Methyl- and Acetylpalladium(II) Complexes Containing a P,N,O Tridentate Hydrazone Ligand

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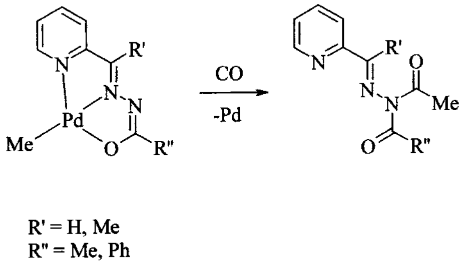
The hydrazone ligand 2-(diphenylphosphanyl)benzaldehyde benzoylhydrazone (HPNO) forms the methyl Pd^{II} complex [Pd(HPN)(Me)Cl] (**1**) in high yield when treated with [(COD)Pd(Me)Cl] in dichloromethane or diethyl ether at room temperature. In complex **1**, the ligand remains neutral and is P,N bidentate. The deprotonation of the ligand by Et_3N affords [Pd(PNO)(Me)] (**2**), in which the anionic ligand is P,N,O tridentate. When **1** is treated with $AgCF_3SO_3$, the cationic complex $[Pd(HPNO)(Me)]^+[CF_3SO_3]^-$ (**3**) is formed; here the neutral ligand coordinates in a tridentate P,N,O fashion. All three methyl complexes were subjected to 30 atm of CO pressure, resulting in the isolation of the corresponding acetyl complexes [Pd(HPN)(MeCO)Cl] (**4**), [Pd(PNO)(MeCO)] (**5**) and $[Pd(HPNO)(MeCO)]^+[CF_3SO_3]^-$ (**6**). Complex **4** is completely stable in solution in the absence of CO, whereas **5** and **6** quickly decarbonylate to regenerate the starting methyl complexes **2** and **3**. Complexes **5** and **6** can also be obtained in high yields by treatment of **4** with Et_3N and $AgCF_3SO_3$, respectively. The X-ray crystal structures of the complexes **2**, **5** and **6** were determined.

Introduction

Recently, we have shown that ionisable tridentate hydrazone ligands of the type HNN′O, derived from the condensation of different hydrazides with 2-formyl- or 2-acetylpyridine, can give rise to two different kinds of methylpalladium(II) complexes: namely [Pd(HNN′)(Me)Cl] and [Pd(NN′O)(Me)], respectively.[1] In the first, the neutral ligands display an N,N′ bidentate behaviour, with the oxygen excluded from the coordination sphere, while in the second the anionic ligands bind palladium through all three donor atoms. Under a CO atmosphere, [Pd(HNN′)(Me)Cl] complexes convert quantitatively into the corresponding acetyl complexes [Pd(HNN′)(MeCO)Cl], and the ligands do not vary their coordination mode. Surprisingly, when the [Pd(NN′O)(Me)] complexes are subjected to a CO atmosphere they quickly decompose to Pd black, with isolation of a new organic molecule corresponding to the ligand acylated at the hydrazone nitrogen (Scheme 1).



Scheme 1

With the aim of isolating acetyl palladium(II) complexes in which the metal is three-coordinated to an anionic ligand, we have introduced a P atom, with a higher affinity towards palladium, into the chelating system. The previously synthesised acylhydrazone ligand 2-(diphenylphosphanyl)benzaldehyde benzoylhydrazone (HPNO in Scheme 2),[2] was used in the synthesis of a series of methylpalladium(II) complexes, which were subsequently carbonylated in order to isolate the corresponding acetyl complexes. The HPNO ligand has already shown its versatility: depending on the experimental conditions it can be either

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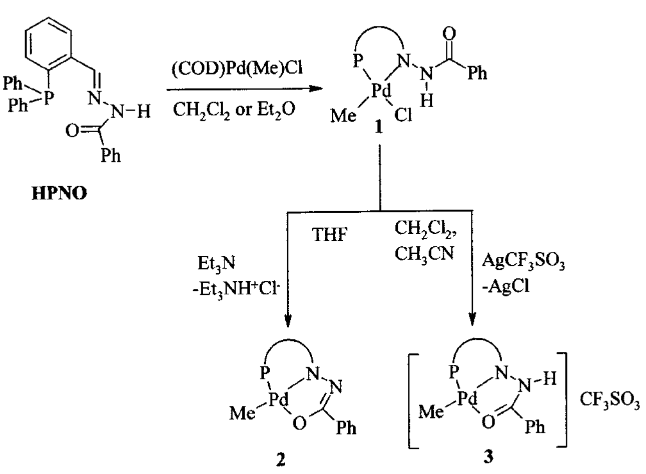
P,N bidentate or P,N,O tridentate when protonated, and P,N,O tridentate when deprotonated.[3]



Scheme 2

We report in this paper on the synthesis and characterisation of a series of methylpalladium(II) complexes possessing HPNO as a ligand, as well as on their reactivity towards CO, with particular regard to the influence that the coordination mode of the ligand exerts on the carbonylation course.

Results and Discussion

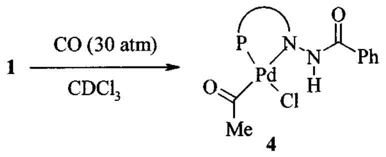
The ligand HPNO reacts at room temperature with [(COD)Pd(Me)Cl], both in dichloromethane and diethyl ether, resulting in the formation of the complex [Pd(HPN)(Me)Cl] (**1**), in which the metal is coordinated by the neutral ligand in a P,N mode (Scheme 2). The large shifts to lower fields both of the signals of the phosphane moiety in the ^{31}P NMR spectrum (from δ = −12.5 to 38.4) and of the HC=N proton in the ^{1}H NMR spectrum (from δ = 8.95 to 9.53), relative to the free ligand, indicate the involvement of both the P and the N atom in the coordination. The exclusion of the oxygen from the coordination sphere is demonstrated by the strong IR stretching band at 1684 cm^{-1}, which is a value typical for an uncoordinated amide C=O group.[1][3a] The neutral character of the ligand is confirmed by a weak IR band at 3206 cm^{-1} and by a singlet at δ = 11.19 in the ^{1}H NMR spectrum recorded in CDCl$_3$. The methyl group bonded to palladium resonates in the ^{1}H NMR spectrum as a doublet at δ = 0.73, with a phosphorous coupling constant of 1.9 Hz; these are typical values for a phosphane and a methyl situated *cis* to one another in a square-planar arrangement around a palladium(II) ion.[4]

The addition of a slight excess of Et$_3$N to a THF solution of **1** causes the deprotonation of the ligand, affording the complex [Pd(PNO)(Me)] (**2**), in which the ligand is now P,N,O tridentate (Scheme 2). Both ν(N−H) and ν(C=O) are absent in the IR spectrum, while in the ^{31}P NMR spectrum there is a singlet at δ = 32.0; the methyl group bonded to palladium is seen as a doublet centred at δ = 0.61 in the ^{1}H NMR spectrum, with a phosphorous coupling constant equivalent to that found in **1**. The shielding of the signals observed in the NMR spectra of **2**, relative to those in **1**, is attributable to the higher electron density due to the anionic tridentate coordination on the metal. The HC=N proton resonates as a singlet at δ = 8.52, a value very similar to those found for palladium(II) complexes of the type [Pd(PNO)X] (X = OAc, Cl, I, C≡C−R).[2,5] Yellow crystals suitable for X-ray analysis were collected after slow diffusion of *n*-hexane into a dichloromethane solution of **2** at −20 °C; the resulting structure confirmed the proposed nature of **2**.

The addition of a chloride scavenger, such as AgCF$_3$SO$_3$, to a dichloromethane solution of **1** resulted in the immediate precipitation of AgCl and isolation of the cationic methyl complex [Pd(HPNO)(Me)]$^+$[CF$_3$SO$_3$]$^-$ (**3**), in which the neutral ligand was P,N,O tridentate (Scheme 2). The ^{31}P NMR spectrum shows a singlet at δ = 36.2, while the HC=N proton resonance is found as a singlet at δ = 9.36. The involvement of the C=O in the coordination is proved by the lowering in frequency of the ν(C=O), which is now visible as a strong bifurcated band at 1560−1597 cm^{-1};[3,6] two strong signals always present at 1298 cm^{-1} and 1240 cm^{-1} in the IR spectrum testify to the presence of a triflate anion.[7] The neutral nature of the hydrazone is indicated both in the IR spectrum and in the ^{1}H NMR spectrum, by a weak band at 3189 cm^{-1} and by a broad singlet at δ = 13.49; the strong deshielding of this last signal is due to the three-coordination of the ligand, which makes the hydrazone proton highly acidic. Finally, the methyl ligand gives rise to a doublet at δ = 0.87, with a phosphorous coupling constant of 3 Hz, which is in agreement with the values found for cationic methylpalladium(II) complexes with phosphanyl-imine ligands.[4b]

All the isolated methyl complexes were treated with CO, with the aim of isolating the corresponding acetyl complexes. Complex **1** did not react either at 1 atm or at 10 atm of CO, but when 30 atm of CO were employed it converted completely into the acetyl [Pd(HPN)(MeCO)Cl] (**4**) within 22 h at room temperature (Scheme 3). The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy, in a single-crystal sapphire high pressure NMR tube. During the carbonylation the disappearance of the singlet of **1** and the simultaneous appearance of a new singlet at δ = 20.2 was observed in the ^{31}P NMR spectrum, while in the ^{1}H NMR spectrum the doublet at δ = 0.73 of **1** progressively disappeared in favour of a singlet at δ = 2.06. These findings agreed with the formation of an acetylpalladium(II) complex,[4] but unfortunately it was not possible to detect any intermediate species. The IR spectrum of **4** in KBr showed a strong ν(C=O) vibration at 1696 cm^{-1}, which indicates the P,N bidentate coordination mode of the ligand; this band was distinguishable from the one due to the ν(MeCO), which was a sharp band at 1665 cm^{-1}. The ν(N−H) vibration was also visible as a weak band at 3204 cm^{-1}. Complex **4** was stable in CDCl$_3$ at room temperature, as demonstrated by the fact that no changes were observed in the ^{1}H

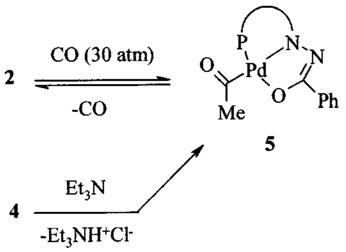
NMR spectrum over 24 h. Slow diffusion of diethyl ether into a $CDCl_3$ solution of **4** refrigerated at −20 °C provided pale yellow crystals suitable for X-ray analysis. Although it was not possible to complete the refinement of the structure, owing to the presence of a disordered solvent molecule, the diffractometric analysis did confirm the proposed structure, with the acetyl group *cis* to the phosphane.



Scheme 3

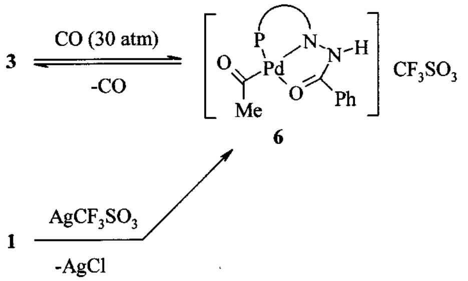
On the basis of these results, all subsequent carbonylations were carried out at a CO pressure of 30 atm.

The carbonylation of **2** was carried out in a steel autoclave at 25 °C for 24 h, with dichloromethane or THF as solvent. After CO release and removal of the solvent, the ^1H NMR spectrum of the residue, recorded in $CDCl_3$, still showed the doublet due to the starting methyl complex **2** at δ = 0.61, together with a new singlet at δ = 2.30, indicative of the formation of the acetyl complex [Pd(PNO)(MeCO)] (**5**) (Scheme 4); the integrals of the two NMR lines were in a 1:2 ratio. However, when the solution was allowed to stand in the absence of CO, the singlet rapidly disappeared in favour of the more shielded doublet, and after a few hours only the signals belonging to **2** were present in the spectrum: in the absence of CO the rapid decarbonylation of **5** took place, without release of palladium black (Scheme 4). The same behaviour was observed in the ^{31}P NMR spectrum recorded in $CDCl_3$, in which there were two different singlets centred at δ = 25.0 (**5**) and δ = 32.0 (**2**). In the IR spectrum of the solid mixture, the ν(MeCO) of **5** was clearly visible at 1675 cm^{-1}; this did not vanish with time, showing that the decarbonylation occurs only in solution.



Scheme 4

The carbonylation of **3** was carried out in a steel autoclave for 24 h at 25 °C, with dichloromethane as solvent. The ^1H NMR spectrum of the residue in $CDCl_3$ again showed the doublet of the starting methyl at δ = 0.87, but in addition there was a singlet centred at δ = 2.35. The two lines were in a 4:1 ratio, indicating that only 20% of **3** had been converted into $[Pd(HPNO)(MeCO)]^+(CF_3SO_3)^-$ (**6** in Scheme 5). As already seen for **5**, but in an even faster process, complex **6** in solution lost CO to regenerate **3**; the decarbonylation process also took place in solution at −18 °C. The rapidity of the decarbonylation prevented the recording of the ^{31}P NMR spectra of **6**. The IR spectrum of the mixture showed a ν(MeCO) band at 1700 cm^{-1} and, as with **5**, decarbonylation in the solid state also did not take place in this case.



Scheme 5

With the aim of obtaining pure **5** and **6**, solutions of **4** in THF and in CH_2Cl_2 were treated with a slight excess of Et_3N and with a stoichiometric amount of $AgCF_3SO_3$, respectively (Schemes 4 and 5). In both cases, in order to prevent decarbonylation, the products were quickly precipitated with a large excess of diethyl ether. In this way **5** and **6** were obtained in good yields and purities. In solution, however, they rapidly lost CO, as already found during the NMR examination, but it was possible in both cases to collect crystals suitable for X-ray analysis from refrigerated THF/*n*-hexane mixtures, thus confirming the proposed structures.

The need to use high CO pressures for the conversion of the methyl complexes into the corresponding acetyl ones is not surprising with phosphane-containing ligands.[4a] Moreover, the decarbonylation undergone by **5** and **6** is a common process for three-coordinate acetylpalladium(II) complexes.[4b,8] However, is worth noting that the carbonylation of the three-coordinate methyl complex **2** did not result in the formation of palladium black and acylation of the ligand, contrary to what was seen with the related [Pd(NN′O)(Me)] complexes (Scheme 1).

The lack of acetyl transfer from palladium to the ligand in this system may be attributable to the presence of the soft phosphorus donor atom in the chelating ligand. The phosphorus coordinates more strongly than nitrogen, thus meaning that breaking of the Pd−P bond is now unlikely, and therefore our previous hypothesis[1] of a unidentate intermediate in the acylation of the N,N′,O ligands is corroborated.

Crystallographic Section

Complexes **2** and **5** are neutral, while complex **6** is cationic and was isolated as a triflate salt. Compound **5** crystallised with two independent, but not significantly different, molecules in the unit cell. The crystal structures and numbering schemes of compounds **2**, **5** (molecule A) and **6** are shown in Figure 1−3 respectively; selections of relevant bond lengths and angles are given in Table 1, Table 2 and Table 3. The ligand behaves in all cases as a tridentate P,N,O donor, and the square planar geometry around palladium is completed by a methyl group in **2** and by an acetyl group in **5** and **6**. Two chelating rings are formed by coordination of the metal: the five-membered N−N−C−O−Pd ring is always strictly planar, while the six-membered N−C−C−C−P−Pd ring shows an envelope conformation with the phosphorus at the flap, a feature common in similar systems.[2,3,5] The distances between P and the mean plane containing the remaining five atoms varies from 0.38 Å in **2** to 0.52 Å in **6**. As commonly observed for analogous compounds,[1] the acyl groups in **5** and **6** are nearly perpendicular to the coordination planes, as indicated by the torsion angles: O1−Pd1−C27−O2 = 90(1)°, O3−Pd2−C55−O4 = 88(1)° (**5**, molecules A and B respectively) and O1−Pd−C27−O2 = −114.0(5)° (**6**). Minor differences due to subtle electronic effects are observed between some distances in the coordination systems among the three compounds: an apparent slight elongation of the Pd−N bond is observed on passing from the *trans* methyl [**2**, 2.058(1) Å] to the *trans* acyl group [**5**, 2.093(9) and 2.089(9) Å for molecules A and B] for the deprotonated form of the PNO ligand. These distances are longer than those observed in complexes with the same or a strictly related hydrazone ligand and containing as groups *trans* to N a chloride [2.001(2) Å],[3a] a *t*Bu-alkynyl [2.028(7) Å],[3a] an iodide [1.99(1), 2.03(1) Å],[5a] an acetate [1.974(4) Å][5b] or a phenylalkynyl [2.010(3) Å] moiety.[2] The major differences between the anionic (**2** and **5**) and the neutral forms (**6**) of the PNO ligand are confined mainly to the carbonyl bond of the N−C=O system. For the deprotonated ligand we observe a shift towards the enol form, as already shown by semiempirical calculations and crystal structures of the chloride and *t*Bu-alkynyl palladium complexes of the ligand.[3a] The contribution of the enol form causes the C−O bond length to be slightly longer in **2** and **5** [1.294(2) Å, **2**, 1.28(1) Å, **5**, both molecules] than in **6** [C−O = 1.246(6)

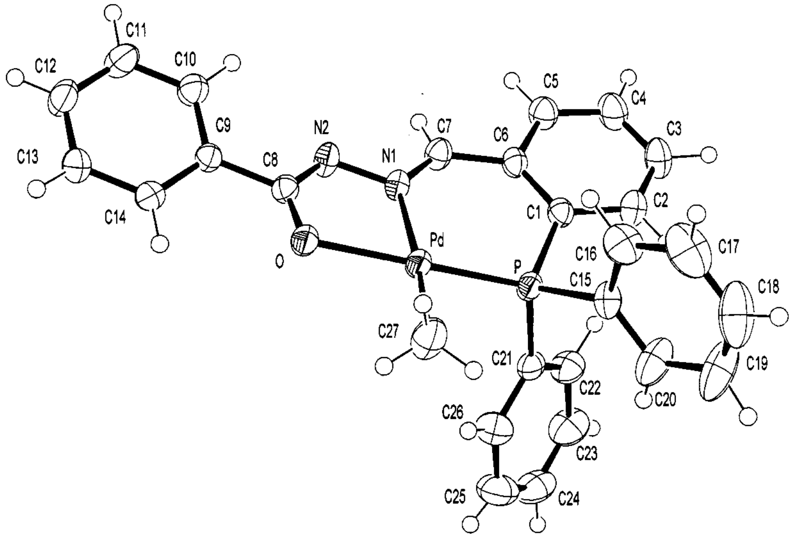


Figure 1. ORTEP diagram of compound **2**

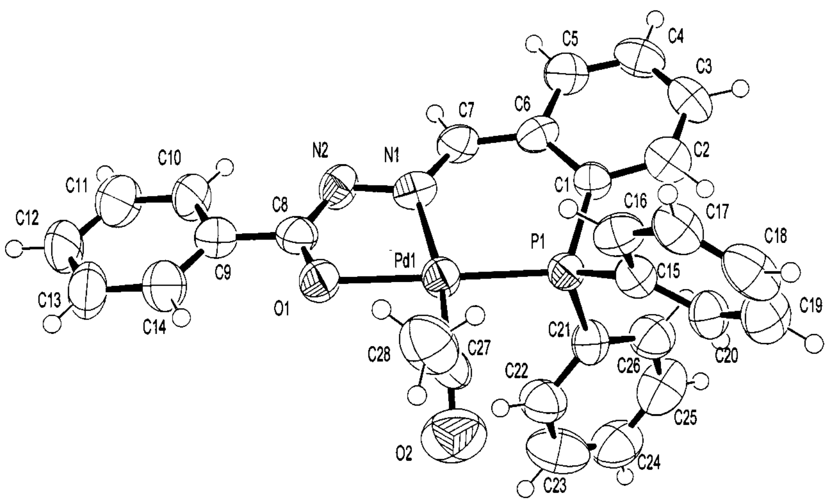


Figure 2. ORTEP diagram of compound **5** (molecule A)

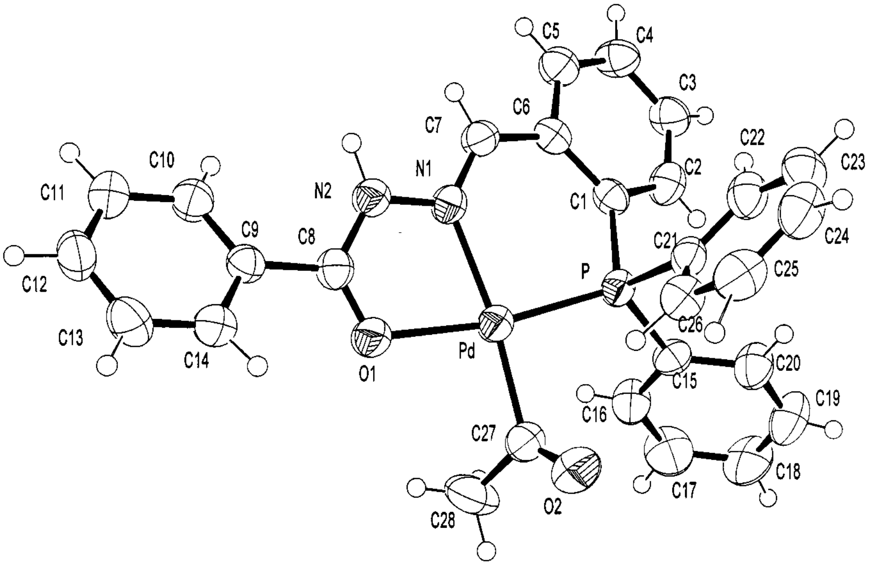


Figure 3. ORTEP diagram of compound **6**; the triflate ion has been omitted

Table 1. Selected bond lengths (Å) and angles (°) for **2**

Pd−C27	2.048(2)	C27−Pd−N1	171.37(8)
Pd−N1	2.058(1)	C27−Pd−O	94.73(7)
Pd−O	2.103(1)	N1−Pd−O	77.84(5)
Pd−P	2.1843(7)	C27−Pd−P	92.09(7)
O−C8	1.294(2)	N1−Pd−P	95.72(4)
N1−C7	1.291(2)	O−Pd−P	171.54(4)
N1−N2	1.398(2)	C1−P−Pd	111.01(5)
N2−C8	1.319(2)	C7−N1−Pd	131.4(1)
		N2−N1−Pd	114.7(1)
		C8−O−Pd	109.3(1)

Table 3. Selected bond lengths (Å) and angles (°) for **6**

Pd−C27	1.988(5)	C27−Pd−N1	172.6(2)
Pd−N1	2.100(4)	C27−Pd−O1	95.9(2)
Pd−O1	2.125(3)	N1−Pd−O1	76.8(1)
Pd−P	2.206(1)	C27−Pd−P	93.3(1)
O1−C8	1.246(6)	N1−Pd−P	94.0(1)
O2−C27	1.200(6)	O1−Pd−P	170.3(1)
N1−C7	1.291(6)	C1−P−Pd	109.7(1)
N1−N2	1.390(5)	C8−O1−Pd	113.0(3)
N2−C8	1.337(7)	C7−N1−Pd	132.2(3)
		N2−N1−Pd	110.5(3)

Table 2. Selected bond lengths (Å) and angles (°) for **5**

Pd1−C27	2.01(1)	Pd2−C55	2.00(1)
Pd1−N1	2.093(9)	Pd2−N3	2.089(9)
Pd1−O1	2.100(8)	Pd2−O3	2.070(8)
Pd1−P1	2.204(3)	Pd2−P2	2.208(3)
O1−C8	1.28(1)	O3−C36	1.28(1)
O2−C27	1.20(2)	O4−C55	1.18(1)
N1−C7	1.29(1)	N3−C35	1.27(1)
N1−N2	1.40(1)	N3−N4	1.41(1)
N2−C8	1.33(1)	N4−C36	1.33(2)
C27−Pd1−N1	171.3(5)	C55−Pd2−N3	172.2(5)
C27−Pd1−O1	93.8(4)	C55−Pd2−O3	93.9(4)
N1−Pd1−O1	77.6(3)	N3−Pd2−O3	78.2(3)
C27−Pd1−P1	93.7(4)	C55−Pd2−P2	93.0(4)
N1−Pd1−P1	95.0(3)	N3−Pd2−P2	94.7(3)
O1−Pd1−P1	169.8(2)	O3−Pd2−P2	169.8(2)
C1−P1−Pd1	111.8(3)	C29−P2−Pd2	111.0(5)
C8−O1−Pd1	109.9(7)	C36−O3−Pd2	109.9(8)
C7−N1−Pd1	130.2(8)	C35−N3−Pd2	132.7(9)
N2−N1−Pd1	113.5(7)	N4−N3−Pd2	112.9(7)

Å]; accordingly, the N−C(O) bond is shorter in the anionic form [1.319(2), 1.33(1), 1.33(2) Å for **2** and **5**, molecules A and B] than in the neutral one [1.337(7) Å for **6**]. Previous calculations[3a] have shown that the anionic charge is largely localized on the oxygen. The Pd−O bond is correspondingly stronger when the ligand has anionic character [2.103(1), 2.100(8), 2.070(8) Å in **2** and **5**] than in the neutral form [2.125(3) Å for **6**].

As observed in the similar compounds above, the terminal phenyl ring C9−C14 apparently has a certain degree of rotational freedom [N2−C8−C9−C10 ranging from −17.8(2) to 25.6(2)°] around the C8−C9 bond that, in all cases, does not appear to be involved in any double bond character delocalization with the hydrazone system [C8−C9 ranging from 1.47(2) to 1.492(2) Å].

The most relevant feature of the crystal packing of the three compounds is given by the charge-assisted hydrogen bond between the cationic complex and the triflate in **6**: N2−H···O5 (N2···O5 = 2.826Å; N2−H−O5 = 121.3°).

Conclusion

The tridentate P,N,O hydrazone ligand HPNO can form three different kinds of methylpalladium(II) complexes, in which it adopts different coordination modes: *i*) neutral P,N (**1**), *ii*) anionic P,N,O (**2**), and *iii*) neutral P,N,O (**3**). The isolation of one or the other depends on the experimental conditions. The methyl complexes **1**, **2** and **3** convert into the corresponding acetyl complexes **4**, **5** and **6** when subjected to high CO pressures; the carbonylations do not affect the coordination modes of the ligand. The stability of the acetyl species in solution towards the loss of CO depends on the chelating behaviour of the ligand: only **4** is completely stable, whereas the three-coordinate acetyl derivatives **5** and **6** quickly decarbonylate to regenerate the starting methyl complexes. In contrast to the carbonylations with HNN′O ligands, no acetylation of HPNO was observed during the carbonylation of **2**. Pure **5** and **6** can be obtained by treating **4** with Et_3N and with $AgCF_3SO_3$, respectively.

Experimental Section

General Remarks: All reactions were performed under an atmosphere of nitrogen, by employing standard Schlenk techniques. Solvents were dried prior to use and stored under nitrogen. Elemental analysis (C, H, N and S) were performed with a Carlo Erba Mod. EA 1108 apparatus. Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer in the 4000−400 cm^{-1} range as KBr disks. ^1H NMR spectra were obtained on a Bruker 300 FT instrument with $SiMe_4$ as internal standard, while $^{31}P\{^1H\}$NMR spectra were recorded on a Bruker CPX 200 FT with H_3PO_4 (85%) as external standard. MS spectra (C.I., methane) were recorded on a Finnigan SSQ 710 spectrometer. 2-(Diphenylphosphanyl)benzaldehyde benzoylhydrazone (HPNO) was synthesised as previously reported.[2] [(COD)Pd(Me)Cl] was prepared according to the literature,[8] while $AgCF_3SO_3$ was purchased from Aldrich.

[Pd(HPN)(Me)Cl] (1). Method a: HPNO (180 mg, 0.441 mmol) was dissolved in CH_2Cl_2 (30 mL), and [(COD)Pd(Me)Cl] (117 mg, 0.453 mmol) was added. The resulting yellow solution was stirred at room temperature for two hours and was then concentrated to a volume of about 5 ml; on addition of 40 mL of diethyl ether a yellow solid precipitated and was filtered off, washed with diethyl ether and dried in vacuum. Yield: 220 mg (88%).

Method b: [(COD)Pd(Me)Cl] (130 mg, 0.490 mmol) was suspended in diethyl ether (20 mL) and HPNO (200 mg, 0.490 mmol) was added; a yellow solid immediately precipitated. The mixture was stirred at room temperature for 2 hours and the solid was then removed by filtration, washed with diethyl ether and dried in vacuum. Yield: 263 mg (95%). $C_{27}H_{24}ClN_2OPPd$ (565.3): calcd. C 57.36, H 4.28, N 4.96; found C 56.98, H 4.22, N 4.84. ^1H NMR ($CDCl_3$): $\delta = 0.73$ (d, $^3J_{P-H} = 1.9$ Hz, 3 H, Pd-Me), 7.40−7.60 (m, 17 H, Ph), 8.25 [d, $^3J = 8.2$ Hz, 2 H, Ph(C=O)], 9.53 (s, 1 H, CH=N), 11.19 (s, 1 H, N−H). ^{31}P NMR ($CDCl_3$): $\delta = 38.4$ (s). IR (KBr): $\tilde{\nu} = 3206$ w (N−H), 1684 s cm^{-1}(C=O). MS-CI: *m/z* = 527 $[M - HCl]^+$.

[Pd(PNO)(Me)] (2). Method a: HPNO (108 mg, 0.264 mmol) was dissolved in THF (20 mL) and Et_3N (40 mg, 0.395 mmol, 0.06 mL) was added. [(COD)Pd(Me)Cl] (70 mg, 0.264 mmol) was added to the pale yellow solution, whereupon triethylamine hydrochloride precipitated; after 3 hours of stirring at room temperature the mixture was filtered to afford a yellow solution, which was concentrated under vacuum to a volume of about 5 mL. Addition of 30 mL of diethyl ether and refrigeration at −20 °C overnight caused the precipitation of a yellow solid, which was filtered off, washed with diethyl ether and dried in vacuum. Yield: 67 mg (48%).

Method b: Compound **1** (70 mg, 0.124 mmol) was dissolved in THF (20 mL), and Et_3N (19 mg, 0.188 mmol, 0.03 mL) was added; the mixture was stirred at room temperature for 3 hours and then filtered, and the resulting yellow solution was worked up as reported in method *a*. Yield: 53 mg (82%). Crystals suitable for X-ray analysis were collected from a CH_2Cl_2/*n*-hexane mixture refrigerated at −20 °C. $C_{27}H_{23}N_2OPPd$ (528.9): calcd. C 61.32, H 4.38, N 5.30; found C 61.17, H 4.32, N 5.42. ^1H NMR ($CDCl_3$): $\delta = 0.61$ (d, $^3J_{P-H} = 1.9$ Hz, 3 H, Pd-Me), 7.39−7.60 (m, 17 H, Ph), 8.22 [dd, $^3J = 7.6$, $^4J = 1.5$ Hz, 2 H, Ph(C=O)], 8.52 (s, 1 H, CH=N). ^{31}P NMR ($CDCl_3$): $\delta = 32.0$ (s). MS-CI: *m/z* = 528 $[M]^+$.

$[Pd(HPNO)(Me)]^+[CF_3SO_3]^-$ (3): Compound **1** (100 mg, 0.177 mmol) was placed in a Schlenk tube and dissolved in CH_2Cl_2 (15 mL). $AgCF_3SO_3$ (45 mg, 0.177 mmol) dissolved in CH_3CN (2 mL) was added, resulting in the immediate precipitation of AgCl. The resulting mixture was stirred at room temperature for 2 h, filtered and concentrated under vacuum; addition of Et_2O and refrigeration at −18 °C overnight afforded **3** as a microcrystalline yellow solid. Yield: 86 mg (72%). $C_{28}H_{24}F_3N_2O_4PPdS$ (678.9): calcd. C 49.53, H 3.56, N 4.13, S 4.72; found C 49.53, H 3.35, N 4.06, S 4.71. ^1H NMR ($CDCl_3$): $\delta = 0.87$ (d, $^3J_{P-H} = 3$ Hz, 3 H, Pd-Me), 7.40−8.03 (m, 17 H, Ph), 8.23 [d, $^3J = 7.9$ Hz, 2 H, Ph(C=O)], 9.36 (s, 1 H, CH=N), 13.49 (s, 1 H, N−H). ^{31}P NMR ($CDCl_3$): $\delta = 36.2$ (s). IR (KBr): $\tilde{\nu} = 3189$ w (N−H), 1597 s − 1560 s (C=N + C=O), 1298 s − 1240 s cm^{-1} (S=O).

Synthesis of the Acetyl Complexes

Carbonylation Reactions: The carbonylation of complex **1** was carried out as described below. **Method a:** A magnetic stirring bar was placed in a 150 mL capacity steel autoclave, together with the complex (30 mg) dissolved in chloroform or dichloromethane (20 mL). The reactor was purged twice with CO and then pressurized to 30 atm. The mixture was stirred overnight at 25 °C, CO was then released, and the solution was filtered through celite in order to remove the traces of palladium black sometimes formed. The resulting yellow solution was treated with diethyl ether until precipitation of [Pd(HPN)(MeCO)Cl] (**4**). This was filtered and washed with diethyl ether. Yield: 37 mg (99%).

The same procedure applied to complexes **2** and **3** did not permit the isolation of pure acetyl complexes because of the decarbonylation that took place when the CO pressure was released.

Method b (Only for Complex 1): Complex **1** (20 mg, 0.035 mmol) was placed in a 5 mm o.d. single-crystal sapphire high-pressure NMR tube and dissolved in about 1 mL of deuterated chloroform. The tube was purged twice with CO and then pressurized at 30 atm. The reaction was followed by ^1H and ^{31}P NMR spectroscopy at 20 °C until the complete disappearance of the starting signals (20 h). The final solution was worked up as reported above.

SAFETY NOTE: Since high gas pressures are involved, safety precautions must be taken at all stages involving HP NMR tubes.[9]

[Pd(HPN)(MeCO)Cl] (4): $C_{28}H_{24}ClN_2O_2PPd{\cdot}CDCl_3$ (713.7): calcd. C 48.80, H 3.53, N 3.93; found C 49.00, H 3.71, N 3.90. ^1H NMR ($CDCl_3$): $\delta = 2.06$ (s, 3 H, MeCO), 7.30−7.59 (m, 17 H, Ph), 8.02 [d, $^3J = 6.9$ Hz, 2 H, Ph(C=O)], 9.63 (s, 1 H, CH=N), 11.84 (s, 1 H, N−H). ^{31}P NMR ($CDCl_3$): $\delta = 20.2$ (s). IR (KBr): $\tilde{\nu} = 3204$ w (N−H), 1696 s (C=O), 1665 s cm^{-1} (MeCO). Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the deuterated chloroform solution of **4** at −20 °C.

[Pd(PNO)(COMe)] (5): Compound **4** (30 mg, 0.051 mmol) was dissolved in THF (20 mL) and treated with Et_3N (8 mg, 0.01 mL, 0.081 mmol). The mixture was stirred at room temperature for 2 h and then filtered; the resulting yellow solution was concentrated in vacuum and **5** was precipitated with diethyl ether, filtered and dried in vacuum. Crystals suitable for X-ray analysis were obtained from a THF/*n*-hexane mixture, refrigerated to −18 °C. $C_{28}H_{23}N_2O_2PPd$ (556.9): calcd. C 60.39, H 4.16, N 5.03; found C 60.52, H 4.24, N 5.11. ^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, MeCO), 8.18 [br. d, 2 H, Ph(C=O)], 8.51 (br, 1 H, CH=N). The other data are obscured by the signals of **2**. ^{31}P NMR ($CDCl_3$): δ = 25.0 (s). IR (KBr): ṽ = 1675 m cm^{-1} (MeCO).

[Pd(HPNO)(MeCO)]$^+$[CF_3SO_3]$^-$ (6): Compound **4** (30 mg, 0.044 mmol) was dissolved in CH_2Cl_2 (20 mL), and $AgCF_3SO_3$ (11.4 mg, 0.044 mmol) dissolved in acetonitrile (1 mL) was added. The mixture was stirred at room temperature for 2 h and then filtered, giving a yellow solution that was concentrated under reduced pressure. The product was precipitated by addition of diethyl ether, filtered and dried in vacuum. Crystals suitable for X-ray analysis were collected from a THF/*n*-hexane mixture refrigerated at −18 °C. $C_{29}H_{24}F_3N_2O_5PPdS$ (706.9): calcd. C 49.27, H 3.42, N 3.96, S 4.53; found C 49.38, H 3.38, N 4.02, S 4.30. ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 3 H, MeCO), 8.20 [br. d, 2 H, Ph(C=O)]. The other data were obscured by signals of **3**. IR (KBr): ṽ = 3183 w (N−H), 1700 s (MeCO), 1602 s (C=N), 1559 vs (C=O), 1296 vs − 1224 vs cm^{-1} (S=O).

X-ray Data Collection, Structure Determination and Refinement of Compounds 2, 5 and 6

Air-stable crystals suitable for structural determination by single-crystal X-ray diffraction were obtained for compounds **2**, **5** and **6**. Relevant details about X-ray experimental conditions, data collection and refinement are given in Table 4. Data for compounds **5** and **6** were collected on Siemens AED diffractometers, while for compound **2** a Philips PW1100 diffractometer was used and the ψ-scan empirical absorption correction was applied. For compounds **2** and **6**, graphite monochromated Mo-K_α radiation was used (λ = 0.71069Å). For the thick crystals of **5**, graphite monochromated Cu-K_α radiation (λ = 1.54184 Å) was chosen for data collection.

Data were corrected for Lorentz and polarisation effects. Crystal decay was observed for **5** and data were rescaled accordingly. The phase problem for all the compounds was solved by direct methods with SIR97.[10] Data refinement was performed by full-matrix, least-squares on *F*2 with SHELXL-97.[11] For compounds **5** and **6**, the Walker and Stewart[12] absorption correction was applied after the last isotropic refinement cycle. In all cases non-hydrogen atoms were refined anisotropically. While in compound **2** all hydrogen atoms were located in the Fourier maps and refined isotropically; in compound **6** some of them were placed in calculated positions. For compound **5**, all hydrogens were placed in calculated positions and constrained to ride on their carrying atoms. The geometry of the structures was inspected and analysed by PARST-97[13] and ORTEP-3[14] and compared with literature data with the aid of the Cambridge Structural Database software.[15]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-155797 (**2**), -155798 (**5**) and -155799 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

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Table 4. Crystal data and structure refinement

	2	**5**	**6**
Empirical formula	$C_{27}H_{23}N_2OPPd$	$C_{28}H_{23}N_2O_2PPd$	$C_{29}H_{24}F_3N_2O_5PPdS$
Formula mass	528.84	556.85	706.93
Wavelength	0.71069 Å	1.54184 Å	0.71069 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*a*
Unit cell dimensions	*a* = 21.465(7) Å	*a* = 16.141(6) Å	*a* = 25.681(8) Å
	b = 12.612(4) Å	*b* = 15.259(6) Å	*b* = 10.919(4) Å
	c = 18.052(5) Å	*c* = 19.674(7) Å	*c* = 10.401(4) Å
	β = 106.31(2)°	β = 94.92(2)°	β = 99.19(2)°
Volume	4690(2) Å^3	4828(3) Å^3	2879(2) Å^3
Z	8	8	4
Calculated density	1.498 Mg/m^3	1.532 Mg/m^3	1.631 Mg/m^3
Absorption coefficient	0.881 mm^{-1}	7.054 mm^{-1}	0.835 mm^{-1}
F(000)	2144	2255	1424
Crystal size	0.4 × 0.4 × 0.3 mm	0.3 × 0.2 × 0.15 mm	0.5 × 0.3 × 0.3 mm
θ range	3.23 to 31.96°	3.67 to 65.12°	3.05 to 30.07°
Reflections collected/unique	13643/7070	8201/8201	8830/8427
Observed reflections [$I > 2\sigma(I)$]	5640	4359	3667
Refinement method	Full-matrix, least-squares on F^2	Full-matrix, least-squares on F^2	Full-matrix, least-squares on F^2
Data/restraints/parameters	7070/0/381	8201/0/615	8427/1/457
Goodness-of-fit on F^2	0.908	1.057	0.886
Final *R* indices	$R1^{[a]} = 0.0258$	$R1^{[a]} = 0.0752$	$R1^{[a]} = 0.0598$
[$I > 2\sigma(I)$]	$wR2^{[b]} = 0.0668$	$wR2^{[b]} = 0.2431$	$wR2^{[b]} = 0.1603$
R indices (all data)	$R1^{[a]} = 0.0383$	$R1^{[a]} = 0.1185$	$R1^{[a]} = 0.1203$
	$wR2^{[b]} = 0.0717$	$wR2^{[b]} = 0.2661$	$wR2^{[b]} = 0.1829$

[a] $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma\,[w(F_0^2)^2]\}^{1/2}$.

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