Potentially Tridentate Ligands in the Synthesis of Methyl- and Acetylpalladium(II) Complexes

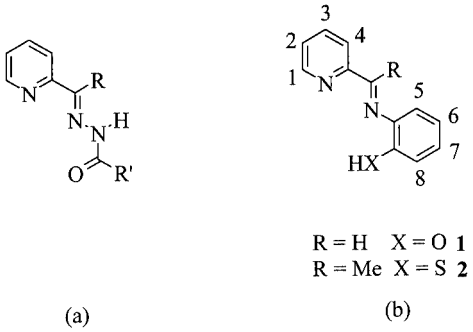
Alessia Bacchi,[a] Mauro Carcelli,[a] Corrado Pelizzi,[a] Giancarlo Pelizzi,[a] Paolo Pelagatti,*[a] and Silvia Ugolotti[a]

Keywords: Carbonylation / Insertion / N ligands / Palladium / Tridentate ligands

The two protic tridentate ligands HNN′O (**1**) and HNN′S (**2**) were treated with [(COD)Pd(Me)Cl], and the corresponding methylpalladium(II) complexes [Pd(η^2-HNN′)(Me)Cl] (**1a** and **2a**) were isolated. The neutral ligands in these complexes coordinated the metal in an NN′ bidentate mode, through the pyridine and imine nitrogens, excluding the O or S atom from the coordination. This behavior was confirmed by X-ray diffraction analysis of the dichloro complex of **1**, [Pd(η^2-HNN′)Cl_2] (**1c**). Complexes **1a** and **2a** easily transformed quantitatively into the corresponding three-coordinate complexes [Pd(η^3-NN′X)(Me)] (**1b**: X = O, **2b**: X = S) in basic medium, with elimination of HCl. The complexes **1a** and **1b** were treated with PPh_3 and $P(CD_3)_3$, respectively, resulting in **1e** and **1h**; **1a** reacted further with a double quantity of PPh_3 to give rise to the diphosphane complex [*trans*-$(PPh_3)_2$Pd(Me)Cl] (**1g**) and free **1**. The three-coordinate complexes **1b** and **2b** were subjected to CO bubbling at room temperature. In the case of **1b**, acylation of the ligand on the phenolic oxygen was observed, with the formation of an organic acetate and release of palladium black. In the case of **2b**, besides the acylated ligand on the thiolic sulfur, the acetylpalladium(II) complex [Pd(η^3-NN′S)(MeCO)] (**2c**) was isolated. The X-ray structures of **1c**·THF, **1b**·1/2$C_6H_6O_2$, **2b**, **2c**·1/2CH_2Cl_2, and **1g** have been solved.

Introduction

There is ongoing interest in the study of CO insertion into Pd−C bonds, because of its importance as a key step in many metal-catalyzed reactions.[1] Much work has been done with both non-hybrid[2] and hybrid[3] bidentate ligands. In contrast, little has been done with tridentate ligands,[4] and there is a lack of data concerning the use of protic tridentate ligands.[5] We have recently shown that the use of protic tridentate HNN′O acylhydrazonic ligands (Scheme 1) resulted in the isolation of two different types of methylpalladium(II) complexes: [Pd(η^2-HNN′)(Me)Cl] and [Pd(η^3-NN′O)(Me)].[6] These complexes showed different reactivities towards CO: the first, in fact, gave rise to the isolation of the corresponding acetyl complexes [Pd(η^2-HNN′)(MeCO)Cl] in excellent yields, whereas the second resulted in the acetylation of the ligands on the hydrazonic nitrogen, with concomitant formation of palladium black; conversion was also quantitative in this case. The presence of the basic hydrazone nitrogen was considered to be responsible for the instability of the complexes under CO atmosphere. With the aim of verifying this hypothesis, we prepared the methylpalladium(II) complexes of the Schiff base ligands 2-[(pyridin-2-ylmethylene)amino]phenol (**1**, HNN′O) and 2-(1-pyridin-2-yl-ethylideneamino)benzenethiol (**2**, HNN′S) (see b in Scheme 1). These chelating agents are potentially tridentate and do not contain a hydrazone nitrogen. Compounds **1** and **2** were treated with [(COD)Pd(Me)Cl], resulting in the isolation, under appropriate conditions, of two different kinds of methylpalladium(II) complexes: [Pd(η^2-HNN′)(Me)Cl] (**1a** and **2a**) and [Pd(η^3-NN′X)(Me)] (**1b**: X = O, **2b**: X = S), which were fully characterized. The reactivity of **1a**−**b** towards phosphanes and, in particular, the reactivity of the three-coordinate complexes **1b** and **2b** towards CO was investigated.



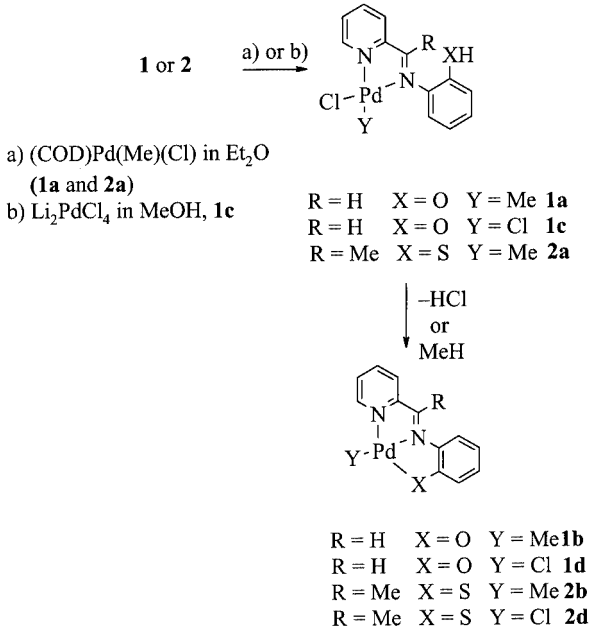
Scheme 1

[a] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma
Parco Area delle Scienze 17/A, 43100 Parma, Italy
Fax: (internat.) +39-0521/905-557
E-mail: paolo.pelagatti@unipr.it

Results and Discussion

Synthesis of the Methyl Complexes 1a and 2a

The ligands HNN′O (**1**) and HNN′S (**2**) reacted with [(COD)Pd(Me)Cl] in diethyl ether at room temperature to afford the complexes [Pd(η^2-HNN′)(Me)Cl] (**1a** and **2a** in Scheme 2). The reactions proceed with rapid displacement of the labile diolefin COD by the incoming chelating pyridylimine ligands. These ligands coordinate to the metal in a bidentate mode through the pyridine and imine nitrogen atoms. The bidentate behavior of the ligand was confirmed by the X-ray structure of the dichloro complex [Pd(η^2-HNN′)Cl_2] (**1c**) (see crystallographic discussion). As previously reported for other methylpalladium(II) complexes containing protic ligands,[6] diethyl ether is the solvent of choice as the fast precipitation of **1a** and **2a** prevents methane elimination caused by ligand deprotonation, a process that takes place easily in solution (vide infra). Complex **1a** is a yellow powder, while complex **2a** is a gray powder. The neutral character of the ligand was indicated by the IR stretching bands of the OH and SH bonds, centered at 3377 cm^{-1} and 3229 cm^{-1}, respectively. The structure of **1a** proposed in Scheme 2 agrees with the ^{1}H NMR spectrum: the sequence of the pyridine protons is normal for pyridylimine ligands in which both nitrogens are involved in coordination.[2b,6] A single isomer was detected, probably that with the methyl ligand *cis* to the imino function. This is in fact the preferred configuration for this type of complex.[2] Moreover, the chemical shift of the methyl group is unusually low (δ = 0.41 ppm in $CDCl_3$ and δ = 0.54 ppm in MeOD, as compared to δ = 0.8−1.1 ppm normally), probably because of the shielding effect of the neighboring aromatic ring.[7] The ^{1}H NMR spectrum of complex **2a** recorded in [D_6]Me_2SO shows a complicated pattern, which prevents unambiguous assignment of the aromatic signals. In the aliphatic region, however, three different species can be distinguished: the expected complex **2a** [singlets at δ = 2.50 and 0.81 ppm, belonging to the C(Me)=N and Pd−Me groups, respectively], and the products of solvent-assisted ligand deprotonation [Pd(η^3-NN′O)(Me)] (**2b**, singlets at δ = 2.70 and 0.20 ppm) and [Pd(η^3-NN′O)Cl] (**2d**, singlet at δ = 2.84 ppm). As far as complex **2a** is concerned, it was not possible to establish the disposition of the methyl and chloride ligands around the metal unequivocally, but we assume that **1a** and **2a** have the same stereochemistry. As a matter of fact, complex **1a** is also not completely stable in solution: in deuterated methanol or dimethyl sulfoxide it slowly converts into the chloride complex [Pd(η^3-NN′O)Cl] (**1d**) with elimination of methane (Scheme 2). This elimination is faster for **2a** than for **1a**, because **2** is more acidic than **1**. Interestingly, methane elimination also takes place in the solid state, as confirmed by TGA analyses (**1a**: 158.3−198.1 °C, weight loss 6%; **2a**, 103.3−149.0 °C, weight loss 5%).



Scheme 2

Synthesis of the Methyl Complexes 1b and 2b

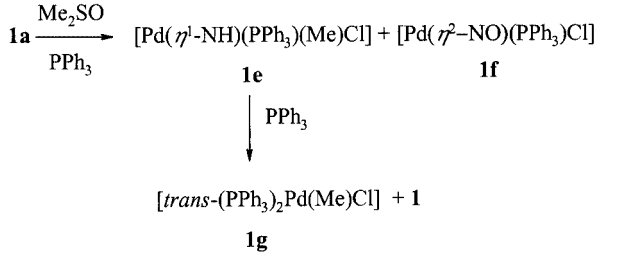
When the reaction between **2** and (COD)Pd(Me)Cl was carried out in THF in the presence of a slight excess of a base, such as NaOMe or Et_3N, elimination of HCl took place and the reaction proceeded with a drastic color change, from yellow to green. During the stirring the solution released the three-coordinate methyl complex [Pd(η^3-NN′S)(Me)] (**2b**) as a green powder (Scheme 2). The anionic character of the ligand was attested to by the disappearance of the IR and ^{1}H NMR signals of the SH group. The methyl ligand resonates at δ = 0.15 ppm, a value similar to those found for other methylpalladium(II) complexes in which the metal is bound to an anionic tridentate ligand.[6]

With **1**, the corresponding process had to be carried out in the presence of *n*BuLi instead of NaOMe or Et_3N. In this way, the deprotonation of the ligand was complete and the reaction was able to proceed smoothly, with a drastic color change from yellow to purple. The three-coordinate methyl complex [Pd(η^3-NN′O)(Me)] (**1b**) precipitated from the solution as a purple solid (Scheme 2). The same product could be obtained by deprotonation of **1a** by *n*BuLi or NaOMe in THF. The tridentate character of the ligand was corroborated by the disappearance of the spectroscopic OH signals; the methyl ligand is found at δ = 0.60 ppm, a higher value than found for **2a**, but still shielded with regard to the value usually found for methylpalladium(II) complexes with bidentate nitrogen ligands.[2b,3,8] The *trans* influence of the methyl attached to palladium is well attested to by the shielding undergone by the imine proton relative to the free ligand: δ = 7.88 ppm for **1b** and δ = 8.71 ppm for **1**.

Single-crystal diffraction analysis of **1b**·1/2$C_6H_6O_2$ and **2b** confirmed the proposed structures (see crystallographic discussion).

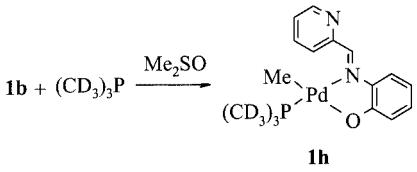
Reactions of 1a and 1b with Phosphanes

In order to investigate the complexation strength of the ligand **1**, and before dealing with the carbonylation reactions, the complexes **1a** and **1b** were treated with PPh_3 and $P(CD_3)_3$. When complex **1a** was treated with a stoichiometric amount of PPh_3 in [D_6]DMSO, an immediate color change took place. The ^{31}P NMR spectrum of the reactant mixture showed a strong signal at $\delta = 40.5$ ppm, a value characteristic for a phosphane coordinated to palladium, and a second, much less intense, singlet at $\delta = 32.5$ ppm. No signals belonging to free PPh_3 were visible. The first resonance was attributable to a species in which the ligand was monodentate through a nitrogen atom and the square-planar coordination was completed by the methyl ligand, the chlorine atom, and PPh_3 (**1e** in Scheme 3). The second signal was tentatively attributed to the chloro(phosphane)-palladium complex **1f** (Scheme 3) , with the deprotonated ligand coordinating palladium through the imine nitrogen and the oxygen, and the square-planar coordination being completed by a PPh_3 molecule and a chlorine atom. Complex **1f** is formed by the reaction between PPh_3 and **1d**, the formation of which has previously been described in Me_2SO solution. The addition of double quantities of PPh_3 resulted in the immediate precipitation of *trans*-[$(PPh_3)_2$Pd(Me)Cl] and the consequent displacement of **1** (Scheme 3). The diphosphane complex is completely soluble in chlorinated solvents, the ^1H NMR spectrum recorded in $CDCl_3$ showing a triplet for the methyl ligand at $\delta = -0.03$ ppm with a $J_{P,H}$ of 5.9 Hz, while in the ^{31}P NMR spectrum the phosphanes generate a singlet centered at $\delta = 27.7$ ppm. The structure of this complex was definitely established by X-ray analysis. Crystals of *trans*-[$(PPh_3)_2$Pd(Me)Cl] were obtained by slow diffusion of *n*-hexane into a refrigerated dichloromethane solution. The methyl is *trans* to the chloride; coordination is planar within 0.08 Å. Relevant coordination features are: Pd−P1 = 2.3272(5), Pd−P2 = 2.3225(6), Pd−Cl = 2.4248(5), Pd−C = 2.0574(4)Å; P1−Pd−P2 = 177.49(2), P1−Pd−Cl = 88.85(1), P1−Pd−C = 91.69(1), P2−Pd−Cl = 89.17(1), P2−Pd−C = 90.43(1), Cl−Pd−C = 174.86(1)°.



Scheme 3

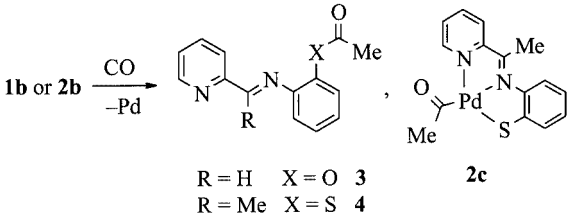
The three-coordinate methyl complex **1b** was treated with a slight excess of $P(CD_3)_3$ in [D_6]DMSO, and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. After the addition of the phosphane, the signals of an uncoordinated pyridine ring appeared: in fact, the sequence of the hydrogen resonances, from low to high field, was 1-H, 4-H, 3-H, 2-H [Scheme 1(b)].[2b,6] The methyl ligand now resonates at $\delta = 0.25$ ppm ($\delta = 0.60$ ppm in **1b**) as a singlet, while the singlet of a coordinated phosphorus is now present in the ^{31}P NMR spectrum at $\delta = 41.3$ ppm. In conclusion, the phosphane replaces the pyridine ring in the coordination sphere, giving rise to the complex [Pd(η^2-NO){$P(CD_3)_3$}(Me)] (**1h**, Scheme 4). On the basis of literature spectroscopic data,[9] we assume that the methyl is *trans* to the oxygen and the phosphane *trans* to the imine nitrogen (Scheme 4).



Scheme 4

Carbonylation Reactions

Dichloromethane solutions of **1b** and **2b** were subjected to CO bubbling at room temperature. In both cases the formation of palladium black was observed. As in the case of the methyl complexes of NN′O acylhydrazone ligands studied previously,[6] the decomposition of **1b** was very fast, and after 5 min the solution was completely bleached. A different behavior was observed in the case of **2b**: after 3.5 h of exposure to CO the solution was still light purple. After removal of palladium, the resulting solutions were analyzed by mass spectrometry: peaks relating to the acylated ligands [$m/z = 240$ (**3**) and 270 (**4**), respectively] were present in both cases (Scheme 5). In the mass spectrum of the carbonylated solution of **1b**, no signals belonging to the starting complex or to an acetylpalladium complex were observed, whereas the peak of the acetylpalladium complex [Pd(η^3-NN′S)(MeCO)] (**2c** in Scheme 4, $m/z = 378$) was present in the corresponding mass spectrum of **2b**. Such a complex was isolated in a crystalline form by slow diffusion of *n*-hexane into the refrigerated mother liquor; X-ray analysis confirmed the proposed structure (see crystallographic discussion). Unfortunately, the few collected crystals did not allow the spectroscopic characterization of the complex.



Scheme 5

The different reactivities shown by the two three-coordinate methyl complexes are due in the case of **2b** to the presence of a *soft* donor (the S atom), making the isolation of

the acetyl complex **2c** possible. This can definitely be viewed as an intermediate in the acetylation of the ligand, as already proposed by other groups for methyl(alkoxo) and methyl(thiolato)palladium(II) and nickel(II) complexes[10] and by us for hydrazonic palladium(II) complexes.[6] On the basis of the reactivity shown by **1b** toward $P(CD_3)_3$ (see complex **1h**), it is plausible to suppose that the CO coordination occurs with concomitant pyridine displacement. The subsequent step could be the migration of the methyl onto the coordinated CO molecule, followed by coupling between the ligand and the acetyl group.

Structures of Complexes 1c·THF, 1b·1/2$C_6H_6O_2$, 2b, and 2c·1/2CH_2Cl_2

Complex **1c** (Figure 1) crystallizes as a 1:1 THF solvate. The ligand is NN′-bidentate [bite angle N1−Pd−N2: 80.1(2)°], the metal square-planar coordination being completed by two chloride ligands. The OH group is not involved in the coordination. The terminal phenyl ring is nearly perpendicular to the chelation plane [Pd−N−C−C(OH): 72.2(8)°], due to the hindrance of the chloride ligand in the coordination plane [Cl2···O1 3.446(5) Å]. The coordination geometry can be summarized as follows: Pd−N2: 2.018(6) Pd−N1: 2.034(6), Pd−Cl1: 2.290(2), Pd−Cl2: 2.300(2) Å; N2−Pd−N1: 80.1(2), N2−Pd−Cl1: 174.0(2), N1−Pd−Cl1: 94.2(2), N2−Pd−Cl2: 94.8(2), N1−Pd−Cl2: 173.4(2), Cl1−Pd−Cl2: 90.93(8)°.

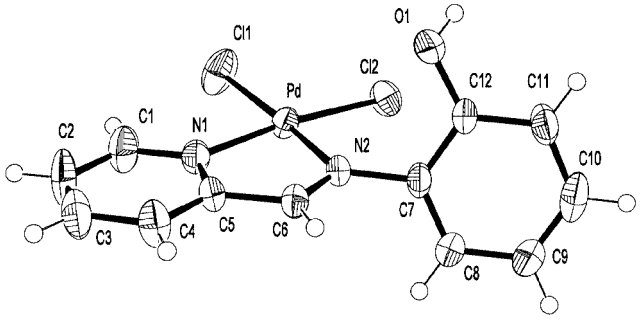


Figure 1. Perspective view of molecule **1c**·THF; thermal ellipsoids are drawn at the 50% probability level; the solvent has been omitted

The molecular structure of **1b**, shown in Figure 2, features NN′O-tridentate coordination for the ligand, with the methyl group *trans* to the iminic nitrogen. The whole complex molecule is perfectly planar (maximum displacement less than 0.08 Å), and two pentaatomic chelation rings are formed upon coordination. Table 1 lists the main bonding features for **1b**. The bite angles involved in the chelation are typical for tridentate chelation in these systems. A survey of the crystal structures of molecules containing a pyridineiminic pentaatomic N(py)−C(py)−C(iminic)−N(iminic)−Pd chelation ring was performed on the Cambridge Crystallographic Database (release of October 2001). The N1−Pd−N2 and Pd−N2−C6 angles appear in the ranges 77.2−82.3° and 108.6−119.2°, respectively, and, as a general trend, they tend to be wider (>80° and >117° respectively) for tridentate NN′X (X = O, S) systems containing two five-membered chelated rings, as in the case of these complexes, than for NN-bidentate systems containing only the Pd−N1−C5−C6−N2 chelation ring (<80° and <116°, respectively). The enlargement of the endocyclic angles upon tridentate coordination correlates well with a shortening of the Pd−N2 bond, ranging between 1.92 and 1.98 Å for tridentate complexes and 1.98 and 2.28 Å for bidentate complexes (with the exception of two NNN-tridentate compounds in which the third donor atom belongs to a flexible six-membered chelation ring). The elongation of the Pd−N2 distance in **1b** [2.009(3) Å] compared to those (1.917−1.944 Å) observed in similar NNO Pd^{II} halogen complexes of phenyl 2-pyridyl ketone benzoylhydrazone[11] is consistent with the *trans* influence of the methyl group, as also attested to by the NMR spectroscopic data. The Pd−O1 distance [2.037(2) Å] is in agreement with those found for the above hydrazone complexes (Pd−O: 2.017−2.033 Å). The growth of good quality crystals of **1b** was favored by co-crystallization with hydroxyquinone, present in traces in the THF used for recrystallization. In the crystal structure, the hydroxyquinone is positioned on a crystallographic center of inversion and bridges two symmetry-related complex molecules through strong O2−H···O1 hydrogen bonds [O2···O1: 2.697(4) Å, O−H···O: 176(3)°], as shown in Figure 3.

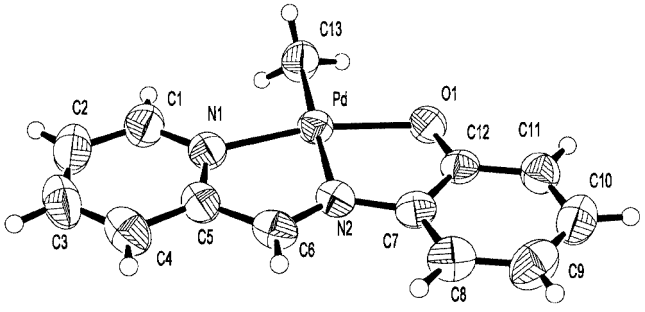


Figure 2. Perspective view of molecule **1b**·1/2$C_6H_6O_2$; thermal ellipsoids are drawn at the 50% probability level

The molecular structure of **2b** is shown in Figure 4, while the most relevant geometric features are listed in Table 1. The coordination is square-planar, with the ligand behaving as NN′S-tridentate, and the methyl *trans* to the iminic N2. The hindrance of the methyl substituent at C6 produces a minor deviation from planarity involving a slight rotation of the benzenethiol group around the C8−N2 bond [C6−N2−C8−C9: −8.0(5)°]. The overall planarity is conserved (maximum deviation 0.16 Å). The presence of the soft and bulkier S donor in the ligand has the effect of opening the S−Pd−N2 angle relative to the analogous O−Pd−N2 angle in **1b** [88.21(6) and 82.7(1)° for **2b** and **1b**, respectively], with a consequent slight weakening of the Pd−N2 bond [2.069(2) for **2b** and 2.009(3) Å for **1b**]. The *trans* effect of the S atom also results in a lengthening of the Pd−N1 bond [2.060(2) in **2b** and 2.033(3) Å for **1b**]. The dimensions of the S atom also seem to induce a compression of the Pd−N2−C6 angle [115.2(2)°] from the usual

Table 1. Selected bond lengths (Å) and angles (°) for compounds **1b**·1/2$C_6H_6O_2$, **2b**, and **2c**·1/2CH_2Cl_2

	1b·1/2$C_6H_6O_2$		**2b**	**2c**·1/2CH_2Cl_2 (two molecules)	
Pd−N1	2.033(3)	Pd−N1	2.060(2)	2.070(7)	2.062(8)
Pd−N2	2.009(3)	Pd−N2	2.069(2)	2.088(7)	2.062(8)
Pd−O1	2.037(2)	Pd−S	2.2382(9)	2.251(3)	2.241(3)
Pd−C13	2.061(4)	Pd−C14	2.045(3)	1.91(1)	1.936(9)
O1−C12	1.327(4)	S−C13	1.762(3)	1.750(9)	1.761(8)
N1−C5	1.350(5)	N1−C5	1.365(3)	1.37(1)	1.36(1)
N2−C6	1.278(4)	N2−C6	1.290(3)	1.27(1)	1.28(1)
N2−C7	1.410(4)	N2−C8	1.436(3)	1.41(1)	1.41(1)
C5−C6	1.474(5)	C5−C6	1.498(4)	1.46(1)	1.47(1)
C7−C12	1.418(5)	C8−C13	1.402(4)	1.36(1)	1.40(1)
N2−Pd−N1	80.9(1)	N2−Pd−N1	80.22(8)	78.7(3)	79.1(3)
N2−Pd−O1	82.7(1)	N2−Pd−S	88.21(6)	86.7(2)	86.8(2)
N1−Pd−O1	163.6(1)	N1−Pd−S	168.43(6)	163.7(3)	165.5(2)
N2−Pd−C13	177.3(1)	N2−Pd−C14	178.3(1)	177.6(4)	173.3(4)
N1−Pd−C13	101.1(1)	N1−Pd−C14	98.3(1)	100.2(4)	100.5(4)
O1−Pd−C13	95.3(1)	S−Pd−C14	93.2(1)	94.0(3)	93.1(3)
C12−O1−Pd	110.1(2)	C13−S−Pd	96.69(9)	96.4(3)	97.9(4)
C5−N1−Pd	111.8(2)	C5−N1−Pd	112.6(2)	110.8(6)	111.0(6)
C6−N2−Pd	115.6(3)	C6−N2−Pd	115.2(2)	114.4(6)	114.0(6)
C7−N2−Pd	112.4(2)	C8−N2−Pd	116.0(2)	114.8(6)	116.1(6)
N1−C5−C6	116.0(3)	N1−C5−C6	115.9(2)	117.5(9)	118.0(9)
N2−C6−C5	115.7(3)	N2−C6−C5	115.9(2)	115.1(9)	114.5(9)
N2−C7−C12	113.0(3)	N2−C8−C13	115.5(2)	117.5(9)	116.7(8)
O1−C12−C7	121.7(3)	S−C13−C8	123.6(2)	123.6(8)	122.3(8)

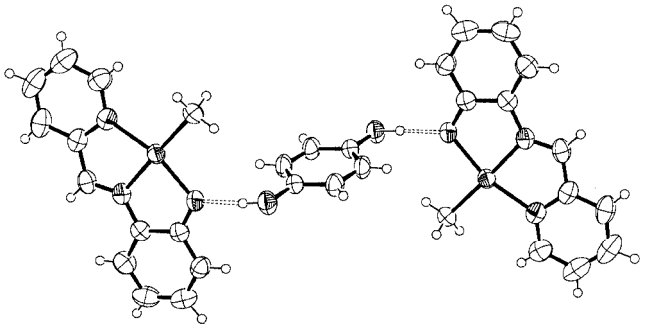


Figure 3. Molecular assembly through hydrogen bonds in the cocrystallization of **1b** with hydroxyquinone

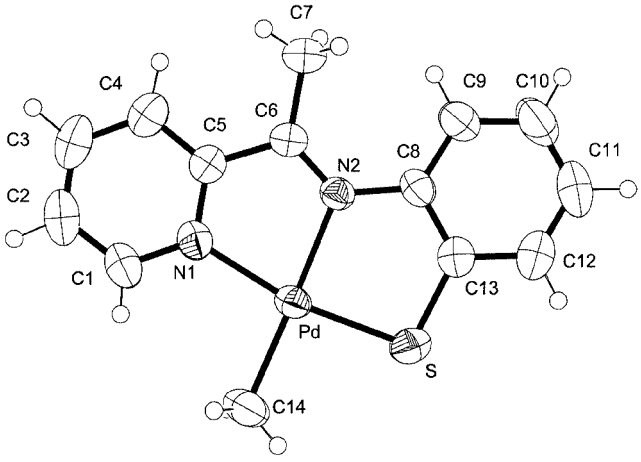


Figure 4. Perspective view of molecule **2b**; thermal ellipsoids are drawn at the 50% probability level

value for tridentate complexes; this has also been observed in some other cases of similar complexes [115.8° in chloro(-pyridine-2-carbaldehyde thiosemicarbazone-*N*,*N*′,*S*)palladium(II),[12] and chloro(2-formylpyridine 3-hexamethylene iminyl thiosemicarbazone-*N*,*N*′,*S*)palladium(II)[13]].

Compound **2c** crystallizes with two independent molecules in the asymmetric unit, one of which is shown in Figure 5. A dichloromethane molecule is also present in the asymmetric unit. The two complex molecules have similar geometries, and their relevant bonding features are listed in Table 1. The insertion of the CO into the Pd−CH_3 bond of **2b** produces a remarkable modification in the geometry of the resulting acylated complex **2c**, the resulting ligand structure being significantly distorted, with deviations from planarity as large as 0.75 Å, due to a rotation of the terminal benzenethiol group around the C−N bond [C6−N2−C8−C9: 33(1) and C21−N4−C23−C24: −30(1)°]. The metal coordination planes (N, N S, C, Pd) are also affected, with maximum deviations from planarity of 0.22 and 0.14 Å, respectively, for the two molecules. The bite geometry of the Pd−N−C−C−S chelation ring is not influenced by this conformational modification, as can be seen by comparison of the corresponding bond angles of **2b** and **2c** (Table 1), whereas angular strains are induced in the Pd−N−C−C−N chelation ring, which in **2c** are generally narrower than in **2b**. In particular, the N−Pd−N bite angle is reduced to values typical for bidentate systems [78.7(3) and 79.1(3)° for the two molecules of **2c**]. The modification

of the coordination geometry upon introduction of the acetyl ligand may be due to a larger *trans* effect determining the elongation of the Pd−N2 bond than in the methyl complex [Pd−C: 2.090(7) and 2.097(7) Å in **2c** and 2.069(2) Å in **2b**], and also to steric reasons involving the orientation of the acetyl group around the Pd−C bond. It has been shown that acetyl groups coordinated to square-planar Pd or Pt atoms tend to orient themselves perpendicularly to the coordination plane, with dihedral angles between the acetyl and the coordination planes varying in the 68−90° range, and Pd−C bonds falling between 1.947 and 2.001 Å.[6] In **2c**, the Pd−C bonds [1.91(1) and 1.936(9) Å] are significantly shorter than average, and the acetyl groups are closer to the coordination planes [dihedral angles of 51.4(4) and 31.7(7)°], thus increasing the steric crowding in the average molecular plane. In both molecules the acetyl optimizes electrostatic interactions with **2** through an orientation of the methyl towards the ligand sulfur atom and the oxygen towards the pyridine C1−H [CH_3(acyl)···S: 3.35(1) and 3.15(1) Å; O(acyl) ···C(py) =3.19(1) and 3.11(1) Å].

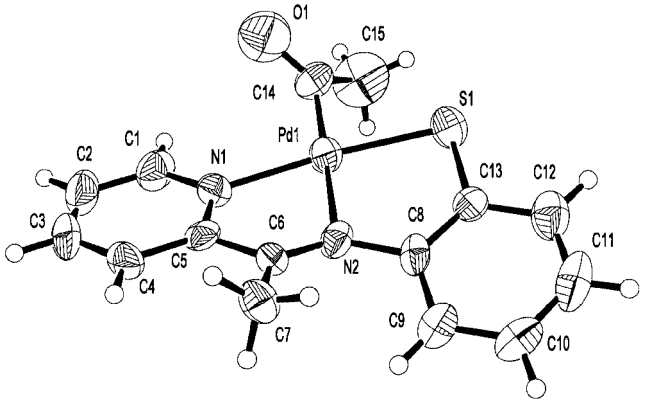


Figure 5. Perspective view of one of the two independent molecules in the crystal structure of **2c**·1/2CH_2Cl_2; thermal ellipsoids are drawn at the 50% probability level; the solvent has been omitted

Conclusions

We have reported the preparation of methylpalladium(II) complexes containing protic tridentate ligands of the HNN′O and HNN′S types. These ligands can adopt two different coordination modes around palladium: η^2-HNN′ when neutral, η^3-NN′X (X = O or S) when deprotonated. The reactivity of the three-coordinate complexes towards phosphanes and CO has been investigated. As far as carbonylation was concerned, in the absence of *soft* donors (**1b**) it was not possible to isolate the corresponding acetyl complex, and the reaction product was an organic molecule derived from the acetylation of the ligand (**3**). In the presence of a *soft* donor (the sulfur atom in **2b**), however, isolation of the carbonylated complex was successful, although the major product of the reaction was the thioacetate **4**, derived from acetylation of the ligand. The formation of the organic derivatives was accompanied by the release of palladium black. According to the results of a study on the reactivity of **1b** toward trimethylphosphane, it seems likely that the CO coordination proceeds by the breaking of the Pd-py bond. The possibility of making such a reaction catalytic is under investigation in our laboratories.

Experimental Section

General: All reactions were performed under an atmosphere of nitrogen by standard Schlenk techniques. Solvents were dried prior to use and stored under nitrogen. Elemental analyses (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. ^{1}H NMR spectra were obtained on a Bruker 300 FT spectrometer with $SiMe_4$ as internal standard at 25 °C, while $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CPX 200 FT with H_3PO_4 (85%) as external standard at 25 °C. MS-CI spectra (methane) were recorded on a Finnigan SSQ 710 spectrometer, collecting negative ions; the relative intensities are reported in brackets. The thermogravimetric analyses were carried out under nitrogen atmosphere on a Perkin−Elmer Delta Series TGA7 apparatus, with a programmed temperature increment of 5 °C/min. The ligands HNN′O (**1**)[14] and HNN′S (**2**)[15] were synthesized by slightly modified literature procedures. The reagents used in the syntheses of the ligands — PPh_3, $P(CD_3)_3$ and *n*BuLi (1.6 M solution in *n*-hexane) — were commercial grade and were used without further purification. [(COD)Pd(Me)Cl] was synthesized as reported in the literature.[4b]

[Pd(η^2-HNN′)(Me)Cl] (1a): Compound **1** (0.050 g, 0.252 mmol) was dissolved in 30 mL of diethyl ether and [(COD)Pd(Me)Cl] (0.066 g, 0.250 mmol) was added. The immediate precipitation of a yellow powder was observed. The mixture was stirred at room temperature for 1 h and then filtered, and the solid was washed repeatedly with diethyl ether and dried under vacuum. Yield: 0.083 g (94%). ^{1}H NMR ([D_6]Me_2SO): δ = 0.41 (s, 3 H, Pd-Me), 6.89 (t, 1 H, 7-H), 6.98 (d, 1 H, 8-H), 7.08 (d, 1 H, 5-H), 7.16 (t, 1 H, 6-H), 7.91 (t, 1 H, 2-H), 8.14 (d, 1 H, 4-H), 8.27 (t, 1 H, 3-H), 8.82 (d, 1 H, 1-H), 8.88 [s, 1 H, C(H)=N], 9.84 (s, 1 H, O−H) ppm. IR: ṽ = 3377 m (OH), 1597 m−1589 m (C=N) cm^{-1}. $C_{13}H_{13}ClN_2OPd$ (355.1): calcd. C 43.97, H 3.69, N 7.89; found C 44.00, H 3.71, N 7.85.

[Pd(η^2-HNN′)(Me)Cl] (2a): Complex **2** (0.050 g, 0.219 mmol) was dissolved in 20 mL of diethyl ether and [(COD)Pd(Me)Cl] (0.058 g, 0.219 mmol) was added. The rapid formation of a gray powder was observed, and this was filtered off after two hours of stirring at room temperature. The filtered solid was washed repeatedly with diethyl ether and then dried under vacuum. Yield: 0.060 g 71%. ^{1}H NMR ([D_6]Me_2SO): δ = 0.81 (s, Pd-Me), 2.50 [s, C(Me)=N] ppm. The other signals overlapped with the signals of **2b** and **2d**. IR: ṽ = 3229 m (SH), 1587 m (C=N) cm^{-1}. $C_{14}H_{15}ClN_2PdS$ (385.2): calcd. C 43.65, H 3.92, N 7.27, S 8.32; found C 43.63, H 3.85, N 7.19, S 8.17.

[Pd(η^3-NN′O)(Me)] (1b). Method a: Complex **1** (0.050 g, 0.252 mmol) was dissolved in 10 mL of THF and [(COD)Pd(Me)Cl] (0.067 g, 0.252 mmol) was added, resulting in a yellow solution that was stirred at room temperature for 5 min. *n*BuLi (0.016 g, 0.252 mmol, 158 μL) was then added, to produce a purple solution that was stirred for 3 h, filtered, concentrated, and then treated with an excess of *n*-hexane. A purple solid was filtered off, washed with *n*-hexane, and then dried under vacuum. Yield: 0.072 g (90%). On slow evaporation of a THF solution of **1b**,

crystals of **1b**·1/2$C_6H_6O_2$ suitable for X-ray analysis were collected.

Method b: Complex **1a** (0.050 g, 0.141 mmol) was dissolved in 10 mL of THF, and NaOMe (0.011 g, 0.211 mmol) or *n*BuLi (0.008 g, 0.141 mmol, 88 μL) was added; the purple solution was stirred at room temperature for 2 h, then filtered and concentrated, and the product was precipitated with *n*-hexane and worked up as described above. Yield: 0.039 g (85%). ^{1}H NMR ([D$_6$]DMSO): δ = 0.60 (s, 3 H, Pd-Me), 6.37 (t, 1 H, 6-H), 6.72 (d, 1 H, 8-H), 7.00 (m, 2 H, 5-H−7-H), 7.21 (t, 1 H, 2-H), 7.38 (d, 1 H, 4-H), 7.76 (t, 1 H, 3-H), 7.88 [s, 1 H, C(H)=N], 8.15 (d, 1 H, 1-H) ppm. IR: $\tilde{\nu}$ = 1600 s (C=N) cm^{-1}. MS: *m*/*z* (%) = 317 (43) [**1b**]$^-$, 301 (19) [**1b** − Me]$^-$, 198 (100) [**1**]$^-$. $C_{13}H_{12}N_2OPd$ (318.7): calcd. C 49.00, H 3.79, N 8.79; found C 49.09, H 3.85, N 8.75.

[Pd(η^3-NN′S)(Me)] (2b): Complex **2** (0.100 g, 0.438 mmol) was dissolved in 30 mL of THF. [(COD)Pd(Me)Cl] (0.116 g, 0.438 mmol) was then added, and the resulting yellow solution was stirred at room temperature for 5 min. NaOMe (0.035 g, 0.656 mmol) or Et_3N (0.066 g, 0.656 mmol, 91 μL) was added, producing a deep green solution that was stirred for 1.5 h and from which a green solid was released. The solid was filtered off, washed with cold methanol and diethyl ether, and then dried under vacuum. Yield: 0.115 g (75%). On slow evaporation of a THF solution of **2b**, crystals suitable for X-ray analysis were collected. ^{1}H NMR ([D$_6$]DMSO): δ = 0.15 (s, 3 H, Pd-Me), 2.70 [s, 3 H, C(Me)=N], 6.78 (t, 1 H, 7-H), 6.91 (t, 1 H, 6-H), 7.15 (d, 1 H, 5-H), 7.23 (d, 1 H, 8-H), 7.66 (t, 1 H, 2-H), 8.01 (d, 1 H, 4-H), 8.13 (t, 1 H, 3-H), 8.35 (d, 1 H, 1-H) ppm. IR: $\tilde{\nu}$ = 1595 m (C=N) cm^{-1}. MS: *m*/*z* (%) = 349 (100) [**2b**]$^-$. $C_{14}H_{14}N_2PdS$ (348.7): calcd. C 48.21, H 4.05, N 8.03, S 9.19; found C 48.25, H 4.10, N 8.05, S 9.14.

[Pd(η^2-HNN′)Cl$_2$] (1c): 1 (0.076 g, 0.383 mmol) was dissolved in 30 mL of methanol, and a methanol solution (30 mL) of Li_2PdCl_4 (0.100 g, 0.383 mmol) was added. The mixture was stirred at room temperature for 2 h, producing a brown solid, which was filtered off, washed with methanol, and dried under vacuum. Yield: 0.111 g (77%). On slow evaporation of a THF solution of **1c**, crystals of **1c**·THF suitable for X-ray analysis were collected. ^{1}H NMR ([D$_6$]DMSO): δ = 6.83 (t, 1 H, 7-H), 6.92 (d, 1 H, 8-H), 7.19 (m, 2 H, 5-H−6-H), 7.95 (t, 1 H, 2-H), 8.20 (d, 1 H, 4-H), 8.39 (t, 1 H, 3-H), 8.72 [s, 1 H, C(H)=N], 9.06 (d, 1 H, 1-H), 10.01 (s, 1 H, O−H) ppm. IR: $\tilde{\nu}$ = 3423 s (O−H), w (C=N) 1615 cm^{-1}. $C_{12}H_{10}Cl_2N_2OPd$·THF (447.62): calcd. C 42.93, H 4.05, N 6.26; found C 42.95, H 4.10, N 6.24.

[Pd(η^3-NN′O)Cl] (1d): Characterization was performed only in solution. ^{1}H NMR ([D$_6$]DMSO): δ = 6.48 (m, 2 H, 7-H−8-H), 7.05 (t, 1 H, 6-H), 7.39 (d, 1 H, 5-H), 7.61 (t, 1 H, 2-H), 7.77 (d, 1 H, 4-H), 8.16 (t, 1 H, 3-H), 8.43 (d, 1 H, 1-H) ppm; the C(H)=N signal was obscured.

Reactions of 1a and 1b with Phosphanes: The complex (0.020 g, 0.056 mmol for **1a** and 0.063 mmol for **1b**, respectively) was dissolved in 0.75 mL of [D$_6$]DMSO in a 5-mm NMR tube. The desired amount of phosphane was added quickly, with the progress of the reaction being monitored by ^{1}H or ^{31}P NMR spectroscopy at 25 °C.

Treatment of 1a with PPh_3: PPh_3 (stoichiometric, 0.015 g, 0.056 mmol) was added; the solution instantaneously turned from yellow to green. **1e:** ^{31}P NMR: δ = 40.5 (s) ppm. **1f:** ^{31}P NMR: δ = 32.5 (s) ppm; (excess of PPh_3): Additional PPh_3 (0.015 g) was added, resulting in the immediate precipitation of a white solid (*trans*-[$(PPh_3)_2$Pd(Me)Cl]), which was filtered off, washed with Me_2SO and diethyl ether, and then dried under vacuum. Yield: 0.035 g (92%). ^{1}H NMR ($CDCl_3$): δ = −0.03 (t, $J_{P\text{-}H}$ = 5.9 Hz, 3 H, Pd−Me), 7.71−7.38 (m, 30 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 27.7 (s) ppm. Crystals suitable for X-ray analysis were collected from a refrigerated THF/*n*-hexane mixture of *trans*-[$(PPh_3)_2$Pd(Me)Cl]. $C_{37}H_{33}ClP_2Pd$ (681.5): calcd. C 65.21, H 4.88, N 4.11; found C 65.20, H 4.85, N 4.10.

Treatment of 1b with $P(CD_3)_3$: $P(CD_3)_3$ (0.007 g, 0.112 mmol, 8.7 μL) was added to the complex solution by micropipette, without observation either of color changes or of solid formation. **1h:** ^{31}P NMR: δ = 43.1 (s) ppm. ^{1}H NMR: δ = 0.25 (s, 3 H, Pd-Me), 6.13 (t, 1 H, 6-H), 6.46 (d, 1 H, 8-H), 6.75 (t, 1 H, 7-H), 7.08 (d, 1 H, 5-H), 7.31 (t, 1 H, 2-H), 7.81 (t, 1 H, 3-H), 8.02 (d, 1 H, 4-H), 8.57 (d, 1 H, 1-H), 9.70 [s, 1 H, C(H)=N] ppm.

Carbonylations of 1b and 2b: The complex (0.050 g, 0.157 mmol for **1b** and 0.144 mmol for **2b**) was placed in a Schlenk tube and dissolved under nitrogen in 15 mL of dichloromethane. CO was bubbled through a glass capillary until complete saturation of the solution (at least 5 min), the vessel was closed, and the CO atmosphere was maintained for the required time. The solution was filtered through Celite in order to remove palladium black, and analyzed by mass spectrometry.

Carbonylation of 1b (3): The formation of palladium black was practically instantaneous, as was the bleaching of the solution. The CO was released after 10 min. MS: *m*/*z* (%) = 241 (48) [**3**]$^-$, 199 (32) [**1**]$^-$.

Carbonylation of 2b (2c and 4): The formation of palladium black was much slower then in the case of **1b**. The CO was released after 2 h. MS: *m*/*z* (%) = 378 (2) [**2c**]$^-$, 270 (100) [**4**]$^-$, 228 (37) [**2**]$^-$. A portion of the solution was dried and redissolved in the minimum amount of dichloromethane, and *n*-hexane was slowly diffused into it at −18 °C; crystals of **2c**·1/2CH_2Cl_2 suitable for X-ray analysis were collected.

Crystal Structure Determinations of 1b·1/2$C_6H_6O_2$, 1c·THF, 2b, 2c·1/2CH_2Cl_2, and *trans*-[$(PPh_3)_2$Pd(Me)Cl]: Single crystals were mounted on glass fibers, and X-ray diffraction data were collected at room temperature on a Bruker−Siemens SMART AXS 1000 equipped with a CCD detector for compounds **1b**·1/2$C_6H_6O_2$, **2b**, and **2c**·1/2CH_2Cl_2, and a Philips PW1100 diffractometer equipped with a scintillation counter for compounds *trans*-[$(PPh_3)_2$Pd(Me)Cl] and **1c**·THF. Graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) was used in all cases. Data collection details for **1b**, **2b**, and **2c** are: crystal to detector distance: 5.0 cm, hemisphere mode, time per frame: 30 s, oscillation Δω = 0.300°. Data reduction was performed by use of the SAINT package[16] and data were corrected for absorption effects by the SADABS[17] procedure. For *trans*-[$(PPh_3)_2$Pd(Me)Cl] and **1c**·THF, data were processed with a peak-profile procedure and corrected for Lorentz, polarization, and absorption effects (Ψ-scan method). Crystal decay was negligible in all cases. The phase problem was solved by direct methods[18] and the structures were refined by full-matrix, least-squares on all F^2,[19] by use of the WinGX package.[20] Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were partly located from Fourier maps and refined isotropically, and partly introduced at calculated positions. Use was made of the Cambridge Crystallographic Database[21] facilities for structure discussion. Final maps were featureless. Data collection and refinement results are summarized in Table 2.

CCDC-178202 (**1b**·1/2$C_6H_6O_2$), -178203 (**2b**), -178204 (**2c**·1/2CH_2Cl_2), -178205 (**1g**), and -178206 (**1c**·THF) contain the

Table 2. Crystal data and structure refinement for **1b**·1/2$C_6H_6O_2$, **2b**, **2c**·1/2CH_2Cl_2, **1g** and **1c**·THF

	1b·1/2$C_6H_6O_2$	**2b**	**2c**·1/2CH_2Cl_2	**1g**	**1c**·THF
Empirical formula	$C_{16}H_{15}N_2O_2Pd$	$C_{14}H_{14}N_2PdS$	$C_{15.5}H_{15}N_2ClOPdS$	$C_{37}H_{33}ClP_2Pd$	$C_{16}H_{18}Cl_2N_2O_2Pd$
Molecular mass	373.70	348.73	419.21	681.47	447.62
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/a$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å, °)	a = 7.124(2) α = 95.40(1) b = 9.301(2) β = 95.43(1) c = 11.408(3) γ = 104.26(1)	a = 7.353(3) b = 18.063(5) β = 107.45(1) c = 10.417(3)	a = 20.188(5) b = 7.665(3) β = 98.66(2) c = 20.209(5)	a = 12.367(3) b = 23.433(5) β = 111.93(2) c = 11.891(3)	a = 10.576(4) b = 15.753(6) β= 103.49(2) c = 10.938(4)
Volume (Å^3)	723.9(3)	1319.9(8)	3091(2)	3197(1)	1772(1)
Z	2	4	8	4	4
$D_{calcd.}$ (Mg/m^3)	1.714	1.755	1.801	1.416	1.678
Absorption coefficient (mm^{-1})	1.287	1.546	1.508	0.789	1.358
F(000)	374	696	1672	1392	896
θ range (°)	1.81−28.22	2.25−28.08	2.04−21.96	3.13−26.10	3−30
Reflections collected	4404	7770	11579	6620	5376
Independent reflections	3068 [R(int) = 0.0161]	2915 [0.0231]	3769 [0.0763]	6320 [0.0572]	5145 [0.3492]
Observed reflections	2579	2378	1959	1434	2644
Data/restraints/ parameters	3068/2/239	2915/0/219	3769/0/392	6320/0/371	5145/0/209
Goodness-of-fit	0.964	0.945	0.810	0.621	0.888
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0316, $wR2$ = 0.0751	0.0258, 0.0582	0.0402, 0.0732	0.0536, 0.1283	0.0735, 0.1770
R indices (all data)	$R1$ = 0.0408, $wR2$ = 0.0790	0.0361, 0.0625	0.1038, 0.0882	0.2031, 0.1565	0.1380, 0.2037
ΔF maximum/ minimum (e/Å^3)	0.482/-0.440	0.528/-0.653	0.537/−0.604	1.164/-0.576	2.440/-4.537

supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The C.I.M. (Centro Interfacoltà di Misure "Giuseppe Casnati") is thanked for technical assistance.

[1] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, California (US), **1987**.

[2] [2a] G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1992**, *430*, 357−372. [2b] R. E. Rülke, J. P. G. Delis, A. M. Groot, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, K. Goubitz, H. Schenk, *J. Organomet. Chem.* **1996**, *508*, 109−120. [2c] J. H. Groen, M. J. M. Vlaar, P. W. N. M. van Leeuwen, K. Vrieze, H. Kooijman, A. L. Spek, *J. Organomet. Chem.* **1998**, *551*, 67−79. [2d] J. H. Groen, B. J. de Jong, J.-M. Ernsting, P. W. N. M. van Leeuwen, K. Vrieze, W. J. J. Smeets, A. L. Spek, *J. Organomet. Chem.* **1999**, *573*, 3−13.

[3] [3a] G. P. C. M. Dekker, A. Bujis, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, W. J. J. Smeets, A. L. Spek, Y. F. Wang, C. H. Stam, *Organometallics* **1992**, *11*, 1937−1948. [3b] P. W. N. M. van Leeuwen, C. F. Roobeek, H. van der Heijden, *J. Am. Chem. Soc.* **1994**, *116*, 12117−12118. [3c] H. A. Ankersmit, B. H. Løken, H. Kooijman, A. L. Spek, K. Vrieze, G. van Koten, *Inorg. Chim. Acta* **1996**, *252*, 141−155. [3d] L. Crociani, G. Bandoli, A. Dolmella, M. Basato, B. Corain, *Eur. J. Inorg. Chem.* **1998**, 1811−1820. [3e] M. J. Green, G. J. P. Britovsek, K. J. Cavell, F. Gerhards, B. F. Yates, K. Frankcombe, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1998**, 1137−1144.

[4] [4a] R. E. Rülke, I. M. Han, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, C. F. Roobeek, M. C. Zoutberg, Y. F. Wang, C. H. Stam, *Inorg. Chim. Acta* **1990**, *169*, 5−8. [4b] R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, *Inorg. Chem.* **1993**, *32*, 5769−5778. [4c] R. E. Rülke, V. E. Kaasjager, D. Kliphuis, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, K. Goubitz, *Organometallics* **1996**, *15*, 668−677. [4d] H. A. Ankersmit, N. Veldman, A. L. Spek, K. Vrieze, G. van Koten, *Inorg. Chim. Acta* **1996**, *252*, 339−354. [4e] R. E. Rülke, V. E. Kaasjager, P. Wehman, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, A. L. Spek, *Organometallics* **1996**, *15*, 3022−3031. [4f] G. J. P. Britovsek, K. J. Cavell, M. J. Green, F. Gerhards, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1997**, *533*, 201−212.

[5] J. Andrieu, B. R. Steele, C. G. Screttas, C. J. Cardin, J. Fornies, *Organometallics* **1998**, *17*, 839−845.

[6] P. Pelagatti, M. Carcelli, F. Franchi, C. Pelizzi, A. Bacchi, A. Fochi, H.-W. Frühauf, K. Goubitz, K. Vrieze, *Eur. J. Inorg. Chem.* **2000**, 463−475.

[7] S. P. Meneghetti, P. J. Lutz, J. Kress, *Organometallics* **1999**, *18*, 2734−2737.

[8] [8a] J. G. P. Delis, J. H. Groen, K. Vrieze, P. W. N. M. van Leeuwen, N. Veldman, L. Spek, *Organometallics* **1997**, *16*, 551−562. [8b] A. Satake, H. Koshino, T. Nakata, *J. Organomet. Chem.* **2000**, *595*, 208−214.

[9] J. L. Hoare, K. J. Cavell, R. Hecker, B. W. Skelton, A. White, *J. Chem. Soc., Dalton Trans.* **1996**, 2197−2206.

[10] [10a] S. Komiya, Y. Akai, K. Tanaka, T. Yamamoto, A. Yamamoto, *Organometallics* **1985**, *4*, 1130−1136. [10b] Y.-J. Kim, H. Osakada, K. Sugita, T. Yamamoto, A. Yamamoto, *Organometallics* **1988**, *7*, 2182−2188.
[11] A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1996**, 4239−4244.
[12] D. Kovala-Demertzi, J. R. Miller, N. Kourkoumelis, S. K. Hadjikakou, M. A. Demertzis, *Polyhedron* **1999**, *18*, 1005−1013.
[13] D. Kovala-Demertzi, M. A. Demertzis, A. Castineiras, D. X. West, *Polyhedron* **1998**, *17*, 3739−3745.
[14] C. G. Pitt, Y. Bao, J. Thompson, M. C. Wani, H. Rosenkrantz, J. Metterville, *J. Med. Chem.* **1986**, *29*, 1231−1237.
[15] J. R. Dilworth, S. D. Howe, A. J. Huston, J. R. Miller, J. Silver, R. M. Thompson, M. Harman, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1994**, 3553−3562.
[16] SAINT: SAX, *Area Detector Integration*, Siemens Analytical instruments Inc., Madison, Wisconsin, USA.
[17] SADABS: *Siemens Area Detector Absorption Correction Software*, G. Sheldrick, University of Göttingen, Germany, **1996**.
[18] Sir97: *A new Program For Solving And Refining Crystal Structures* − A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G. Polidori, R. Spagna, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche C. N. R., Bari, **1997**.
[19] Shelxl97. *Program for structure refinement.* G. Sheldrick, University of Göttingen, Germany, 1997.
[20] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
[21] F. H. Allen, O. Kennard, R. Taylor, *Acc. Chem. Res.* **1983**, *16*, 146−153.

Received January 29, 2002
[I02048]