–C14 [1.947(3) Å] is the shortest ever observed among the seven palladium-acetyl complexes structurally characterised, whose bond lengths range between 1.948 and 2.001 Å. The influence of the acetyl group on the Pd–N bond lengths can be analysed by comparing **13** with acetyl(2,2′-bipyridine)chloropalladium[8a] and acetylchloro-[2-(*N*-isopropyl)carbaldiminopyridine]palladium.[8a] The coordination geometry of **13** is very close to that observed in the former (Pd–acetyl = 1.948, Pd–N1 = 2.067, Pd–N2 = 2.162 Å, with the acetyl group *trans* to N2). On the contrary, in acetylchloro[2-(*N*-isopropyl)carbaldiminopyridine]palladium the acetyl group is *trans* to the pyridine nitrogen, causing the elongation of the Pd–N1 bond (2.171 Å), while the bond length between palladium and the iminic nitrogen (2.062 Å), *trans* to a chloride, is shorter than in **13** and similar to the Pd–pyridine distances of **13** and acetyl(2,2′-bipyridine)chloropalladium.

The geometry of compound **3** (Figure 2) is identical to that of **13** (see Table 4); the coordinated atoms are coplanar with the metal within 0.06 Å. Also, the entire ligand is coplanar within 0.18 Å to the coordination plane. There are two intramolecular hydrogen bonds N3–H···Cl [N3···Cl =

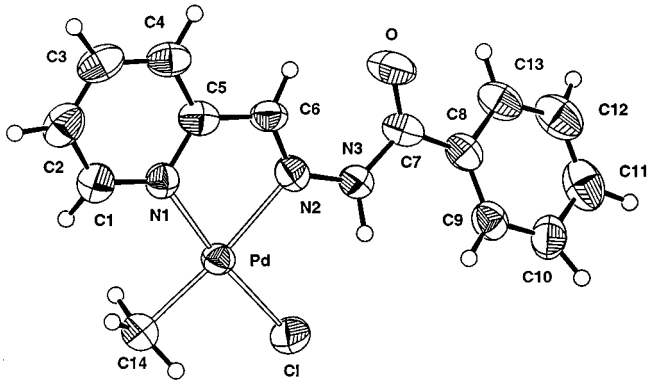
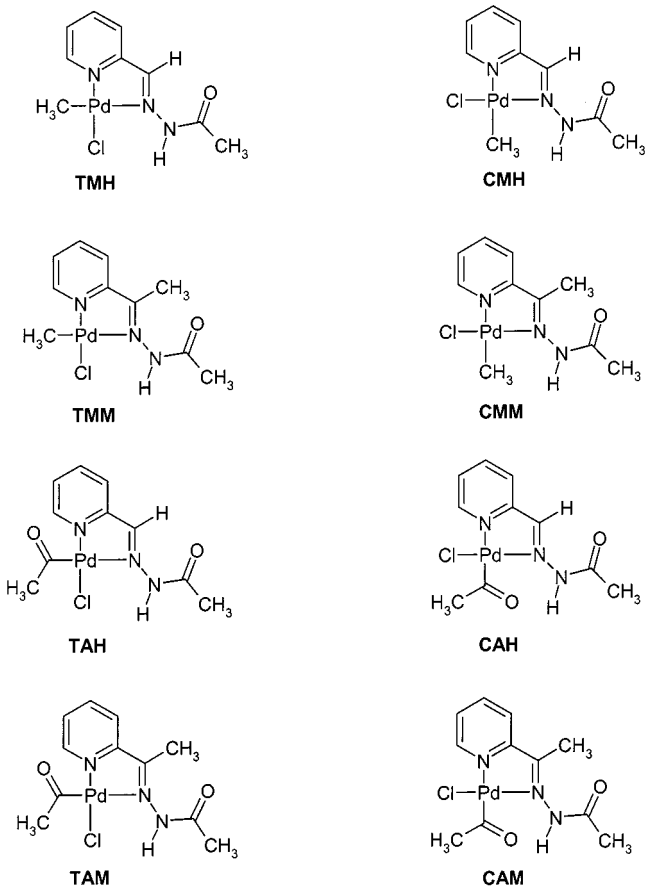


Figure 2. ORTEP view of **3**, with thermal ellipsoids at the 50% probability level

Table 4. Selected bond lengths [Å] and angles [°] with s.u.'s in parentheses for compound **3**; parameters in bold italic were not varied in the energy minimisation

Bond Lengths		Bond Angles	
***Pd–Cl*[2]**	***2.309(3)***	***Cl–Pd–N1***	***172.5(2)***
Pd–N1	***2.048(7)***	***Cl–Pd–N2***	***93.1(2)***
Pd–N2	***2.143(7)***	***Cl–Pd–C14***	***93.4(4)***
Pd–C14	***2.04(1)***	***N1–Pd–N2***	***79.8(3)***
O–C7	1.24(1)	***N1–Pd–C14***	***93.7(4)***
N1–C1	***1.35(1)***	***N2–Pd–C14***	***173.4(4)***
N1–C5	***1.38(1)***	***Pd–N1–C1***	***129.1(6)***
N2–N3	1.38(1)	***Pd–N1–C5***	***113.0(6)***
N2–C6	***1.31(1)***	***C1–N1***–C5	***117.8(8)***
N3–C7	1.38(1)	Pd–N2–N3	121.0(5)
C1–C2	***1.40(2)***	***Pd–N2–C6***	***112.2(6)***
C2–C3	***1.37(2)***	N3–N2–C6	126.8(7)
C3–C4	***1.40(2)***	N2–N3–C7	127.2(8)
C4–C5	***1.39(1)***	***N1–C1–C2***	***123.1(9)***
C5–C6	***1.45(1)***	***C1–C2–C3***	***119(1)***
–	–	***C2–C3–C4***	***119(1)***
–	–	***C3–C4–C5***	***120.3(9)***
–	–	***N1–C5–C4***	***120.8(8)***
–	–	***N1–C5–C6***	***117.1(8)***
–	–	***C4–C5–C6***	***122.1(8)***
–	–	***N2–C6–C5***	***117.9(7)***
–	–	O1–C7–N3	119.9(9)
–	–	O1–C7–C8	123.8(8)
–	–	N3–C7–C8	116.3(8)



Scheme 4. Molecular schemes of the compounds considered in the theoretical calculations; the numbering of the atoms follows that shown in Figure 1 and 2 for the crystal structures

3.183(8) Å, H···Cl = 2.43(12) Å, N3–H···Cl = 131(13)°] and C6–H···O [C6···O = 2.779(11) Å, C6–H···O = 118(6)°]. The terminal phenyl C8–C13 makes a dihedral angle of 27° with the average molecular plane.

Molecular Modelling

As shown by NMR spectroscopy, the proportion of *cis*/*trans* isomers in solution for compounds Pd(HL)(R)Cl (HL = **HL1–HL5**) [R = Me, C(O)Me] is related to the nature of the R group coordinated to the metal and to the steric hindrance of the substituent R′′ attached to the iminic carbon. Some factors that can affect the preference for one or the other forms involve the different *trans* influence of the pyridinic and iminic nitrogens, the steric hindrance of the ligand *cis* to the hydrazonic N–H group, and the repulsion between the carbonylic oxygen and the alkyl substituents on the iminic carbon. In order to elucidate the relative importance of these factors on the observed isomer distributions, we analysed the conformational energy of different model systems by semi-empirical calculations. The systems considered in the analysis are shown in Scheme 4: they comprise the *cis* and *trans* isomers, referring to the hydrazonic N–H, of methyl- and acetyl- derivatives of complexes containing the ligands **HL1** and **HL3′**. [**NB** The ligand HL3′ is modelled by replacing the terminal phenyl of HL3 with a methyl group (see Experimental Section)].

These differ in the presence of a hydrogen or a methyl on the iminic carbon. The simultaneous effect of the *cis* ligand and of the iminic substituent on the NH–C=O system has been studied by calculating the energetic profile for the rotation of the rigid terminal NH–C(O)Me group around the N–N single bond. The C6–N2–N3–C7 torsion angle (for labelling see Figure 1 and Figure 2) has been varied from –120° to +120°, in increments of 5°, and at each step the torsion angle has been held fixed, and the other parameters have been released to minimise the energy. Then, the most stable conformations have been found by minimising the energy of the molecular geometries close to the minima in the path.

Methyl Complexes

Figure 3 shows the energetic profile for molecules TMH, CMH, TMM, and CMM.

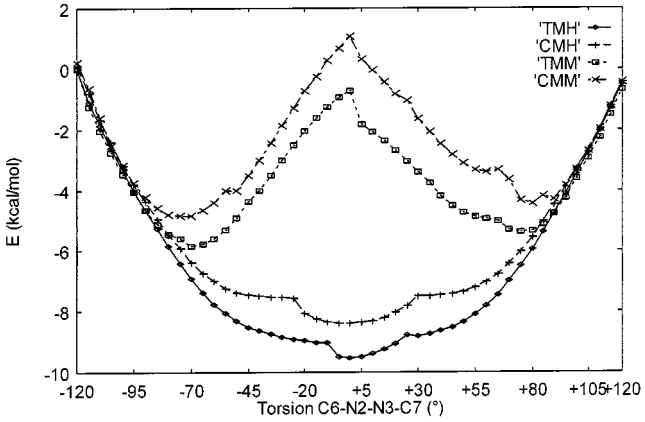


Figure 3. Energetic profiles for the rotation of the terminal NH(CO)–Me group around the N–N bond for methyl complexes TMH, CMH, TMM, and CMM; all energies have been rescaled referring to the value found for TMH at torsion = –120°

TMH and CMH do not present any steric obstacle for the carbonyl oxygen to lie in the ligand plane, and for both *cis* and *trans* isomers the conformation with minimum energy is planar, with the hydrazonic group practically coplanar to the coordination plane (C6–N2–N3–C7 = –19 and –11°, respectively), and the N–H group pointing towards the *cis* ligand. The *trans* form is about 1.2 kcal/mol more stable than the *cis* form due to the intramolecular hydrogen-bond N–H···Cl (H···Cl = 2.47 Å). This interaction is effective in the torsion angle window between –70° and +70° where the N–H dipole detects the stabilising attraction of the chloride, as shown by the fact that the curves for the two isomers coincide when the N–H group is oriented almost perpendicularly to the coordination plane (as for C6–N2–N3–C7 <–70° and >+70°). The introduction of a methyl group on the iminic carbon produces a remarkable destabilisation (about 9.3 kcal/mol) of the planar conformation, due to the repulsion between the carbonyl and the methyl (O···C = 2.76 and 3.15 Å for the most stable conformations of TMM and CMM, respectively). Two equivalent minima are found in the energy profile (Figure 3), corresponding to

torsion angles C6–N2–N3–C7 of –58° and +58° for TMM and –73° and +73° for CMM. Again, the molecule with the chloride *cis* to the N–H (TMM) is about 1 kcal/mol more stable than the molecule with the methyl close to the N–H (CMM), because of the N–H···Cl hydrogen bond (H···Cl = 2.52 Å), that can also explain the difference of about 15° between the positions of the energy minima for the two configurations. The optimisation of this interaction is favoured by a slight pyramidalisation of the bonding geometry for N3, expressed as the sum of the bond angles around it, which works out to 348.5° and 342.8° for TMM and CMM, respectively, whereas it is close to 360° for the sp^2-hybridized N3 in TMH and CMH (357.9° and 359.2°, respectively).

Acetyl Complexes

The oxygen of the acetyl group bound to the metal can compete with the chloride as a hydrogen-bond acceptor towards the N–H group. The acetyl complexes have an additional degree of freedom, represented by the orientation of the acetyl group around the Pd–C bond. The analysis of the energetic profile for the rotation shows that for the *trans* complex TAH there is a broad range of favoured orientations lying in a shallow minimum, with values of N1–Pd–C14–O2 ranging between –90° and +90°. For these conformations the acetyl oxygen is oriented towards the pyridine, and does not feel the repulsion of the negative charge localised on the chloride. Within this range two local minima are found, corresponding to –60° and +60°, as observed in the crystal structure of **13**, separated by a rotational barrier of about 5 kcal/mol, at N1–Pd–C14–O2 = 0° (with the acetyl in the square coordination plane). When the acetyl is bonded *cis* to the N–H group (CAH), the preferred orientations are situated in a shallow minimum with the torsion angle N2–Pd–C14–O2 ranging between –30° and +30° (Figure 4), which brings the acetyl oxygen close to the coordination plane and in proximity to the N3–H dipole.

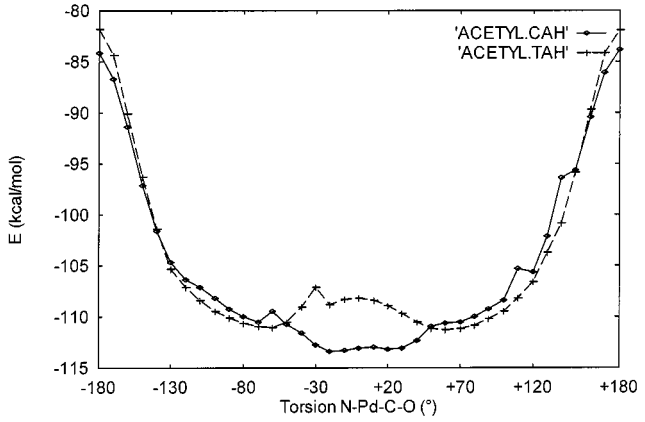


Figure 4. Energetic profiles for the rotation of the acetyl ligand around the Pd–C bond for TAH and CAH; torsion N–Pd–C–O refers to N2 for CAH and to N1 for TAH

These data suggest that the interaction between the acetyl and the N–H can stabilise the *cis* isomer. The relative stability of the *cis* and *trans* isomers when the steric hindrance on the iminic carbon is varied have been studied for compounds TAH, CAH, TAM, and CAM (Scheme 4), with the same procedure as in the case of the methyl complexes. The results are shown in Figure 5.

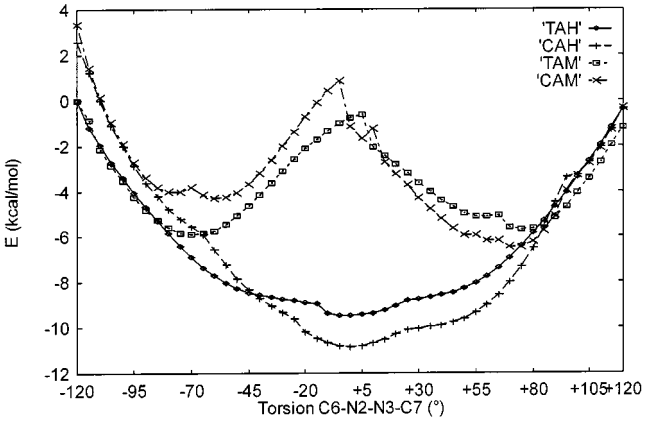


Figure 5. Energetic profiles for the rotation of the terminal NH(CO)–Me group around the N–N bond for acetyl complexes TAH, CAH, TAM, and CAM; all energies have been rescaled referring to the value found for TAH at torsion = –120°

As already observed for the methyl complexes, in the absence of steric hindrance for O1, for the most stable conformations the plane containing the NH–C(O)Me terminal group is coplanar with the metal coordination plane, and the N–H points towards the *cis* ligand (C6–N2–N3–C7 = –15° and –9° for TAH and CAH, respectively). However, the hydrogen-bond acceptor capabilities of the acetyl ligand produce a relevant inversion in the stability of the *cis* and *trans* isomers: when the terminal group is almost perpendicular to the coordination plane (C6–N2–N3–C7 < –50°) the *trans* isomer TAH is slightly more stable than the *cis* isomer CAH, but, as the N–H dipole enters in the range of interaction of the *cis* acetyl, at C6–N2–N3–C7 = –45°, the *cis* isomer CAH gains stability by the incipient formation of the N–H···O hydrogen bond (H···O = 1.80 Å at the minimum), which is much stronger than the N–H···Cl hydrogen bond present in the *trans* isomer TAH (H···Cl = 2.48 Å). The asymmetry of the profile relative to the *cis* isomer is due to the fact that the acetyl orientation is held fixed at N2–Pd–C14–O2 = –30°, meaning that at C6–N2–N3–C7 = –45° the N–H is on the opposite side of the acetyl oxygen with respect to the coordination plane, while at C6–N2–N3–C7 = +45° it is on the same side. The asymmetry of the energetic profile for the rotation of the torsion angle C6–N2–N3–C7 is even more significant for CAM and TAM, where the orientations with the hydrazonic group coplanar with the coordination plane are destabilised by the repulsion between O1 and C16 (Figure 5). Both molecules have two preferred conformations, as seen for CMM and TMM, but in the case of the acetyl complexes the *cis* complex CAM (with N2–Pd–C14–O2 = –30°) is about 1.9 kcal/mol less stable than the *trans* complex when the NH is oriented on the opposite side of the acetyl oxygen with respect to the coordination plane (C6–N2–N3–C7 = –56°). The stabilisation of TAM is due to the interaction N–H···Cl (H···Cl = 2.50Å), as found for TMM. The relative stability

of TAM and CAM is inverted when the torsion angle C6–N2–N3–C7 has positive values: in CAM the optimisation of the hydrogen bond to the *cis* group involves a gain of about 0.9 kcal/mol, relative to TAM, for the most stable conformation (C6–N2–N3–C7 = 66°, N2–Pd–C14–O2 = –31°, H···O = 1.79Å). This conformation is also the global minimum for CAM, and is about 2.0 kcal/mol more stable than the one with C6–N2–N3–C7 = –56°. For TAM the two minima are energetically equivalent, due to the local symmetry of the NH···Cl system with respect to the coordination plane.

These results show that the conformational preferences for compounds in Scheme 4 are mainly influenced by the hydrogen bond between the NH group and the *cis* ligand. When the choice is between Cl and Me, the hydrogen bond with the former is favoured in all cases (CMH, TMH, CMM, TMM). In TAH, CAH, CAM, TAM, the chloride must compete with the acetyl, and it has been seen that the latter is generally more suited to optimise the hydrogen bond, provided that it is correctly oriented.

Conclusions

We have shown that HNNO tridentate hydrazonic ligands can form two different kinds of methyl palladium(II) complexes, depending on the experimental conditions. Thus, in the absence of a basic medium, the ligands adopt a neutral bidentate HNN coordination, whereas in the presence of a base a tridentate NNO behaviour is preferred. In solution the bidentate complexes tend to eliminate methane in relation to the acidic character of the ligand. The reactivity towards CO of the bidentate and tridentate complexes is drastically different. The bidentate complexes form the corresponding acetyl complexes, where the ligand maintains a neutral bidentate HNN behaviour. On the contrary, the carbonylation of the tridentate complexes results in their fast and complete decomposition to palladium black together with the formation of the acylated ligand, the acetyl group being bonded to the hydrazonic nitrogen.

A molecular modelling study indicates that not only steric effects determine the isomeric *cis*/*trans* distribution observed in both bidentate methyl and acetyl complexes, but also that electronic considerations must be taken into account. Thus, for the methyl complexes the possibility of formation of a N–H···Cl hydrogen bond favours the *trans* isomer, whereas in the acetyl complexes the formation of a N–H···O_{acyl} hydrogen bond favours the *cis* isomer.

Experimental Section

General: All the manipulations were carried out under a purified dry nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried prior to use and stored under nitrogen. 2-Acetylpyridine and 2-pyridinecarboxaldehyde were purchased (Aldrich), whereas 6-methyl-2-pyrdinecarboxaldehyde was synthesised by the oxidation of 6-methyl-2-pyridinemethanol with SeO_2 in dioxane.[20] The hydrazides were synthesised by reaction between the corresponding methyl or ethyl esters and hydrazine monohydrate (Fluka). (COD)PdMeCl was synthesised following literature methods.[11a] Silver acetate was purchased (Aldrich).

Proton NMR spectra were recorded on a Bruker 300 FT spectrometer, with $SiMe_4$ as internal standard, at 25 °C. IR spectra were obtained by a Nicolet 5PCFT-IR spectrophotometer in the 4000–400 cm^{-1} range with KBr disks. Mass spectra were recorded on a FINNIGAN SSQ 710 spectrometer. Elemental analysis (C,H,N) were performed by using a Carlo Erba Model EA 1108 apparatus. GC-MS spectra were obtained with a Hewlett–Packard 5890 series II gas chromatograph with a Gerstel CIS III temperature-controllable injector, an HP 5971A mass-selective detector with electron-impact ionisation at 70 eV, and an HP Ultra-2 column (25 m, 0.20 mm inner diameter, 0.33 μm film thickness).

Synthesis of Ligands HL1–HL4. – General Procedure: Ligands **HL1**–**HL4** were synthesised by refluxing a solution containing the ketone or the aldehyde (0.5 g) with a stoichiometric amount of the corresponding hydrazide, in the presence of a few drops of glacial acetic acid. The end of the reaction was determined by TLC, monitoring the disappearance of the stain corresponding to the pyridinic system. After concentration and cooling of the solution, the pure ligands crystallised as colourless needles which were washed with a few millilitres of diethyl ether and dried in vacuum.

Methyl 2-Pyridyl Ketone Acetylhydrazone (HL1): Yield: 0.571 g (78%). – M.p. 153 °C. – IR (cm^{-1}): ν(N–H) = 3198 m, ν(C=O) = 1678 vs, AMIDE II $\tilde{\nu}$ = 1580 s, AMIDE III = 1371 s. – ^{1}H NMR ($CDCl_3$): (*E*) isomer δ = 2.40 [s, 3 H, MeC(O)], 2.36 [s, 3 H, C(Me)=N]; (*Z*) isomer δ = 2.37 [s, 3 H, MeC(O)], 2.33 [s, 3 H, C(Me)=N]. – MS (C.I.): 178 [M^+ + 1]. – $C_9H_{11}N_3O$ (177.21): calcd. C 61.00, H 6.26, N 23.71; found C 60.88, H 6.23, N 23.81. – log β_1^H = 12.51(1).

Methyl 2-Pyridyl Ketone Benzoylhydrazone (HL2): Yield: 0.741 g (75%). – m.p.: 150–152 °C. – IR (cm^{-1}): ν(N–H) = 3180 br, ν(C=O) = 1654 vs, AMIDE II $\tilde{\nu}$ = 1544 s, AMIDE III = 1282 s. – ^{1}H NMR ($CDCl_3$): (*E*) isomer δ = 7.90 [d, 2 H, Ph *o*–C(O)], 7.51–7.46 [m, 4 H, H^3 + Ph *m* and *p*-C(O)], 2.49 [s, 3 H, C(Me)=N]; (*Z*) isomer δ = 7.95 [dd, 2 H, Ph *o*-C(O)], 7.52–7.43 [m, 3 H, Ph *m* and *p*-C(O)], 2.50 [s, 3 H, C(Me)=N]. – MS (C.I.): 240 [M^+ + 1]. – $C_{14}H_{13}N_3O$ (239.28): calcd. C 70.35, H 5.47, N 17.56; found C 70.36, H 5.67, N 17.86. – log β_1^H = 11.35(1).

2-Pyridyl Carboxaldehyde Benzoylhydrazone (HL3): Yield: 0.864 g (78%). – m.p.: 107–109 °C. – IR (cm^{-1}): ν(N–H) = 3193 w, ν(C=O) = 1662 vs, AMIDE II $\tilde{\nu}$ = 1553 vs, AMIDE III = 1286 vs. – ^{1}H NMR ($CDCl_3$): (*E*) isomer δ = 7.97 [d, 3 H, H^3 + Ph *o*-C(O)], 7.27 [s, 1 H, C(H)=N]; (*Z*) isomer δ = 8.02 [d, 3 H, H^3 + Ph *o*-C(O)], 7.61–7.50 [m, 5 H, Ph *m* and *p*-C(O)], 7.27 [s, 1 H, C(H)=N]. – MS (C.I.): 226 [M^+ + 1]. – $C_{13}H_{11}N_3O$ (225.25): calcd. C 69.32, H 4.92, N 18.66; found C 69.35, H 4.97, N 18.64. – log β_1^H = 11.48(1).

Ethyl 2-Pyridyl Ketone Benzoylhydrazone (HL4): Yield: 0.500 g (53%). – m.p.: 146 °C. – IR (cm^{-1}): ν(N–H) = 3174 m, ν(C=O) = 1653 vs, AMIDE II $\tilde{\nu}$ = 1548 s, AMIDE III = 1300 s. – ^{1}H NMR ($CDCl_3$): (*E*) isomer δ = 7.90 [d, 2 H, Ph *o*-C(O)], 7.53–7.48 [m, 3 H, Ph *m*- and *p*-C(O)], 3.04 (q, 2 H, Et), 1.25 (t, 3 H, Et). – (*Z*) isomer δ = 7.97 [d, 2 H, Ph *o*-C(O)], 7.49–7.45 [m, 3 H, Ph *m*- and *p*-C(O)], 2.94 (q, 2 H, Et), 1.31 (t, 3 H, Et). – MS (C.I.): 254 [M^+ + 1]. – $C_{13}H_{15}N_3O$ (229.28): calcd. C 71.13, H 5.97, N 16.59; found C 71.16, H 6.03, N 16.52.

Synthesis of Ligand HL5: The synthesis was carried out in situ introducing the correct amount of benzoylhydrazide into the solu-

tion coming from the synthesis of 6-methyl-2-pyridylcarboxyaldehyde. The solution was then refluxed for 30 minutes. After cooling a pale pink solid was filtered and washed with diethyl ether.

6-Methyl-2-pyridyl Aldehyde Benzoylhydrazone (HL5): Yield: 0.593 g (60%). – m.p.: 108 °C. – IR (cm^{-1}): ν(N–H) = 3187 m, ν(C=O) = 1653 vs, AMIDE II $\tilde{\nu}$ = 1560 s, AMIDE III = 1296 s. – ^1H NMR ($CDCl_3$): (*E*) isomer δ = 8.30 [s, 1 H, C(H)=N], 7.88 [d, 2 H, Ph *o*-C(O)], 7.45 [t, 2 H, Ph *m*-C(O)], 7.54 [t, 1 H, Ph *p*-C(O)]. – MS (C.I.): 240 [M^+ + 1]. – $C_{14}H_{13}N_3O$ (239.28): calcd. C 70.28, H 5.48, N 17.56; found C 70.31, H 5.53, N 17.60. – log β_1^H = 11.61(1).

Synthesis of the Bidentate Methyl Complexes Pd(HNN)MeCl 1–5. – General Procedure: To a vigorously stirred ethereal ligand suspension (0.100 g) was added a stoichiometric amount of (COD)PdMeCl. Instantaneously a pale yellow solid precipitated and the resulting mixture was stirred for two hours at room temperature. After filtration the isolated solid was repeatedly washed with diethyl ether and then dried in vacuum.

Complexes **1** and **3** can also be prepared with CH_2Cl_2 as solvent by the following procedure: 0.100 g of ligand are dissolved in 20 mL of CH_2Cl_2 and a stoichiometric amount of (COD)PdMeCl is added. The yellow solution is stirred at room temperature for two hours. Concentration of the solution and precipitation with *n*-hexane gives the desired products as a yellow powder, which is filtered off, washed with *n*-hexane and then dried under vacuum for several hours. The yields are lower then those obtained using diethyl ether (65%).

The yields reported below are those from the synthesis carried out in diethyl ether.

[PdMeCl(HL1)] (1): Yield: 0.106 g (92%). – IR (cm^{-1}): ν(N–H) = 3291 s, ν(C=O) = 1699 vs, AMIDE II $\tilde{\nu}$ = 1478 m, AMIDE III = 1374 m. – ^1H NMR ($CDCl_3$): δ = 2.26 [s, 3 H, MeC(O)], 2.20 [s, 3 H, C(Me)=N]. – $C_{10}H_{14}ClN_3OPd$ (334.09): calcd. C 35.95, H 4.22, N 12.58; found C 35.86, H 4.08, N 12.68.

[PdMeCl(HL2)] (2): Yield: 0.155 g (93%). – IR (cm^{-1}): ν(N–H) = 3195 w, ν(C=O) = 1673 vs, AMIDE II $\tilde{\nu}$ = 1499m–1460 s, AMIDE III = 1271 m. – ^1H NMR ($CDCl_3$): *trans* isomer δ = 7.99 [d, 2 H, Ph *o*-C(O)], 7.60–7.50 [m, 4 H, H^1 + Ph *m* and *p*-C(O)], 2.37 [s, 3 H, C(Me)=N]; *cis* isomer δ = 2.42 [s, 3 H, C(Me)=N]. – $C_{15}H_{16}ClN_3OPd$ (396.17): calcd. C 45.48, H 4.07, N 10.61; found C 45.51, H 4.01, N 10.60.

[PdMeCl(HL3)] (3): Yield: 0.153 g (91%). – IR (cm^{-1}): ν(N–H) = 3247 w, ν(C=O) = 1669 vs, AMIDE II $\tilde{\nu}$ = 1506vs–1485 s, AMIDE III = 1266 vs. – ^1H NMR (CD_2Cl_2): δ = 9.96 [s, 1 H, C(H)=N], 7.96 [d, 2 H, Ph *o*-C(O)], 7.52 [t, 3 H, Ph *m*- and *p*-C(O)]. – $C_{14}H_{14}ClN_3OPd$ (382.14): calcd. C 44.00, H 3.69, N 11.00; found C 43.99, H 3.53, N 10.85.

[PdMeCl(HL4)] (4): Yield: 0.115 g (91%). – IR (cm^{-1}): ν(N–H) = 3206 w, ν(C=O) = 1668 vs, AMIDE II $\tilde{\nu}$ = 1466 m, AMIDE III = 1268 m. – ^1H NMR ($CDCl_3$): *trans* isomer δ = 8.02 [d, 2 H, Ph *o*-C(O)], 7.50 [m, 3 H, Ph *m* and *p*-C(O)], 2.84 (q, 2 H, Et); *cis* isomer δ = 7.99 [d, 2 H, Ph *o*-C(O)], 2.89 (s, 2 H, Et). The triplets of the Et groups are fused in a multiplet centred at δ = 1.25 – $C_{16}H_{18}ClN_3OPd$ (410.19): calcd. C 46.85, H 4.42, N 10.24; found C 46.800, H 4.29, N 10.46.

[PdMeCl(HL5)] (5): Yield: 0.141 g (85%). – IR (cm^{-1}): ν(N–H) = 3234 w, ν(C=O) = 1674 vs, AMIDE II $\tilde{\nu}$ = 1483 m, AMIDE III = 1263 m. – ^1H NMR ($CDCl_3$): δ = 7.96 [d, 2 H, Ph *o*-C(O)], 7.60 [t, 1 H, Ph *p*-C(O)], 7.47 [t, 2 H, Ph *m*-C(O)], 9.96 [s, 1 H, C(H)=N]. – $C_{15}H_{16}ClN_3OPd$ (396.17): calcd. C 45.48, H 4.10, N 10.61; found C 45.45, H 4.08, N 10.46.

Synthesis of the Chloride Complex Pd(NNO)Cl 6: HL2 (0.020 g, 0.084 mmol) was dissolved in 30 mL of CH_2Cl_2 and (COD)PdMeCl (0.022 g, 0.084 mmol) was added. Immediately a yellow solution was formed from which a yellow solid precipitated within 20 minutes of stirring at room temperature. After two hours of reaction the solid was filtered, repeatedly washed with diethyl ether and then dried in vacuum.

[PdCl(L2)] (6): Yield: 0.260 g (82%). – IR (cm^{-1}) $\tilde{\nu}$: AMIDE II = 1498 s, AMIDE III = 1364 s. – ^1H NMR ($CDCl_3$): δ = 8.11 [d, 2 H, Ph *o*-C(O)], 7.38–7.30 [m, 4 H, H^3 + Ph *m*- and *p*-C(O)], 2.46 [s, 3 H, C(Me)=N]. $C_{14}H_{12}ClN_3OPd$ (380.12): calcd. C, 44.24, H 3.18, N 11.05; found C 44.43, H 2.99, N 11.12.

Synthesis of the Tridentate Methyl Complexes Pd(NNO)Me 7–10: i): Compound **1**, **2**, **3**, or **5** (0.050 g) was dissolved in 20 mL of THF together with a threefold excess of NaOMe. Soon after the base had been added, a colour change of the solution from yellow to orange was observed. The solution was then stirred at room temperature for two hours. The unchanged NaOMe and the formed NaCl were removed by filtration and the resulting solution was concentrated in vacuum. By adding *n*-hexane an orange powder precipitated which was filtered off and dried in vacuum for several hours. ii): Compound **1**, **2**, **3**, or **5** (0.050 g) was dissolved in 20 mL of CH_2Cl_2 and a fivefold excess of silver acetate was added. The resulting mixture was stirred in the dark overnight. After removal of the silver salts the solution was concentrated in vacuum and the product precipitated by adding diethyl ether. For both methods the yields vary from 55% to 75%.

[PdMe(L1)] (7): IR (cm^{-1}) $\tilde{\nu}$: AMIDE II = 1582 vs, AMIDE III = 1370 m. – ^1H NMR ($CDCl_3$): δ = 2.31 [s, 3 H, MeC(O)], 2.28 [s, 3 H, C(Me)=N]. $C_{10}H_{13}N_3OPd$ (297.63): calcd. C 40.35, H 4.40, N 14.12; found C 40.30, H 4.46, N 14.10.

[PdMe(L2)] (8): IR (cm^{-1}) $\tilde{\nu}$: AMIDE II = 1499 s, AMIDE III = 1365 s. – ^1H NMR (CD_2Cl_2): δ = 8.06 [d, 2 H, Ph *o*-C(O)], 7.30–7.26 [m, 3 H, Ph *m* and *p*-C(O)], 2.41 [s, 3 H, C(Me)=N]. $C_{15}H_{15}N_3OPd$ (359.70): calcd. C 50.09, H 4.20, N 11.68; found C 49.99, H 4.15, N 11.50.

[PdMe(L3)] (9): IR (cm^{-1}) $\tilde{\nu}$: AMIDE II = 1501 s, AMIDE III = 1380 s. – ^1H NMR ($CDCl_3$): δ = 9.21 [s, 1 H, C(H)=N], 8.19 [d, 2 H, Ph *o*-C(O)], 7.33–7.30 [m, 3 H, Ph *m* and *p*-C(O)]. $C_{14}H_{13}N_3OPd$ (345.68): calcd. C 48.64, H 3.79, N 12.16; found C 48.61, H 3.82, N 12.10.

[PdMe(L5)] (10): IR (cm^{-1}) $\tilde{\nu}$: AMIDE II = 1462 m, AMIDE III = 1366 vs. – ^1H NMR ($CDCl_3$): δ = 9.06 [s, 1 H, C(H)=N], 8.13 [d, 2 H, Ph *o*-C(O)], 7.41–7.33 [m, 3 H, H^2 + Ph *m* and *p*-C(O)].

Carbonylation Reactions of the Bidentate Methyl Palladium Complexes Pd(HNN)MeCl. General Procedure for the Preparation of Complexes 11, 13, 14, and 15: Compound **1**, **3**, **4**, or **5** (0.050 g) was placed in a 50 mL Schlenk tube and dissolved in about 10 mL of CH_2Cl_2; CO was then bubbled through this solution for about 5–10 minutes through a glass capillary. After filtration of the solution through celite the acetyl complexes were precipitated by addition of *n*-hexane.

{Pd[C(O)Me]Cl(HL1)} (11): Yield: 0.024 g (45%). – IR (cm^{-1}): ν(N–H) = 3174 s, ν(C=O) = 1692br, ν{Pd[C(O)Me]} = 1670 sh–1646 s, AMIDE II $\tilde{\nu}$ = 1501 s, AMIDE III = 1371 m. – ^1H NMR

($CDCl_3$): *trans* isomer δ = 2.28 [s, 3 H, MeC(O)], 2.20 [s, 3 H, C(Me)=N]; *cis* isomer δ = 2.48 [s, 3 H, MeC(O)], 2.19 [s, 3 H, C(Me)=N]. – $C_{11}H_{13}ClN_3O_2Pd$ (361.10): calcd. C 36.49, H 3.90, N 11.60; found C 36.43, H 3.54, N 11.43.

{Pd[C(O)Me]Cl(HL3)} (13): Yield: 0.043 g (80%). – IR (cm^{-1}): ν(N–H) = 3266 w, ν(C=O) + ν{Pd[C(O)Me]} = 1692 vs, AMIDE II $\tilde{\nu}$ = 1503 vs–1486 s, AMIDE III = 1250 s. – ^{1}H NMR ($CDCl_3$): *trans* isomer δ = 9.90 [s, 1 H, C(H)=N], 7.96 [d, 2 H, Ph *o*-C(O)], 7.67–7.51 [m, 5 H, H^1+H^3 + Ph *m* and *p*-C(O)]; *cis* isomer δ = 10.24 [s, 1 H, C(H)=N], 8.11 [d, 2 H, Ph *o*-C(O)]. – $C_{15}H_{14}ClN_3O_2Pd$ (410.15): calcd. C 43.93, H 3.44, N 10.24; found C 44.00, H 3.52, N 10.26.

{Pd[C(O)Me]Cl(HL4)} (14): Yield: 0.033 g (62%). – IR (cm^{-1}): ν(N–H) = 3206 m, ν(C=O) = 1692 vs, ν[Pd(C(O)Me)] = 1668 sh–1645 s, AMIDE II $\tilde{\nu}$ = 1462 s, AMIDE III = 1368 m. – ^{1}H NMR ($CDCl_3$): *trans* isomer δ = 2.92 (q, 2 H, Et); *cis* isomer δ = 2.98 (q, 2 H, Et). The low resolution of the spectrum does not allow a correct attribution of the signals of the pyridine and phenyl rings. For both isomers the Pd–Me signals are overlapped with the triplets generated by the methyl group of the R substituent in a multiplet centred at 1.27 ppm. – $C_{17}H_{18}ClN_3O_2Pd$ (438.20): calcd. C 47.14, H 3.03, N 9.70; found C 47.10, H 3.00, N 9.75.

{Pd[C(O)Me]Cl(HL5)} (15): Yield: 0.016 g (45%). – IR (cm^{-1}): ν(N–H) = 3234 m, ν(C=O) + ν(Pd(C(O)Me)] = 1700 vs, AMIDE II $\tilde{\nu}$ = 1509 s, AMIDE III = 1262 s. – ^{1}H NMR ($CDCl_3$): δ = 7.96 [d, 2 H, Ph *o*-C(O)], 7.61 [t, 1 H, Ph *p*-C(O)], 7.52 [t, 2 H, Ph *m*-C(O)], 6.94 [s, 1 H, C(H)=N]. – $C_{15}H_{16}ClN_3O_2Pd$ (412.16): calcd. C 45.31, H 3.80, N 9.91; found C 45.25, H 3.71, N 9.89.

Procedure for the Preparation of 12: Compound **2** (0.060 g, 0.150 mmol) was placed in a 50 mL schlenk tube and dissolved in 20 mL of cold CH_2Cl_2 (0 °C). The reactor was evacuated and filled with CO for three consecutive times. The solution was stirred for 15 minutes maintaining the temperature at 0 °C and then the solvent was removed in vacuum without varying the temperature. The solid residue was re-dissolved in CH_2Cl_2, filtered through celite and dried again in vacuum.

{Pd[C(O)Me]Cl(HL2)} (12): Yield: 0.042 g (78%). – IR (cm^{-1}): ν(N–H) = 3200 w, ν(C=O)+ν[Pd(C(O)Me)] = 1689 vs, AMIDE II $\tilde{\nu}$ = 1474 s, AMIDE III = 1261 s. – ^{1}H NMR ($CDCl_3$): *trans* isomer δ = 2.38 [s, 3 H, C(Me)=N]; *cis* isomer δ = 2.52 [s, 3 H, C(Me)=N]. In both isomers the residual protons are overlapped with other signals.

Carbonylation Reactions of the Tridentate Methyl Palladium Complexes Pd(NNO)Me. – General Procedure: Complexes **7–10** (0.020 g) were dissolved in 20 mL of CH_2Cl_2 in a 50 mL schlenk tube. CO was bubbled through the solution at room temperature for 5 minutes through a glass capillary. Immediately palladium black was formed. The solution was stirred under CO atmosphere until it was completely colourless and then filtered through celite. After evaporation of the solution a pale yellow solid was filtered off.

The characterisation of the formyl 2-pyridyl aldehyde *N*-acetyl benzoylhydrazone is reported: Yield: 0.015 g (complete conversion). – m.p: 116 °C. – IR (cm^{-1}) $\tilde{\nu}$: AMIDE II = 1459s–1421 m, AMIDE III = 1262 m. – ^{1}H NMR (CD_2Cl_2): δ = 8.63 (d, 1 H, R′), 7.78 (td, 1 H, H^2), 7.34 (td, 1 H, H^1), 7.88 [dd, 2 H, Ph *o*-C(O)], 7.55–7.43 [m, 4 H, H^3 + Ph *m* and *p*-C(O)], 7.02 [s, 1 H, C(H)=N], 2.33 [s, 3 H, C(O)Me]. – MS (CI): 268 (M^+ + 1). – $C_{15}H_{13}N_3O_2$ (267.29): calcd. C 67.41, H 4.90, N 15.72; found C 67.45, H 5.01, N 15.77.

Synthesis of Formyl 2-Pyridyl Aldehyde *N*-acetyl Benzoylhydrazone: Compound **HL3** (0.500 g, 2.220 mmol) was dissolved in 20 mL of pyridine under a nitrogen atmosphere. The obtained solution was stirred in an ice bath and acetyl chloride (0.871 g, 11.100 mmol) was added dropwise to the solution. Immediately pyridinium hydrochloride precipitated. The mixture was refluxed for 24 hours after which 30 mL of water was slowly added. From the solution a brown solid precipitated which was filtered off and dried in vacuum. Recrystallisation from ethanol gave 0.400 g (67%) of microcrystalline product.

X-ray Structure Determination of 13 and 3:[21] A single crystal of **13** suitable for X-ray analysis was glued to a glass fibre and mounted on a Philips PW100 diffractometer employing Mo-K_α radiation. The instrument was equipped with a graphite monochromator. Intensities were collected at room temperature, and corrected for absorption using the ψ-scan method. During data collection, no intensity decay was observed. Corrections for Lorenz and polarisation effects were applied. Relevant data collection and structure refinement parameters are summarised in Table 5.

Table 5. Crystal data and structure refinement for compounds **3** and **13**

Compound	**3**	**13**
Empirical formula	$C_{14}H_{14}ClN_3OPd$	$C_{15}H_{14}ClN_3O_2Pd$
Formula weight	382.1	410.15
Radiation, λ [Å]	Cu-K_α, 1.5418	Mo-K_α, 0.71069
Crystal system	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/c$
Unit cell dimensions [Å, °]	a = 5.9876(7)	a = 10.372(4)
	b = 12.776(2)	b = 7.146(3)
	c = 19.396(3)	c = 21.985(7)
	β = 96.20(1)	β = 102.83(2)
Volume [Å^3]	1475.1(4)	1589(1)
Z	4	4
Density (calculated) [g/cm^3]	1.72	1.71
F(000)	760	816
Crystal size [mm]	0.03 × 0.05 × 0.40	0.13 × 0.14 × 0.38
θ range [°]	4–75	3–30
Index ranges	$0 \le h \le 7$	$-14 \le h \le 14$
	$-15 \le k \le 0$	$-10 \le k \le 10$
	$-24 \le l \le 24$	$0 \le l \le 30$
Independent reflections	3277	4626
		R(int) = 0.0538
Observed reflections	2366 [$F_o > 2.5\sigma(F_o)$]	2308 [$F_o > 4\sigma(F_o)$]
Data/restraints/parameters	2366/14/238	2308/0/244
Goodness of fit	0.80	0.80
Final R indices [$I > 2\sigma(I)$]		
R_1[a]	0.052	0.038
R_w[b]	0.057	0.0906

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

The phase problem was solved by direct methods employing SIR97.[22] Atom coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms by full-matrix least-squares on F^2 with the SHELXL97 program.[23] All hydrogen atoms were located in the difference Fourier maps and refined isotropically. The final geometry was analysed with the program PARST97.[24] The calculations were performed on a DIGITAL Alpha255 workstation at the "Centro di Studio per la Strutturistica Diffrattometrica del C.N.R." in Parma.

A wedge-shaped crystal of compound **3** was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu-Kα radiation. Corrections for Lorentz and polarisation effects were applied. During data collection, no intensity decay was observed. The structure was solved by the PATTY op-

tion of the DIRDIF96 program system.[25] The hydrogen atoms were calculated and restrained so that the distance to their carrier remained constant at approximately 1.0 Å. Structure was refined by full-matrix least-squares on *F*, using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The DIFABS empirical absorption correction[26] was applied with coefficients in the range of 0.64–2.02. The secondary isotropic extinction coefficient[27] refined to $R = 70.(2)$. A final difference Fourier map revealed a residual electron density between –1.8 and 1.2 eÅ^{-3}, in the vicinity of the heavy atoms. Scattering factors were taken from Cromer and Mann,[28a] International Tables for X-ray Crystallography (1974).[28b] The anomalous scattering of Cl and Pd was taken into account.[29] The calculations were performed with XTAL.[30] All drawings were made with ZORTEP[31] an extensive use was made of the Cambridge Structural Database software.[32]

Molecular Energy Calculations: All the calculations were performed with the program MOPAC 6.00[33] running on a Pentium 200 MHz personal computer. The model compounds (Scheme 4) were built based on the geometry of the crystal structure of **3** (Figure 2, Table 4), which presented a *trans* configuration. In all cases the terminal phenyl has been replaced by an idealised methyl group. The atomic labelling refers to Figure 2. The acetyl derivatives were built by inserting the acetyl group on the metal, with geometry taken from the X-ray structure of **13**. The atomic labelling refers to Figure 1. The *cis* derivatives were built by exchanging the –R and –Cl ligands, preserving the original bond lengths. The iminomethyl molecules (TMM, CMM, TAM, CAM) have been built by substituting the H atom with an idealised methyl group. All hydrogen atoms were introduced in idealised geometry with the exception of the iminic and hydrazonic ones, which were taken from the crystal structure. The geometries of all models have been optimised by minimising the molecular energy using the PM3 Hamiltonian.[34] The metal was treated as a dummy bivalent cation, and the geometry of the molecular core around the metal was held fixed, as observed in the crystal (Table 4 indicates all the parameters which were not modified in the minimisation). The geometric parameters which were optimised are all the bond lengths, angles and torsions starting from the N2–N3 bond and proceeding towards the terminal methyl. The geometries of the iminic hydrogen and methyl, the NH group, and the rotation of the coordinated methyl and acetyl groups around the Pd–C bonds were also optimised.

The energetic profiles for the rotation of the terminal NH–C(O)–Me group around the N–N bond, and for the rotation of the acetyl around the Pd–C bond have been calculated by varying the torsion considered (C6–N2–N3–C7 for the former and N1–Pd–C14–O3 and N2–Pd–C14–O3 for the latter, *trans* and *cis*, respectively) in steps of 5° and 10°, respectively, and by optimising the rest of the molecule at each step, with the constraints described above. The acetyl was also constrained to remain planar during its rotation. In all cases a correction of 14*sin(τ) kcal/mol was applied to the rotational barrier for the N–C(O) bond, introducing an additional molecular mechanics energetic contribution due to the partial double-bond character of the amidic bond as implemented in MOPAC, depending on the torsion angle τ = C6–N2–N3–C7.

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