DALTON
FULL PAPER

Coordination properties of novel hemilabile acetamide-derived *P,O* phosphine ligands. Crystal structures of $Ph_2PNHC(O)Me$ and $[PdMe\{PPh_2NHC(O)Me\}\{PPh_2NHC(O)Me\}][O_3SCF_3]$†

Pierre Braunstein,[a] Céline Frison,[a] Xavier Morise[a] and Richard D. Adams[b]

[a] *Laboratoire de Chimie de Coordination (UMR CNRS 7513), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France*
[b] *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208*

Received 27th March 2000, Accepted 10th May 2000
Published on the Web 14th June 2000

Cationic methyl Pd(II) complexes are described in which the new heterofunctional phosphine ligands $Ph_2PNHC(O)Me$ **1** or $Ph_2PN(Me)C(O)Me$ **3** behave as rigid and/or hemilabile *P,O* chelates. The chelating ability of **3** is higher than that of **1** and both are compared to that of other *P,O* ligands, such as the keto- and amido-phosphines $Ph_2PCH_2C(O)Ph$ and $Ph_2PCH_2C(O)NPh_2$, respectively. The crystal structure of **1** reveals the presence in the solid-state of an intermolecular hydrogen-bonded network N–H · · · O and that of $[PdMe\{PPh_2NHC(O)Me\}\{PPh_2NHC(O)Me\}][O_3SCF_3]$ **12b** establishes the presence of both a chelating and a monodentate ligand **1** in the same complex. Carbonylation of the cationic methyl complexes **8a**, **17**, **18a** and **20a** afforded the corresponding acetyl complexes in which this ligand occupies a position *cis* to phosphorus, irrespective of that of the alkyl ligand in the precursor complex.

Introduction

Since ligands largely govern the stoichiometric and catalytic reactivity of metal complexes, the continuing interest in the design of new functional ligands is not surprising and applies in particular to phosphines, which are ubiquitous in coordination and organometallic chemistry, and various *P,O* systems have been studied, which combine a soft phosphine moiety with a hard oxygen functionality.[1,2] Their chelating ability confers additional stability during catalysis, whereas their dissymmetrical nature may be of interest for a stereo-electronic control of the active metal centre. For example, anionic *P,O* ligands have been shown to play a key role in the nickel-catalyzed ethene oligomerization into linear α-olefins (Shell Higher Olefin Process), where subtle ligand variations strongly influence the reactivity and/or the selectivity of the active metal centre,[3–5] in the rhodium-catalyzed activation of alkanes[6] or in the reversible CO_2 fixation and catalytic lactone synthesis by palladium complexes.[7] Furthermore, neutral *P,O* ligands may display a hemilabile behaviour, involving the weak donor functionality, which leads to the storage of a potential vacant coordination site suitable for substrate activation.[1,2,8–11]

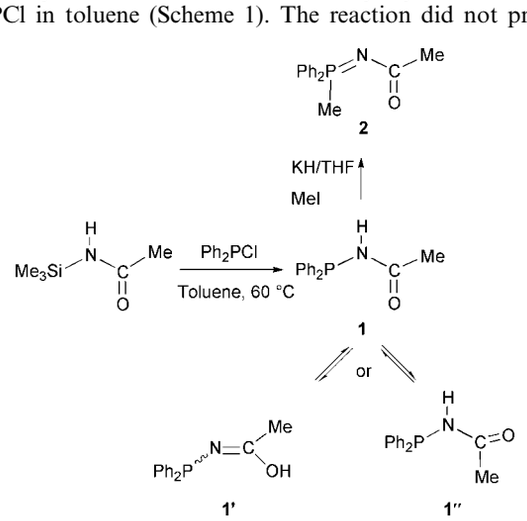
By analogy with the interesting properties brought about by the NH group of dppa (bis(diphenylphosphino)amine) compared with the CH_2 group of dppm (bis(diphenylphosphino)methane),[12–15] it appeared interesting to investigate the corresponding effect on heteroditopic *P,O* ligands. We therefore set out to study the coordination properties of ligands of the type $Ph_nP\{NHC(O)CH_3\}_{3-n}$ ($n = 1$, 2), *i.e.* acetamido analogues of the ketophosphines $Ph_nP\{CH_2C(O)R\}_{3-n}$. Modifications of the chelating ability and of the hemilabile behaviour were anticipated, owing to the different electronic influences of the NH and CH_2 groups and to changes in the P–N–C *vs.* P–C–C bond angle in α position to the P atom,[16] which could influence the reactivity of the corresponding complexes. We have recently reported Ni complexes with the anionic chelating ligand $[Ph_2PN\cdots C(\cdots NPh)Ph]^-$ which is isoelectronic with the phosphino enolate $[Ph_2PCH\cdots C(\cdots O)Ph]^-$.[17]

We report here investigations on the coordination properties of the new acetamido derived phosphine ligand $Ph_2PNHC(O)Me$ **1** and its *N*-methyl derivative $Ph_2PN(Me)C(O)Me$ **3**. Cationic Pd(II) complexes in which **1** or **3** act as rigid *P,O* chelate and/or a hemilabile ligand are described. The chelating ability of these ligands is compared to that of other potential *P,O* chelates, such as the keto- and amido-phosphines $Ph_2PCH_2C(O)Ph$[18] and $Ph_2PCH_2C(O)NPh_2$,[19] respectively. The crystal structures of **1** and $[PdMe\{PPh_2NHC(O)Me\}\{PPh_2NHC(O)Me\}][O_3SCF_3]$ **12b** are also reported.

Results

Synthesis and characterization of the ligands

The new acetamido phosphine $Ph_2PNHC(O)Me$ **1** was prepared by condensation of *N*-trimethylsilylacetamide with Ph_2PCl in toluene (Scheme 1). The reaction did not proceed



Scheme 1

† Part of the Doctoral Thesis of C. F.

Table 1 Selected IR and NMR data for compounds **1**–**20**

Complex	IR [a]/cm^{-1} ν(C=O)	^{1}H NMR,[b] δ (ppm), J (Hz) Ligand **1** or **3**	Other	^{31}P{^{1}H}NMR,[b] δ (ppm), J (Hz)
1	1715s	2.13 [s, 3H, C(O)Me], 6.15 (br, 1H, NH)		21.6
1′		2.30 [s, 3H, C(O)Me], OH not observed		31.1
2	1672m	2.18 [d, 3H, $^4J_{PH}$ = 3, C(O)Me], 2.24 (d, 3H, $^2J_{PH}$ = 13, PMe)		19.8
3	1669s	2.54 (d, 3H, $^3J_{PH}$ = 4.8, NMe), 2.74 [s, 3H, C(O)Me]		55.1
4	1698s	2.10 [s, 3H, C(O)Me], 9.7 (br, 1H, NH) (298 K); 2.06 [s, 3H, C(O)Me], 9.2 (d, 1H, $^2J_{PH}$ = 16, NH) (220 K)	2.87 (d, 6H, $^4J_{PH}$ = 2.8, NMe_2), 3.99 (d, 2H, $^4J_{PH}$ = 6.9, NCH_2) (298 K); 2.87 (s, br, 6H, NMe_2), 3.98 (s, br, 2H, NCH_2) (220 K)	61.8 (br) (298 K) 60.7 (220 K)
4′		2.52 [s, 3H, C(O)Me], 12.9 (br, 1H, NH) (220 K)	2.93 (s, br, 6H, NMe_2), 4.07 (s, br, 2H, NCH_2) (220 K)	79.7 (220 K)
5	1604s	2.43 [s, 3H, C(O)Me], 10.74 (br, 1H, NH)[c]	2.93 (d, 6H, $^4J_{PH}$ = 2.8, NMe_2), 4.06 (d, $^4J_{PH}$ = 2.1, NCH_2)[c]	79.0[c]
6	1672s	2.38 [s, 3H, C(O)Me], 2.99 (d, 3H, $^3J_{PH}$ = 6.6, NMe)	2.85 (d, 6H, $^4J_{PH}$ = 3.0, NMe_2), 4.03 (d, 2H, $^4J_{PH}$ = 2.4, NCH_2)	85.8
7	1584s	2.56 [s, 3H, C(O)Me], 3.11 (d, 3H, $^3J_{PH}$ = 5.4, NMe)	2.92 (d, 6H, $^4J_{PH}$ = 3.0, NMe_2), 4.03 (d, 2H, $^4J_{PH}$ = 2.4, NCH_2)	97.8
8a	1614s	2.40 [s, 3H, C(O)Me], 10.06 (br, 1H, NH)[c]	0.74 (s, 3H, PdMe), 2.27 (s, 3H, NCMe)[c]	79.8[c]
8b	1602s	2.35 [s, 3H, C(O)Me], 10.23 (br, 1H, NH)	0.76 (s, 3H, PdMe), 2.31 (s, 3H, NCMe)	79.3
9	1675m,[d] 1606m[e]	2.37 [s, 3H, C(O)Me], 8.88 (br, 1H, NH)	0.65 (dd, 3H, $^3J_{PH}$ = 6.0, 5.9, PdMe), 4.27 (dd, 2H, $^2J_{PH}$ = 9.3, $^3J_{PH}$ = 1.6, CH_2)	14.0 (d, 1P, CP), 70.1 (d, 1P, $^2J_{PP}$ = 417, NP)
10	1659m,[d] 1604m[e]	2.34 [s, 3H, C(O)Me], 9.55 (br, 1H, NH)	0.62 (dd, 3H, $^3J_{PH}$ = 6.3, 6.0, PdMe), 3.60 (d, 2H, $^2J_{PH}$ = 9.0, CH_2)	17.2 (d, 1P, CP), 69.0 (d, 1P, $^2J_{PP}$ = 418, NP)
11	1611s	—	0.83 (s, 3H, PdMe), 2.31 (s, 3H, MeCN), 4.48 (d, 2H, $^2J_{PH}$ = 11.4, CH_2)	36.0
12a	1687, 1611[f]	2.27 [s, 6H, C(O)Me], 8.07 (br, 2H, NH)	0.59 (t, 3H, $^3J_{PH}$ = 5.7, PdMe)	60.2
12b	1689s, 1612s[f]	2.33 [s, 6H, C(O)Me], 9.08 (br, 2H, NH)	0.64 (m, 3H, PdMe)	59.0
13	1674s, 1607s	—	0.73 (br, 3H, PdMe), 4.48 (s, br, 2H, CH_2)	20.9
14	1591s	2.37 [s, 3H, C(O)Me], 2.98 (d, 3H, $^3J_{PH}$ = 5.4, NMe)[g]	0.60 (d, 3H, $^3J_{PH}$ = 2.4, PdMe), 2.04 (s, 3H, MeCN)[g]	98.0[g]
15	1665m, 1582s[b]	2.37 [s, 6H, C(O)Me], 2.95 (virtual t, 6H, $\lvert^3J_{PH} + {}^5J_{PH}\rvert$ = 6.0, NMe)[g]	0.47 (t, 3H, $^3J_{PH}$ = 6.0, PdMe)[g]	77.7[g]
16	1701m, 1589s	2.20 [s, 3H, C(O)Me], 2.44 [s, 3H, C(O)Me], 3.06 (br, 3H, NMe), 8.33 (br, 1H, NH)[g]	0.46 (br, 3H, PdMe)[g]	49.6 (d, 1P, HNP), 90.7 (d, 1P, $^2J_{PP}$ = 444, MeNP)[g]
17	1604s	2.38 [s, 3H, C(O)Me], 10.71 (s, 1H, NH)	0.61 (dd, 3H, $^3J_{PH}$ = 6.5, 5.6, PdMe)	24.8 (d, 1P, PPh_3), 70.7 (d, 1P, $^2J_{PP}$ = 405, NP)
cis-**18a**	1596s	2.49 [s, 3H, C(O)Me], 8.75 (br, 1H, NH)	1.07 (d, 3H, $^3J_{PH}$ = 7.7, PdMe), 3.62 [d, 9H, $^3J_{PH}$ = 13.3, $P(OMe)_3$]	67.8 (d, 1P, NP), 121.3 [d, 1P, $^2J_{PP}$ = 43, $P(OMe)_3$]
trans-**18a**	1652m	2.45 [s, 3H, C(O)Me], 8.72 (br, 1H, NH)	0.86 (dd, 3H, $^3J_{PH}$ = 6.1, 5.9, PdMe), 3.81 [d, 9H, $^3J_{PH}$ = 12.2, $P(OMe)_3$]	68.7 (d, 1P, NP), 119.0 [d, 1P, $^2J_{PP}$ = 603, $P(OMe)_3$]
cis-**18b**	1589s	2.23 [s, 3H, C(O)Me], 10.27 (br, 1H, NH)	0.76 (d, 3H, $^3J_{PH}$ = 7.5, PdMe), 3.43 [d, 9H, $^3J_{PH}$ = 13.3, $P(OMe)_3$][c]	67.3 (d, 1P, NP), 121.2 [d, 1P, $^2J_{PP}$ = 46, $P(OMe)_3$][c]
trans-**18b**	1608s	2.18 [s, 3H, C(O)Me], 10.01 (br, 1H, NH)	0.68 (br, 3H, PdMe), 3.54 [d, 9H, $^3J_{PH}$ = 11.4, $P(OMe)_3$]	68.3 (d, 1P, NP), 119.7 [d, 1P, $^2J_{PP}$ = 607, $P(OMe)_3$][c]
cis-**19b**	1592m	2.51 [s, 3H, C(O)Me], 10.72 (br, 1H, NH)	1.00 (d, 3H, $^3J_{PH}$ = 7.62, PdMe), 1.17 [d, 6H, $^3J_{HH}$ = 3.0, $CH(CH_3)_2$], 4.68 [M, 1H, $CH((CH_3)_2)$]	67.7 (d, 1P, NP), 111.4 [d, 1P, $^2J_{PP}$ = 36, $P(O^iPr)_3$]
trans-**19b**	1610m	2.44 [s, 3H, C(O)Me], NH not identified	0.88 (dd, 3H, $^3J_{PH}$ = 7.2, 6.6, PdMe), 1.27 [d, 6H, $^3J_{HH}$ = 3.2, $CH(CH_3)_2$], 4.68 [m, 1H, $CH((CH_3)_2)$]	68.3 (d, 1P, NP), 110.8 [d, 1P, $^2J_{PP}$ = 598, $P(O^iPr)_3$]
cis-**20b**	1589m	2.46 [s, 3H, C(O)Me], 10.74 (br, 1H, NH)	0.93 (d, 3H, $^3J_{PH}$ = 7.7, PdMe)	69.3 (d, 1P, NP), 110.2 [d, 1P, $^2J_{PP}$ = 46, $P(OPh)_3$]
trans-**20b**	1613m	2.26 [s, 3H, C(O)Me], 10.47 (br, 1H, NH)	0.68 (dd, 3H, $^3J_{PH}$ = 6.7, 5.6, PdMe)	70.5 (d, 1P, NP), 107.5 [d, 1P, $^2J_{PP}$ = 593, $P(OPh)_3$]

[a] Recorded in CH_2Cl_2 unless otherwise stated. [b] Recorded in $CDCl_3$ unless otherwise stated. [c] Recorded in $CD_3C(O)CD_3$. [d] ν_{CO} of $Ph_2PCH_2C(O)R$. [e] ν_{CO} of $Ph_2PNHC(O)Me$. [f] Recorded as KBr disk. [g] Recorded in CD_2Cl_2.

until the temperature of the mixture was raised to 60 °C. Then the solution became cloudy and vapours of chlorotrimethylsilane were noticed, which were evacuated under reduced pressure. Upon slow cooling, **1** deposited as a colourless crystalline material which was recovered by decantation. Its ^{31}P{^{1}H} NMR ($CDCl_3$) spectrum consisted of two signals at δ 21.6 and 31.1 (ratio 60/40). This could be explained by a tautomeric equilibrium between the acetamido and the iminol forms **1** and **1′**, respectively (Scheme 1), which is supressed in the corresponding *N*-methyl derivative (see below). The N=C bond having a deshielding effect on the nearby atoms, the ^{31}P{^{1}H} signal of **1′** is expected to occur at lower field than that of **1**. We therefore assign the signal at δ 21.6 (major tautomer) to the acetamido ligand **1**. In the ^{1}H NMR spectrum the signals due to the CH_3 protons of **1** and **1′** occurred at δ 2.13 and δ 2.30, respectively (Table 1). The ^{13}C signal of the HN–C=O moiety in **1** was observed at δ 173.31 and that of N=C–OH in **1′** at δ 174.33, the latter showing a $^2J_{PC}$ value of 13 Hz. The suggested tautomeric equilibrium **1**⇌**1′** appears solvent dependent: in CD_2Cl_2, the acetamido form **1** represents more than 75% (60% in $CDCl_3$),

whereas in acetone-d_6 the iminol form **1′** was not detected. Alternatively, the second isomer could have a structure such as **1′′** formed by rotation about the partial C–N double bond. We cannot distinguish between these two possibilities with the available data. The crystal structure of **1** has been determined by X-ray diffraction (*vide infra*). Interestingly, *N*-methylation of **1** did not occur upon treatment with KH followed by addition of MeI. Instead, the phosphorus ylide **2** was formed (Scheme 1, Table 1). Its $^{31}P\{^1H\}$ NMR spectrum consisted of a singlet at δ 19.8, whereas in the ^1H NMR spectrum two doublets at δ 2.18 ($^4J_{PH} = 3$ Hz) and 2.24 ($^2J_{PH} = 13$ Hz) were ascribed to the C(O)Me and PMe protons, respectively. In the IR spectrum the ν(CO) vibration was observed at 1672 cm^{-1}.

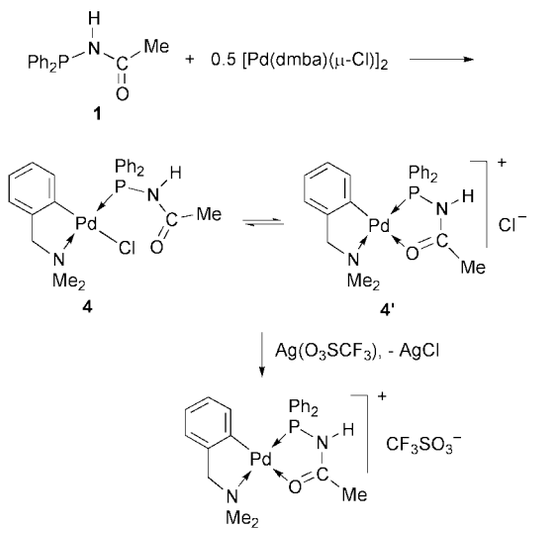
The *N*-methyl acetamido phosphine **3** could, however, be prepared from $Me_3SiN(Me)C(O)Me$ and Ph_2PCl (eqn. 1). The

3 (1)

reaction proceeded at ambient temperature in CH_2Cl_2, whereas in toluene, thermal activation was needed, which led to the formation of by-products such as $Ph_2PP(O)Ph_2$ (δ −21.4 and 35.3, $^1J_{PP} = 228$ Hz). In contrast to the case of **1**, only one species was detected in the ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** (Table 1), which would be in accord with the involvement of the NH proton in the equilibrium shown in Scheme 1.

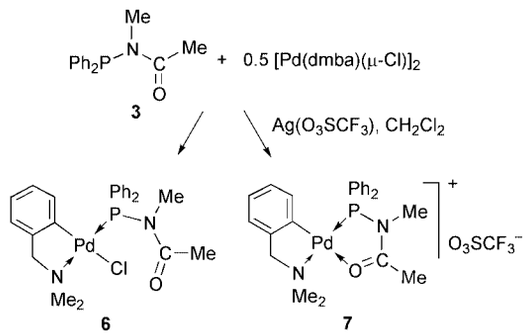
Cationic Pd complexes

Reaction of $[Pd(dmba)(\mu\text{-}Cl)]_2$ (dmba-H = *N,N*-dimethylbenzylamine) with 2 molar equiv. of **1** afforded [(dmba)PdCl{$PPh_2NHC(O)Me$}] **4** as a pale green solid. At room temperature its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) consisted of a broad signal at δ 61.8, a feature which suggested the occurence of a dynamic behaviour. Indeed, at 220 K two $^{31}P\{^1H\}$ resonances are observed at δ 79.7 and 60.7 (ratio: 45/55). The presence of two species, in this temperature range, was confirmed by ^1H NMR spectroscopy (Table 1). These observations suggest the existence in solution of an equilibrium between **4** and **4′** resulting from the hemilability of coordinated **1** (Scheme 2).



Scheme 2

Formation of the ionic species **4′** resulted from chelation of **1** and concomittant displacement of Cl^-. We assigned to this complex the $^{31}P\{^1H\}$ NMR signal at lower field (δ 79.7). Note that **4′** was not detected when the NMR spectra were run in toluene-d_8. This solvent dependence of the equilibrium **4**⇌**4′** is consistent with the ionic nature of **4′**. Addition of $Ag(O_3SCF_3)$ to a **4**/**4′** mixture led to anion metathesis and induced a shift of the equilibrium towards the cationic species which afforded [(dmba)Pd{$PPh_2NHC(O)Me$}][O_3SCF_3] **5** in quantitative yield (Scheme 2). Reaction of the more electron donating ligand **3** with $[Pd(dmba)(\mu\text{-}Cl)]_2$ gave a single product. This was evidenced by the presence of a sharp $^{31}P\{^1H\}$ NMR signal at δ 85.8 and of only one set of signals in the ^1H NMR spectrum. No additional resonances were observed upon cooling. The IR spectrum showed a ν(CO) vibration at 1672 cm^{-1}, which indicates that the amide oxygen atom is not coordinated to the Pd centre. These data are in agreement with the formation of [(dmba)PdCl{$PPh_2N(Me)C(O)Me$}] **6** in which **3** acts as a monodentate phosphine ligand (Scheme 3). For comparison, the cationic complex [(dmba)Pd{$PPh_2N(Me)C(O)Me$}][O_3SCF_3] **7** was prepared from **3**, $[Pd(dmba)(\mu\text{-}Cl)]_2$ and $Ag(O_3SCF_3)$. Its spectroscopic data are clearly different from those of **6** (Scheme 3, Table 1).

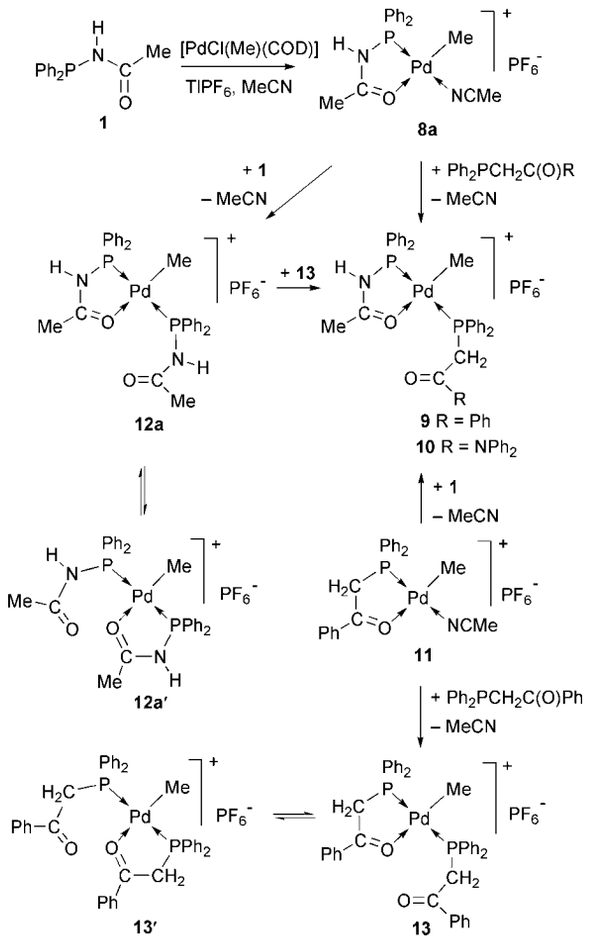


Scheme 3

The reaction of **1**, [PdCl(Me)(COD)] (COD = 1,5-cyclooctadiene) and $TlPF_6$ in acetonitrile afforded the cationic complex [PdMe{$PPh_2NHC(O)Me$}(NCMe)][PF_6] **8a** in 90% yield (Scheme 4) in which chelation of **1** to the electron deficient Pd(II) centre has occurred ($^{31}P\{^1H\}$ NMR: δ 79.8, IR (CH_2Cl_2): ν(CO) 1614 cm^{-1}). The Pd-bound methyl resides in *cis* position to the P atom, as indicated by the absence of any detectable $^3J_{PH}$ coupling (Table 1). The triflate analogue of **8a** [PdMe{$PPh_2NHC(O)Me$}(NCMe)][O_3SCF_3] **8b**, was prepared in a similar manner by use of $Ag(O_3SCF_3)$ instead of $TlPF_6$.

Treatment of **8a** with 1 molar equiv. of $Ph_2PCH_2C(O)R$ afforded almost quantitatively [PdMe{$PPh_2NHC(O)Me$}-{$PPh_2CH_2C(O)R$}][PF_6] **9** (R = Ph) and **10** (R = NPh_2) (Scheme 4). In these complexes the added *P,O* phosphine behaves as a monodentate ligand whereas **1** remains chelated to the Pd centre. Both $^{31}P\{^1H\}$ NMR spectra showed an AX pattern with a large $^2J_{PP}$ value of *ca.* 420 Hz, indicative of a *trans* arrangement of the two P nuclei with respect to the metal centre (Table 1). Complex **9** was also obtained by addition of 1 molar equiv. of **1** to [PdMe{$PPh_2CH_2C(O)Ph$}(NCMe)][PF_6] **11** (Scheme 4). The latter was prepared in a similar manner to **8a**, from [PdCl(Me)(COD)], $Ph_2PCH_2C(O)Ph$ and $TlPF_6$ in acetonitrile (see Experimental section and Table 1). However, it appeared less stable in solution than **8a** ($^{31}P\{^1H\}$ NMR monitoring).

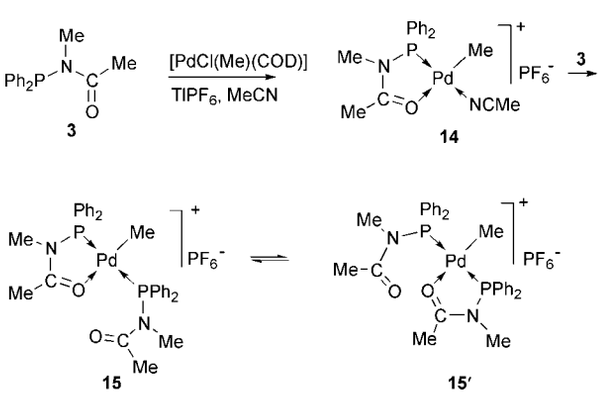
Complex **12a** was obtained by reaction of **8a** with 1 molar equiv. of **1** and showed only a broad $^{31}P\{^1H\}$ NMR signal at δ 60.2 (Scheme 4). This value is intermediate between the chemical shifts observed for **1** when it behaves as a chelate (δ *ca.* 80) or a monodentate ligand (δ *ca.* 45) in other cationic Pd(II) complexes (see below). This indicates the occurrence in solution of a fast equilibrium on the NMR time scale **12a**⇌**12a′** in which



Scheme 4

each phosphine ligand alternatively acts in a chelate or monodentate manner (Scheme 4). The ^{1}H NMR data were consistent with the proposed structure (Table 1). Low temperature NMR experiments did not slow the exchange rate sufficiently to show separate resonances. However, the fact that each phosphine ligand adopts a different coordination mode in **12a** was clearly evidenced in the solid state IR spectrum (KBr), which showed two ν(CO) vibrations at 1687 cm^{-1} (free C=O) and 1611 cm^{-1} (coordinated C=O), and was further confirmed by a crystal structure determination of the triflate salt **12b** (see below). Note that a similar hemilabile behaviour was found for the ketophosphine ligands $Ph_2PCH_2C(O)Ph$ in complex **13** which was prepared from **11** and $Ph_2PCH_2C(O)Ph$ (Scheme 4). Interestingly, when **12a** was reacted with **13** in a 1 : 1 ratio, a ligand redistribution was observed and the mixed phosphine complex **9** was formed quantitatively (Scheme 4).

Complex **14** was obtained in a similar manner to **7**, from **3**, [PdCl(Me)(COD] and $TlPF_6$ (Scheme 5). Formation of a *P*,*O* chelate around the Pd centre resulted in the occurrence of the ν(CO) vibration at 1591 cm^{-1} (1669 cm^{-1} in the case of uncoordinated **3**) and a low field ^{31}P{^{1}H} NMR resonance at δ 98.0. Addition of a second molar equiv. of **3** led to the formation of **15** in which a dynamic behaviour similar to that described above in **12a** (see **15**⇌**15′**, Scheme 5) also occurs and only a broad ^{31}P{^{1}H} NMR resonance was observed (δ 77.7).



Scheme 5

To compare the chelating ability of **1** with that of **3**, complex **8a** was reacted with 1 molar equiv. of **3**. Although the new, mixed phosphine complex **16** was obtained as the main product, formation of **12a** and **15** was also observed (Scheme 6). Spectroscopic data support the structure proposed for **16**. The ^{31}P{^{1}H} NMR spectrum showed two doublets at δ 90.7 and 49.6, whose values are characteristic for the P atom of **3** being part of a chelate ring in contrast to that of **1**, respectively. Furthermore, the large $^2J_{PP}$ value of 444 Hz indicates a mutual *trans* arrangement of these nuclei.

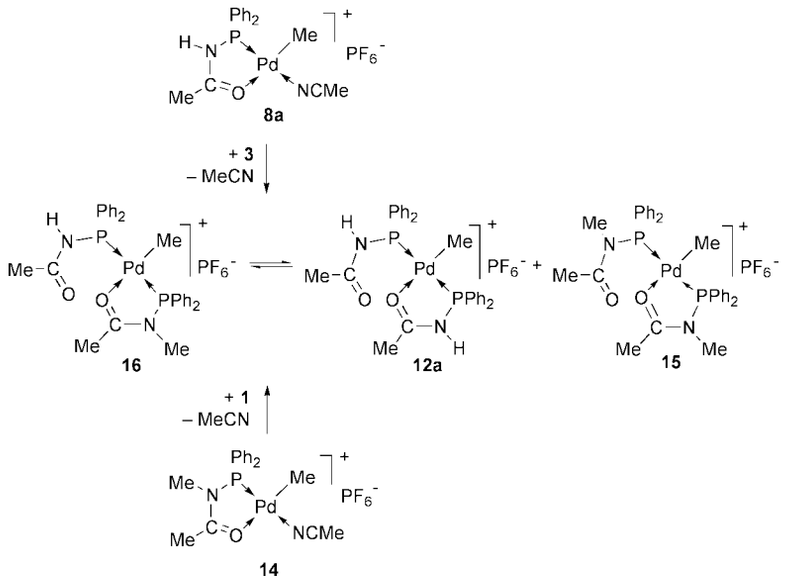
Interestingly, when complex **14** was treated with 1 molar equiv. of **1** or when stoichiometric amounts of **12a** and **15** were reacted together, the same reaction mixture as that obtained in the reaction between **8a** and **3** was obtained (Scheme 6). This suggests the rapid establishment of a thermodynamic equilibrium (Scheme 6) between **16** and **12a** and **15** and *in situ* ^{31}P{^{1}H} NMR spectroscopy gave a relative ratio of 3 : 1 : 1, respectively. Note that in the mass spectrum, the molecular peaks of **12a**, **15** and **16** were also observed, with their expected isotopic pattern.

No ligand redistribution was observed with monodentate phosphorus ligands but *cis*–*trans* isomerizations were evidenced. Thus, whereas reaction of the cation $[PdMe\{PPh_2NHC(O)Me\}(NCMe)]^+$ with PPh_3 afforded $[PdMe\{PPh_2NHC(O)Me\}(PPh_3)]^+$ (see **17**) in which the P atoms are in mutual *trans* position ($^2J_{PP}$ = 405 Hz) (Table 1), reaction with $P(OMe)_3$, $P(O^iPr)_3$ or $P(OPh)_3$ yielded an isomeric mixture, **18**–**20**, respectively, in which the *cis* isomer was always the major species (see Experimental section). This gives rise in their ^{31}P{^{1}H} NMR spectrum to two independent AX patterns with $^2J_{PP}$ values of *ca.* 45 Hz or 595 Hz for the *cis* and *trans* isomers, respectively. The ratio between the two isomers was not sensitive to the nature of the counter ion but to that of the solvent, as shown by ^{31}P{^{1}H} NMR: the *cis*/*trans* ratio varies from 90 : 10 in $CDCl_3$ to 70 : 30 in acetone-d_6 in the case of *cis*-**18a**. The existence of such isomers allowed the study of the possible influence of the *trans* ligand on the reactivity of the Pd–Me bond towards *e.g.* carbonylation.

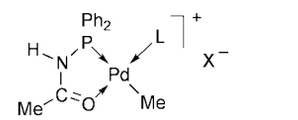
Carbonylation reactions. Carbonylation of the methyl derivatives **8a, 17, 18a** and **20a** in CH_2Cl_2 was monitored by ^{31}P{^{1}H} NMR and IR spectroscopies. In all cases, only one isomer of the acetyl derivatives is observed, in which the C(O)Me group is in the *cis* position to the P donor atom of coordinated **1**. This is established by a characteristic upfield shift of *ca.* 20 for its resonance[20] and the high value of the $^2J_{PP}$ coupling constant in **22**–**24**. Two ν_{CO} absorptions are observed, at *ca.* 1611 cm^{-1} for the coordinated amide and *ca.* 1710 cm^{-1} for the acyl ligand (see Experimental section).

Crystal structures of 1 and 12b

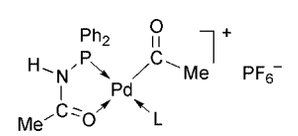
Selected bond distances and angles for **1** are given in Table 2. An ORTEP representation of two adjacent molecules of **1** is presented in Fig. 1. Bond distances and angles are within the range of those reported for related amide and phosphine derivatives. Note, however, that the P–N bond (1.728(2) Å) is longer than that found in PhP(O)(OMe)NHC(O)Ph (1.674 Å)[21] and in (MeO)P(O)(SMe)NHC(O)Me (1.641 Å)[22] and similar to that of $Ph_2P(S)NHC(O)Ph$ (1.72(1)Å).[23] The P–N–C(13) bond angle (122.3(1)°) is more obtuse than the P–C–C angle found in $Ph_2PCH_2CO_2Et$ (113.24°)[24] and $Ph_2PCH_2CO_2H$ (110.188°).[25]



Scheme 6



cis-**18a** L = $P(OMe)_3$; X = PF_6
cis-**18b** L = $P(OMe)_3$; X = O_3SCF_3
cis-**19b** L = $P(O^iPr)_3$; X = O_3SCF_3
cis-**20a** L = $P(OPh)_3$; X = PF_6
cis-**20b** L = $P(OPh)_3$; X = O_3SCF_3



21 L = NCMe
22 L = PPh_3
23 L = $P(OMe)_3$
24 L = $P(OPh)_3$

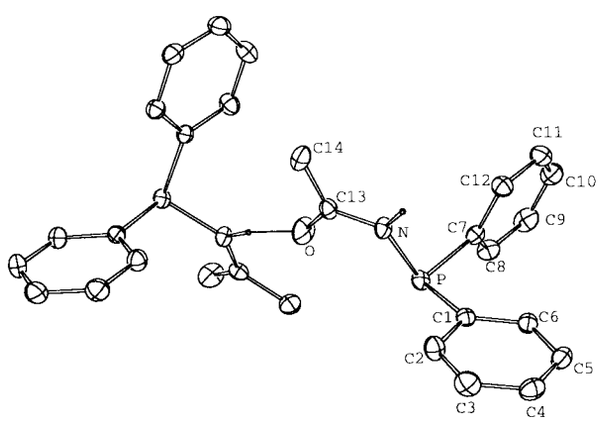


Fig. 1 View of the molecular structure of $Ph_2PNHC(O)Me$ **1** showing the dimeric unit resulting from intermolecular hydrogen bonding N–H · · · O. Hydrogen H(14) is bonded to N.

Table 2 Selected intramolecular distances (Å) and angles (°) for $Ph_2PNHC(O)Me$ **1**

P(1)–C(1)	1.836(2)	N(1)–C(13)	1.346(3)
P(1)–C(7)	1.828(2)	C(13)–O(1)	1.218(3)
P(1)–N(1)	1.728(2)		
C(1)–P(1)–C(7)	101.71(9)	P(1)–N(1)–C(13)	122.3(1)
C(1)–P(1)–N(1)	98.33(8)	N(1)–C(13)–O(1)	120.8(2)
C(7)–P(1)–N(1)	101.66(9)	N(1)–C(13)–C(14)	117.1(2)

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3 Selected intramolecular distances (Å) and angles (°) for **12b**

Pd(1)–P(1)	2.307(2)	Pd(1)–P(2)	2.265(2)
Pd(1)–O(2)	2.181(4)	Pd(1)–C(50)	2.022(7)
P(1)–N(1)	1.700(5)	P(1)–C(1)	1.810(6)
P(1)–C(7)	1.813(6)	P(2)–N(2)	1.718(5)
P(2)–C(13)	1.807(6)	P(2)–C(19)	1.808(7)
O(1)–C(31)	1.198(8)	O(2)–C(41)	1.244(7)
N(1)–C(31)	1.379(8)	N(2)–C(41)	1.353(8)
C(31)–C(32)	1.51(1)	C(41)–C(42)	1.492(9)
P(1)–Pd(1)–P(2)	178.20(6)	P(2)–N(2)–C(41)	118.3(4)
P(1)–Pd(1)–O(2)	98.0(1)	P(1)–Pd(1)–C(50)	89.0(2)
P(2)–Pd(1)–O(2)	80.5(1)	P(2)–PD(1)–C(50)	92.5(2)
O(2)–Pd(1)–C(50)	172.4(2)	Pd(1)–P(1)–N(1)	114.4(2)
Pd(1)–P(2)–N(2)	99.8(2)	Pd(1)–O(2)–C(41)	116.9(4)
P(1)–N(1)–C(31)	122.3(5)	O(1)–C(31)–N(1)	122.3(6)
O(1)–C(31)–C(32)	123.6(7)	N(1)–C(31)–C(32)	114.1(6)
O(2)–C(41)–N(2)	122.4(5)	O(2)–C(41)–C(42)	120.1(6)
N(2)–C(41)–C(42)	117.4(6)		

Estimated standard deviations in the least significant figure are given in parentheses.

The most notable feature is the fact that molecules pack to form H-bonded chains due to strong intermolecular N–H(14) · · · O=C hydrogen bonding [N · · · O 2.828 Å, H(14) · · · O 1.882 Å; N–H · · · O 173.68°]. A view along the *y* axis shows a head to tail disposition for adjacent molecules, with the P, N, C(13), O, H(14) and C(14) atoms being coplanar, thus giving the arrangement pictured in Fig. 2a. A view along the *z* axis shows the layer stacking due to hydrogen bonding (Fig. 2b).

Selected bond distances and angles for **12b** are given in Table 3. An ORTEP representation of the cation of **12b** is presented in Fig. 3. It clearly evidences the different coordination modes of the two phosphine ligands. The Pd–P bond distance of the monodentate phosphine (2.307(2) Å) is slightly longer than that of the chelate (2.265(2) Å). The bond distances within the coordinated phosphine ligands are similar to those observed for free **1**. Note that the C(41)–O(2) distance (1.244(7) Å) is slightly longer than C(31)–O(1) (1.198(8) Å) as a result of the coordination of the O(2) atom to the Pd centre. The Pd–O(2) distance of 2.181(4) Å is in the expected range for the carbonyl

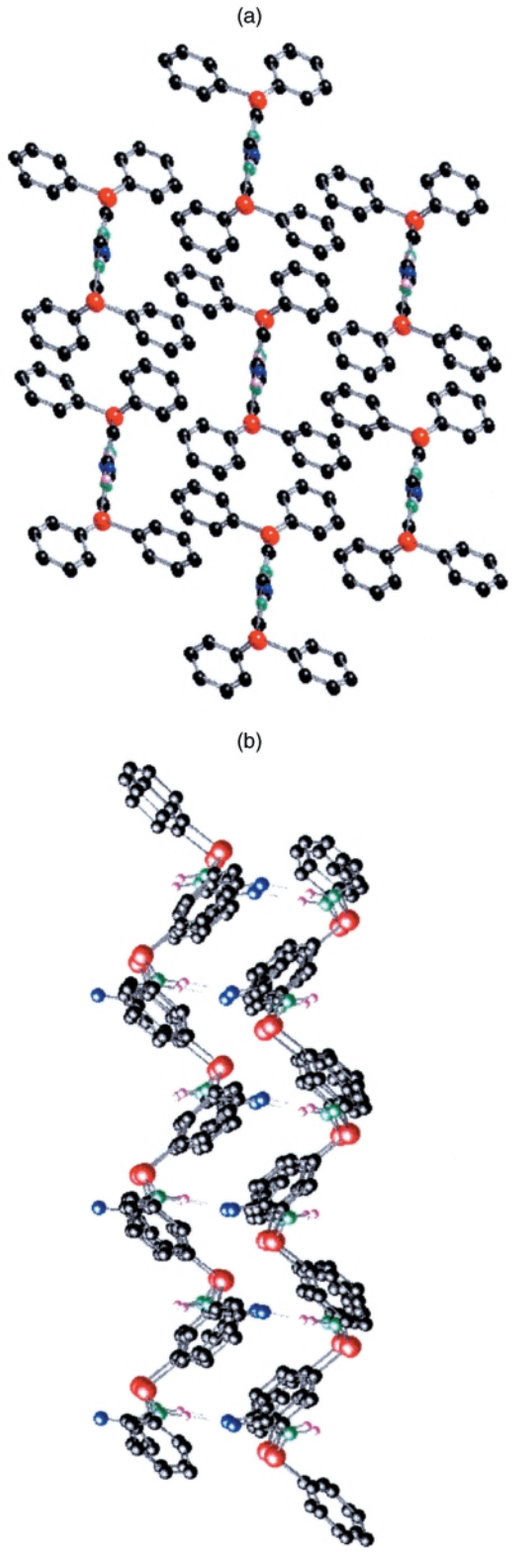


Fig. 2 Views of the packing of **1**: (a) along the *y* axis and (b) along the *z* axis. Colour code: P red, O blue, N green and H (NH) pink.

group of a *P*,*O* chelate coordinated to a Pd centre.[26–28] The latter has a square planar geometry, with a *trans* arrangement of the P atoms (P(1)–Pd–P(2) 178.20(6)°) and of the methyl group and the O atom of the chelating *P*,*O* ligand (O(2)–Pd–C(50) 172.4(2)°). As a result of the occurence of the P(2)–N(2)–C(41)–O(2)–Pd(1) five-membered ring, the P(2)–N(2)–C(41) angle (118.3(4)°) is more acute than the P(1)–N(1)–C(31) angle (122.3(5)°) and the P(1)–N(1)–C(13) angle of the free phosphine **1** (122.3(1)°). There are no other significant differences in the bond angle values between coordinated phosphines and free **1**.

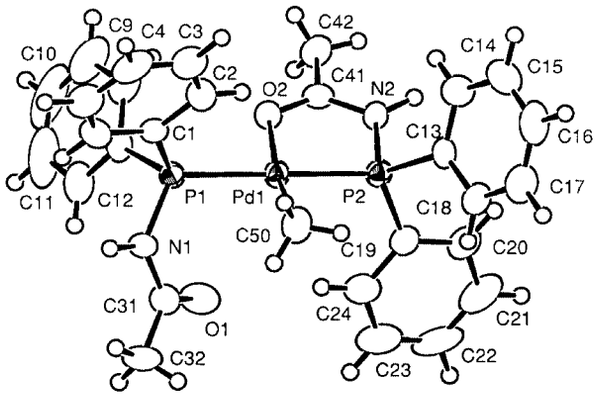


Fig. 3 View of the molecular structure of [PdMe{$PPh_2NHC(O)Me$}-{$PPh_2NHC(O)Me$}][O_3SCF_3] **12b**.

Discussion

In spite of the extensive studies carried out during the past decade on organophosphorus compounds containing a P–N bond, such as dppa and its oxidized derivatives,[29–31] the chemistry of amido derived phosphine ligands remains relatively unexplored. To the best of our knowledge, phosphine **1** represents one of the rare examples of an acetamido-derived phosphine. During the course of our work, Woollins *et al*. have reported a 34% yield synthesis of $Ph_2P(S)NHC(O)Ph$ from the benzamide phosphine $Ph_2PNHC(O)Ph$, which was not isolated but reacted *in situ* with sulfur.[23] Our synthesis of ligand **1**, from *N*-trimethylsilylacetamide and Ph_2PCl, is straightforward and almost quantitative. The driving force for the reaction is the formation of chlorotrimethylsilane. This approach is related to that described by Schmutzler *et al.* for the preparation of urea- and thiourea-derived phosphines.[32] It is interesting to note that treatment of **1** with KH and MeI only gave the phosphorus ylide derivative **2** (Scheme 1), a similar observation was reported for the alkylation of dppa ($Ph_2PNHPPh_2$).[33]

The hemilabile properties of **1** and **3** were evidenced by their dynamic behaviour in complexes **4** and **12a** and in complex **15**, respectively. Yet, the situation in **4** was quite unexpected, since it has been observed that the reaction of $[Pd(dmba)(\mu\text{-}Cl)]_2$ with *P*,*O* phosphines, such as $Ph_2PCH_2C(O)R$ (R = Ph, NPh_2, *etc.*), only gave neutral species in which the latter acted as a monodentate ligand.[30] The existence of the equilibrium between **4** and **4′** revealed a certain propensity of **1** to chelate metal centres (Scheme 2). The reaction of **3** with $[Pd(dmba)(\mu\text{-}Cl)]_2$ only produced **6**, in which the *P*,*O* ligand acts as a monodentate phosphine. This observation is quite surprising since **3** displays an increased chelating ability with respect to **1** due to *N*-methylation, as evidenced in the structure of complex **16**. Interaction between the N–H proton and Cl^- in **4′**, which cannot occur in **6**, may be invoked in order to account for the existence of the equilibrium **4**⇌**4′**. It became therefore of interest to evaluate the chelating ability of **1** by introducing in the coordination sphere of the Pd centre a second, potentially competing *P*,*O* chelate. This was achieved by substitution of the labile acetonitrile ligand in **8a** with the desired *P*,*O* phosphine. In the presence of the ketophosphine $Ph_2PCH_2C(O)Ph$, or its amido analogue $Ph_2PCH_2C(O)NPh_2$, the P–N–C–O–Pd five membered ring present in **8a** was retained and complexes **9** and **10** were obtained, respectively (Scheme 4). Furthermore, the displacement by **1** of the pre-existent *P*,*O* chelate in **11** and the ligand exchange reaction, which occurred between **12a** and **13**, confirmed the higher chelating ability of **1** than $Ph_2PCH_2C(O)Ph$. Both reactions led to **9** as a sole product (Scheme 4). It is interesting to note that the chelation of **1** or **3** in **8a** or **14**, respectively, gives rise to more stable complexes than that of $Ph_2PCH_2C(O)Ph$ in **11**.

When the two acetamido derived phosphine ligands **1** and **3** are present in the same complex, as in **16**, chelation of the *N*-methyl derivative **3** is preferred over that of **1**. It is, however, interesting to note that ligand redistribution occurs in solution since a mixture of the bis(acetamido-phosphine) complex **12a** and the bis(*N*-methylacetamido-phosphine) complex **15** is in equilibrium with **16**. It is interesting to note that these 3 species could also be identified in the solid state by mass spectroscopy.

The cationic methyl complexes **17**–**20** did not give rise to redistribution reactions between the monodentate phosphines, in contrast to the situation observed with **16** or in related work between $Ph_2PCH_2C(O)NPh_2$ and PCy_3.[34] Whereas in such Pd(II) complexes with *P*,*O* or *P*,*N* chelates the alkyl ligand tends to avoid the position *trans* to phosphorus,[35] as also observed with the PPh_3 derivative **17**, the phosphite derivatives **18**–**20** exist as a mixture of the *cis* (major) and *trans* (minor) isomers which does not appear to be dependent on the counter ion. The availability of two isomeric alkyls in the case of the phosphite derivatives suggested the study of their reactivity towards CO insertion to see whether one isomer would react preferentially. Such studies are relevant to current interest in CO/olefin coupling reactions.[36,37] We found that only one isomer is produced, which suggests that either one of the isomeric precursors has reacted faster, leading to a displacement of its equilibrium with the other isomer, or that a very fast isomerization between two isomeric acetyl derivatives leads to the observed one. Low energy processes are readily available for ligand isomerization in penta-coordinated Pd(II) intermediates. *In situ* experiments only showed the presence of one acetyl isomer throughout carbonylation. The preference for a soft carbon ligand (either alkyl or acyl) to avoid a position *trans* to phosphorus is consistent with Pearsons antisymbiotic effect.[38–40]

Experimental

All reactions were performed using Schlenk-tube techniques under dry nitrogen. Solvents were dried and distilled prior to use under nitrogen. The ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.1, 121.5 and 50.0 MHz, respectively, on a FT Bruker AC 300 instrument. Chemical shifts are positive downfield from external tetramethylsilane (TMS) for ^1H and ^{13}C, and from H_3PO_4 (85% in H_2O) for ^{31}P. IR spectra were recorded in the 4000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer. Elemental C, H and N analyses were performed by the service de microanalyse du CNRS (ULP) and at the University of Saarbrücken (Germany). Electrospray mass spectra were run on a HP 1100 series LC/MSD spectrometer.

Syntheses

The complexes [PdCl(Me)COD],[41] $[Pd(dmba)(\mu\text{-}Cl)]_2$[42] and the ligands $Ph_2PCH_2C(O)Ph$[18] and $Ph_2PCH_2C(O)NPh_2$[19] were prepared according to published procedures. Ph_2PCl, $TlPF_6$ (Strem), $MeC(O)NHSiMe_3$, $AgBF_4$ and KPF_6 (Aldrich) were purchased and used as received.

$Ph_2PNHC(O)Me$ 1. The compound $MeC(O)NHSiMe_3$ (10.893 g, 0.083 mmol) was dissolved in toluene (150 mL), Ph_2PCl (15 mL, 0.083 mmol) was added to the solution and the mixture was placed under vacuum for 30 s, before being heated to 60 °C. The mixture was placed under vacuum for 10 s every 5 min in order to eliminate $ClSiMe_3$ which was formed. After 30 min, the solution was allowed to cool to ambient temperature, during which **1** deposited as a colourless crystalline material. The solution was filtered and **1** was dried under vacuum. Suitable crystals for X-ray diffraction were obtained by allowing the reaction mixture to cool from 60 °C to room temperature by keeping the Schlenk tube in the oil bath. Then, hexane (100 mL) was added to the filtrate and the resulting mixture was placed at −20 °C for 48 h, affording a second crop of **1**. Overall yield: 16.96 g (84%). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 22.35 [s, C(O)Me], 24.18 [s, C(O)Me of **1′**], 128.43–138.19 (aromatics), 173.31 (s, C=O), 174.33 (d, N=C–OH of **1′**, $^2J_{PC}$ = 13 Hz). Calc. for $C_{14}H_{14}NOP$: C, 69.13; H, 5.80; N, 5.76. Found: C, 69.28; H, 5.92; N, 5.85%.

$(Me)Ph_2P{=}NC(O)Me$ 2. The ligand $Ph_2PNHC(O)Me$ **1** (0.395 g, 1.612 mmol) was dissolved in THF (30 mL) and KH (0.065 g, 1.612 mmol) was added at −30 °C. The solution was stirred for 1 h at this temperature before excess MeI (2 mL) was added. The mixture was allowed to warm to ambient temperature. The solution was filtered and volatiles were removed under vacuum, giving **2** as a white powder which was washed with diethyl ether (15 mL) and pentane (15 mL) and dried *in vacuo*. Yield: 0.310 g (75%). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 13.00 (d, $^1J_{PC}$ = 64 Hz, PMe), 27.45 [d, $^3J_{PC}$ = 18.4 Hz, C(O)Me], 183.52 (d, $^2J_{PC}$ = 9.7 Hz, C=O). Calc. for $C_{15}H_{16}NOP$: C, 70.03; H, 6.27; N, 5.44. Found: C, 70.04; H, 6.27; N, 5.27%.

$Ph_2PN(Me)C(O)Me$ 3. The compound $MeC(O)NMeSiMe_3$ (475 μL, 2.950 mmol) was dissolved in CH_2Cl_2 (15 mL). Pure Ph_2PCl (530 μL, 2.950 mmol) was added to the solution and the mixture was stirred for 15 min. The volatiles were removed under reduced pressure, giving **3** as a white powder which was washed with diethyl ether (15 mL) and dried *in vacuo*. Yield: 0.540 g (71%). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 23.61 (d, $^2J_{PC}$ = 64 Hz, NMe), 31.82 [d, $^3J_{PC}$ = 6.5 Hz, C(O)Me], 176.4 (d, $^2J_{PC}$ = 6.0 Hz, C=O). Calc. for $C_{15}H_{16}NOP$: C, 70.03; H, 6.27; N, 5.44. Found: C, 69.86; H, 6.38; N, 4.80%.

$[(dmba)PdCl\{PPh_2NHC(O)Me\}]$ 4. Solid **1** (0.976 g, 3.984 mmol) was added to a solution of $[Pd(dmba)(\mu\text{-}Cl)]_2$ (1.100 g, 1.991 mmol) in CH_2Cl_2 (100 mL) at ambient temperature. The mixture was stirred for 20 min. The solution was filtered and the volatiles were evaporated to leave a pale green powder, which was washed with diethyl ether (20 mL) and pentane (2 × 20 mL) and dried under vacuum. Yield: 1.856 g (90%). Calc. for $C_{23}H_{26}ClN_2OPPd$: C, 53.20; H, 5.05; N, 5.39. Found: C, 53.37; H, 5.04; N, 5.50%.

$[(dmba)Pd\{PPh_2NHC(O)Me\}][O_3SCF_3]$ 5. Complex **4** (0.160 g, 0.308 mmol) was treated with $Ag(O_3SCF_3)$ (0.079 g, 0.308 mmol) in CH_2Cl_2 (200 mL) at ambient temperature. The solution was filtered and the solvent was removed under reduced pressure. The residue was washed with pentane (10 mL) and **5** was obtained as a pale yellow-green solid. Yield: 0.179 g (92%). Calc. for $C_{24}H_{26}F_3N_2O_4PPdS$: C, 45.55; H, 4.14; N, 4.43. Found: C, 45.26; H, 4.02; N, 4.35%.

$[(dmba)PdCl\{PPh_2N(Me)C(O)Me\}]$ 6. Ligand **3** (0.058 g, 0.225 mmol) was added to a solution of $[Pd(dmba)(\mu\text{-}Cl)]_2$ (0.062 g, 0.113 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 20 min at ambient temperature. The solution was filtered and the solvent was evaporated to leave a white powder, which was washed with diethyl ether (10 mL) and pentane (10 mL) and dried under vacuum. Yield: 0.112 g (93%). Calc. for $C_{24}H_{28}ClN_2OPPd$: C, 53.95; H, 5.47; N, 5.24. Found: C, 53.86; H, 5.28; N, 5.00%.

$[(dmba)Pd\{PPh_2N(Me)C(O)Me\}][O_3SCF_3]$ 7. Complex **6** (0.160 g, 0.299 mmol) was treated with $Ag(O_3SCF_3)$ (0.077 g, 0.299 mmol) in CH_2Cl_2 (50 mL) at ambient temperature. The solution was filtered and the solvent was removed under reduced pressure. The residue was washed with pentane (10 mL) and **7** was obtained as a pale yellow-green solid. Yield: 0.170 g (88%). Calc. for $C_{25}H_{28}F_3N_2O_4PPdS$: C, 46.42; H, 4.36; N, 4.33. Found: C, 46.22 ; H, 4.34; N, 4.18%.

[PdMe{$PPh_2NHC(O)Me$}(NCMe)][PF_6] 8a. Solid [PdCl(Me)(COD)] (1.086 g, 4.098 mmol) was added to a solution of **1** (0.996 g, 4.098 mmol) in MeCN (300 mL). The mixture was stirred for 30 min, before $TlPF_6$ (1.432 g, 4.098 mmol) was added. The solution was then stirred for 30 min. The white suspension was filtered and the solvent was evaporated under vacuum to leave a beige solid which was washed with diethyl ether (15 mL) and dried *in vacuo*. Yield: 2.03 g (90%). Calc. for $C_{17}H_{20}F_6N_2OP_2Pd$: C, 37.08; H, 3.66; N, 5.09. Found: C, 36.86; H, 3.61; N, 4.83%.

[PdMe{$PPh_2NHC(O)Me$}(NCMe)][O_3SCF_3] 8b. Solid [PdCl(Me)(COD)] (0.506 g, 1.909 mmol) was added to a solution of **1** (0.468 g, 1.909 mmol) in MeCN (200 mL). The mixture was stirred for 30 min, before $Ag(O_3SCF_3)$ (0.491 g, 1.909 mmol) was added. The solution was then stirred for 30 min. The white suspension was filtered and the solvent was evaporated *in vacuo* to leave a beige solid which was washed with diethyl ether (15 mL) and dried *in vacuo*. Yield: 0.974 g (92%). Calc. for $C_{18}H_{20}F_3N_2O_4PPdS{\cdot}0.5Et_2O$: C, 40.59; H, 4.26; N, 4.73. Found: C, 40.24; H, 3.50; N, 4.36%.

[PdMe{$PPh_2NHC(O)Me$}{$PPh_2CH_2C(O)Ph$}][PF_6] 9. *Method (a).* Solid $Ph_2PCH_2C(O)Ph$ (0.033 g, 0.108 mmol) was added at ambient temperature to a solution of **8a** (0.060 g, 0.108 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 30 min. The solvent was evaporated under reduced pressure to leave a brown oil which was washed with diethyl ether (20 mL) and pentane (20 mL) and dried to give **9** as a beige powder. Yield: 0.072 g (82%). Calc. for $C_{35}H_{34}F_6NO_2P_3Pd{\cdot}0.5MeCN$: C, 51.81; H, 4.29; N, 2.52. Found: C, 51.77; H, 4.34; N, 2.55%.

Method (b). In a NMR tube were placed **11** (see below, 0.010 g, 0.016 mmol) and **1** (0.004 g, 0.016 mmol) in $CDCl_3$. The spectroscopic data obtained were identical to those of complex **9** prepared using method (a).

Method (c). In a NMR tube were placed **12a** (see below, 0.015 g, 0.020 mmol) and **13** (see below) (0.017 g, 0.020 mmol) in $CDCl_3$. The spectroscopic data obtained were similar to those of complex **9** prepared using method (a).

[PdMe{$PPh_2NHC(O)Me$}{$PPh_2CH_2C(O)NPh_2$}][PF_6] 10. In a NMR tube were placed **8a** (0.017 g, 0.031 mmol) and solid $Ph_2PCH_2C(O)Ph$ (0.012 g, 0.030 mmol) in $CDCl_3$. Complex **10** was characterized by comparison of its spectroscopic data with those of **9** (see Table 1).

[PdMe{$PPh_2CH_2C(O)Ph$}(NCMe)][PF_6] 11. Solid [PdCl(Me)(COD)] (0.385 g, 1.453 mmol) was added to a solution of $Ph_2PCH_2C(O)Ph$ (0.442 g, 1.453 mmol) in MeCN (100 mL) at ambient temperature. The mixture was stirred for 30 min, before solid $TlPF_6$ (0.507 g, 1.453 mmol) was added. The solution was then stirred for 30 min before it was filtered. The solvent was evaporated under vacuum to leave a beige solid which was washed with diethyl ether (15 mL) and dried under vacuum. Yield: 0.765 g (86%). Calc. for $C_{23}H_{23}F_6NOP_2Pd$: C, 45.16; H, 3.79; N, 2.29. Found: C, 45.44; H, 3.71; N, 2.21%.

[PdMe{$PPh_2NHC(O)Me$}{$PPh_2NHC(O)Me$}][PF_6] 12a. Solid **1** (0.051 g, 0.208 mmol) was added to a solution of **8a** (0.115 g, 0.208 mmol) in CH_2Cl_2 (15 mL) at ambient temperature. After being stirred for 30 min, the solution was filtered, and the solvent was evaporated under vacuum to leave **12a** as a yellow oil which was washed with diethyl ether (15 mL) and pentane (15 mL). Yield: 0.154 g (97%). Calc. for $C_{29}H_{31}F_6N_2O_2P_3Pd$: C, 46.26; H, 4.15; N, 3.72. Found: C, 46.07; H, 3.98; N, 3.54%.

[PdMe{$PPh_2NHC(O)Me$}{$PPh_2NHC(O)Me$}][O_3SCF_3] 12b. Solid **1** (0.073 g, 0.298 mmol) and [PdCl(Me)(COD)] (0.039 g, 0.149 mmol) were placed in a Schlenk flask and CH_2Cl_2 (10 mL) was added. The solution was stirred for 5 min before solid $Ag(O_3SCF_3)$ (0.038 g, 0.149 mmol) was added in one portion. The mixture was stirred for 30 min. After filtration, the solvent was evaporated under vacuum to leave **12b** as a pale yellow sticky material. Crystallization from CH_2Cl_2/pentane afforded yellow crystals suitable for X-ray diffraction study. Yield: 0.083 g (74%). Calc. for $C_{30}H_{31}F_3N_2O_5P_2PdS$: C, 47.60; H, 4.13; N, 3.70. Found: C, 47.61; H, 4.28; N, 3.40%.

[PdMe{$PPh_2CH_2C(O)Ph$}{$PPh_2CH_2C(O)Ph$}][PF_6] 13. Solid $Ph_2PCH_2C(O)Ph$ (0.054 g, 0.178 mmol) was added to a solution of **11** (0.110 g, 0.178 mmol) in CH_2Cl_2 (10 mL) at ambient temperature. The solution was stirred for 30 min, filtered and the solvent was evaporated under reduced pressure, affording **13** as a beige powder. It was washed with diethyl ether (20 mL) and hexane (20 mL) and dried under vacuum. Yield: 0.129 g (82%). Calc. for $C_{41}H_{37}F_6O_2P_3Pd$: C, 56.28; H, 4.26. Found: C, 56.49; H, 4.36%.

[PdMe{$PPh_2N(Me)C(O)Me$}(NCMe)][PF_6] 14. Solid [PdCl(Me)(COD)] (0.277 g, 1.045 mmol) was added to a solution of $Ph_2PN(Me)C(O)Me$ (0.268 g, 1.045 mmol) in MeCN (40 mL) at ambient temperature. The mixture was stirred for 30 min, before solid $TlPF_6$ (0.365 g, 1.045 mmol) was added. The solution was then stirred for 30 min before it was filtered. The solvent was evaporated under vacuum to leave an orange solid which was washed with diethyl ether (15 mL) and dried under vacuum. Yield: 0.530 g (90%). Calc. for $C_{18}H_{22}F_6N_2OP_2Pd$: C, 38.28; H, 3.93; N, 4.96. Found: C, 38.52; H, 4.08; N, 4.94%.

[PdMe{$PPh_2N(Me)C(O)Me$}{$PPh_2N(Me)C(O)Me$}][PF_6] 15. Solid **3** (0.050 g, 0.194 mmol) was added to a solution of **14** (0.110 g, 0.194 mmol) in CH_2Cl_2 (15 mL) at ambient temperature. After being stirred for 30 min, the solution was filtered, and the solvent was evaporated under reduced pressure, giving **15** as a yellow powder which was washed with diethyl ether (15 mL) and pentane (15 mL). Yield: 0.120 g (80%). Calc. for $C_{31}H_{35}F_6N_2O_2P_3Pd$: C, 47.68; H, 4.52; N, 3.59. Found: C, 47.83; H, 4.56; N, 2.90%.

[PdMe{$PPh_2N(Me)C(O)Me$}{$PPh_2NHC(O)Me$}][PF_6] 16. *Method (a).* Solid **3** (0.051 g, 0.198 mmol) was added to a solution of **8a** (0.110 g, 0.198 mmol) in CH_2Cl_2 (10 mL) at ambient temperature. The solution was stirred for 30 min, filtered and the solvent was evaporated under vacuum to leave a beige powder which was washed with pentane (10 mL) and dried under vacuum. Compound **16** could not be separated from **12a** and **15** which were formed in lower yields (see text). A mass spectrum of the mixture contained the molecular peaks of each complex, with the expected isotopic pattern. ES-MS: *m*/*z*: [M^+]: 635 (**15**), 623 (**16**), 607 (**12a**).

Method (b). Solid **1** (0.029 g, 0.120 mmol) was added to a solution of **14** (0.068 g, 0.120 mmol) in CH_2Cl_2 (10 mL) at ambient temperature. The solution was stirred for 30 min, filtered and the solvent was evaporated under vacuum to leave a yellow powder which was washed with pentane (10 mL) and dried under vacuum. The spectroscopic data obtained were identical to those of complex **16** prepared using method (a). The presence of **12a** and **15** was also observed, in an identical ratio to that obtained using method (a).

Method (c). Solid **12a** (0.026 g, 0.033 mmol) and **15** (0.027 g, 0.033 mmol) were mixed together in CD_2Cl_2 (2 mL) at ambient temperature. The spectroscopic data obtained were identical to those of complex **16** prepared using method (a). Compounds **12a** and **15** were also observed, in an identical ratio to that observed using method (a).

[PdMe{$PPh_2NHC(O)Me$}(PPh_3)][O_3SCF_3] 17. Solid PPh_3 (0.236 g, 0.901 mmol) was added to a solution of **8b** (0.500 g,

0.901 mmol) in CH_2Cl_2 (100 mL). After the solution was stirred for 30 min, it was filtered and the solvent was removed under reduced pressure to leave a white powder which was washed with diethyl ether (30 mL) and pentane (30 mL) and dried under vacuum. Yield 0.615 g (88%). Calc. for $C_{34}H_{32}F_3NO_4P_2SPd$: C, 52.62; H, 4.16; N, 1.80. Found: C, 52.44; H, 4.30; N, 1.85%.

[PdMe{PPh$_2$NHC(O)Me}{P(OMe)$_3$}][PF$_6$] 18a. Using a similar procedure to that detailed below for **20a**, **8a** (0.202 g, 0.367 mmol) was treated with pure $P(OMe)_3$ (43 μL, 0.367 mmol) in CH_2Cl_2 (75 mL). Complexes *cis*- and *trans*-**18a** were obtained as a brown powder in a 90:10 ratio. Yield 0.203 g (87%). Calc. for $C_{18}H_{26}F_6NO_4P_3Pd$: C, 34.12; H, 4.14; N, 2.21. Found: C, 34.37; H, 4.11; N, 2.08%.

[PdMe{PPh$_2$NHC(O)Me}{P(OMe)$_3$}][O$_3$SCF$_3$] 18b. In a similar manner, but using **8b** instead of **8a**, complexes *cis*- and *trans*-**18b** were obtained in a 90:10 ratio (80% yield). Since the spectroscopic data obtained were identical to those of *cis*- and *trans*-**18a**, no further analysis was performed.

[PdMe{PPh$_2$NHC(O)Me}{P(O^{i}Pr)$_3$}][O$_3$SCF$_3$] 19b. Pure $P(O^iPr)_3$ (71.4 μL, 0.289 mmol) was added to a solution of **8b** (0.160 g, 0.289 mmol) in CH_2Cl_2 (40 mL). After being stirred for 30 min, the solution was filtered, and the solvent was removed under vacuum to leave a white residue which was washed with diethyl ether (15 mL) and pentane (15 mL) and dried under vacuum to give a white powder. Yield 0.185 g (89%). Complexes *cis*- and *trans*-**19b** were obtained in a 85:15 ratio. Calc. for $C_{34}H_{32}F_3NO_7P_2SPd$: C, 49.56; H, 3.91; N, 1.70. Found: C, 49.51; H, 4.07; N, 1.51%.

[PdMe{PPh$_2$NHC(O)Me}{P(OPh)$_3$}][PF$_6$] 20a. Pure $P(OPh)_3$ (210 μL, 0.809 mmol) was added to a solution of **8a** (0.446 g, 0.809 mmol) in CH_2Cl_2 (100 mL). After being stirred for 30 min, the solution was filtered, and the solvent was evaporated under reduced pressure to leave a brown oil which was washed with diethyl ether (15 mL) and pentane (15 mL) and dried under vacuum to give a brown powder. Complexes *cis*- and *trans*-**20a** were obtained as a brown powder in a 60:40 ratio. Yield: 0.498 g (75%). *cis*-**20a**: IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1586s; $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 69.7 (d, 1P, NP), 109.9 [d, 1P, J_{PP} = 46 Hz, $P(OPh)_3$]. *trans*-**20a**: IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1641m; $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 71.0 (d, 1P, NP), 107.3 [d, 1P, J_{PP} = 595 Hz, $P(OPh)_3$]. Calc. for $C_{33}H_{32}F_6NO_4P_3Pd$: C, 48.34; H, 3.93; N, 1.71. Found: C, 48.54; H, 3.89; N, 1.52%.

[PdMe{PPh$_2$NHC(O)Me}{P(OPh)$_3$}][O$_3$SCF$_3$] 20b. A procedure similar to that used for **20a** starting from **8b** (0.118 g, 0.210 mmol) in CH_2Cl_2 (40 mL) and $P(OPh)_3$ (55.7 μL, 0.210 mmol) yielded *cis*- and *trans*-**20b** in a 60:40 ratio. Yield 0.129 g (75%). Calc. for $C_{34}H_{32}F_3NO_7P_2SPd$: C, 49.56; H, 3.91; N, 1.70. Found: C, 49.51; H, 4.07; N, 1.51%.

Carbonylation reactions

A solution of the appropriate monocationic methyl complex (**8a**, **17**, **18a** or **20a**) in CH_2Cl_2 (20 mL) was treated with CO at room temperature to give the acetyl complexes **21**–**24** which were characterized by spectroscopic methods.

[Pd{C(O)Me}{PPh$_2$NHC(O)Me}(NCMe)][PF$_6$] 21. IR (CH_2Cl_2, cm^{-1}):ν_{CO} = 1716s, 1618w; ^1H NMR (acetone-d_6): δ 2.27 [s, 3H, PdC(O)Me], 2.30 (s, 3H, NCMe), 2.35 [s, 3H, C(O)Me], 8.79 (s, 1H, NH); $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 58.95.

[Pd{C(O)Me}{PPh$_2$NHC(O)Me}(PPh$_3$)][PF$_6$] 22. IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1705s, 1608w; ^1H NMR ($CDCl_3$): δ 1.64 [s, 3H, PdC(O)Me], 2.35 [s, 3H, C(O)Me], 10.64 (s, 1H, NH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.2 (d, 1P, PPh_3), 52.8 (d, 1P, J_{PP} = 270 Hz, NP).

[Pd{C(O)Me}{PPh$_2$NHC(O)Me}{P(OMe)$_3$}][PF$_6$] 23. IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1712s, 1611w; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.0 (d, 1P, NP), 115.4 [d, 1P, J_{PP} = 411 Hz, $P(OMe)_3$].

[Pd{C(O)Me}{PPh$_2$NHC(O)Me}{P(OPh)$_3$}][PF$_6$] 24. IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1719s, 1613w; ^1H NMR ($CDCl_3$): δ 2.00 [s, 3H, PdC(O)Me], 2.17 [s, 3H, C(O)Me], 8.57 (s, 1H, NH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 53.9 (d, 1P, NP), 106.0 [d, 1P, J_{PP} = 392 Hz, $P(OPh)_3$].

X-Ray crystallographic analyses

The relevant data for **1** and **12b** are summarized in Table 4. For **1** all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions ($d_{C\text{-}H}$ = 0.95 Å, $B_H = 1.3B_{equiv}$ for the carbon to which it was attached), except for the NH proton which was located in the difference Fourier map and refined with a fixed isotropic B = 4 Å^2. For **12b** all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions ($d_{C\text{-}H}$ = 0.95 Å). Fig. 1 and 3 were generated using ORTEP.[43]

CCDC reference number 186/1980.

See http://www.rsc.org/suppdata/dt/b0/b002386h/ for crystallographic files in .cif format.

Table 4 Crystallographic data of $Ph_2PNHC(O)Me$ **1** and [PdMe{PPh$_2$NHC(O)Me}{PPh$_2$NHC(O)Me}][O$_3$SCF$_3$] **12b**

	1	**12b**
Formula	$C_{14}H_{14}NOP$	$C_{30}H_{31}F_3N_2O_5P_2PdS$
M	243.25	756.99
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
T/K	294	294
a/Å	8.094(1)	9.542(1)
b/Å	9.5744(5)	15.538(4)
c/Å	17.020(1)	22.717(3)
β/°	97.513(7)	92.21(1)
V/Å^3	1307.5(3)	33.65.8(9)
Z	4	4
ρ (calcd)/g cm^{-3}	1.24	1.49
Radiation, λ Mo-Kα/Å	0.71073	0.71073
μ/mm^{-1}	0.187	0.765
No. of reflcns measured	3021	4623
No. of reflcns	1725	2951
Residuals	0.042; 0.063 (R; R_w)	0.042; 0.051 (R; R_w)

Acknowledgements

We are grateful to Professor J. Fischer, Dr A. DeCian and N. Gruber (Strasbourg) for the crystal structure determination of **1**. This work was supported by the Centre National de la Recherche Scientifique and the Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche (PhD grant to CF). We are grateful to NATO (research grant CRG 920073) for financial support and to Johnson Matthey PLC for a generous loan of $PdCl_2$.

References

1 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
2 C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233.
3 W. Keim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235.
4 J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.*, 1998, **22**, 467.

5 P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2203.
6 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 1996, **15**, 5551.
7 P. Braunstein, D. Matt and D. Nobel, *J. Am. Chem. Soc.*, 1988, **110**, 3207.
8 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian and J. Fischer, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 863.
9 G. J. P. Britovsek, W. Keim, S. Mecking, D. Sainz and T. Wagner, *J. Chem. Soc.*, *Chem. Commun.*, 1993, **21**, 1632.
10 H. Werner, M. Schulz and B. Windmuller, *Organometallics*, 1995, **14**, 3659.
11 P. Braunstein, Y. Chauvin, J. Nähring, Y. Dusausoy, D. Bayeul, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 851.
12 I. Bachert, I. Bartusseck, P. Braunstein, E. Guillon, J. Rosé and G. Kickelbick, *J. Organomet. Chem.*, 1999, **588**, 144.
13 J. T. Mague, *J. Cluster Sci.*, 1995, **6**, 217.
14 P. Braunstein, R. Hasselbring, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 37.
15 P. Braunstein, R. Hasselbring, A. DeCian and J. Fischer, *Bull. Soc. Chim. Fr.*, 1995, **132**, 691.
16 P. Braunstein, J. Pietsch, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3571.
17 P. Braunstein, J. Pietsch, Y. Chauvin, A. DeCian and J. Fischer, *J. Organomet. Chem.*, 1999, **582**, 371.
18 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.
19 J. Andrieu, P. Braunstein and A. D. Burrows, *J. Chem. Res.* (*S*), 1993, 380.
20 J. H. Groen, B. J. de Jong, J.-M. Ernsting, P. W. N. M. van Leeuwen, K. Vrieze, W. J. J. Smeets and A. L. Spek, *J. Organomet. Chem.*, 1999, **573**, 3.
21 E. Breuer, A. Schlossman, M. Safadi, D. Gibson, M. Chorev and H. Leader, *J. Chem. Soc.*, *Perkin Trans. 1*, 1990, 3263.
22 V. N. Solovyov, I. V. Matynov and N. G. Zabirov, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1991, **57**, 135.
23 T. Q. Ly, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2501.
24 H. Arzoumanian, A. Baldy, R. Lai, A. Odreman, J. Metzger and M. Pierrot, *J. Organomet. Chem.*, 1985, **295**, 343.
25 L. M. Shkol'nikova, A. A. Masuyk, N. M. Dyatlova and Y. Podlaga, *Zh. Strukt. Khim.*, 1987, **28**, 156.
26 P. Braunstein, L. Douce, J. Fischer, N. C. Graig, G. Goetz-Grandmont and D. Matt, *Inorg. Chim. Acta*, 1992, **194**, 151.
27 J. Andrieu, P. Braunstein, M. Drillon, Y. Dusausoy, F. Ingold, P. Rabu, A. Tiripicchio and F. Ugozzoli, *Inorg. Chem.*, 1996, **35**, 5986.
28 P. H. Leung, S. K. Loh, J. J. Vittal, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1997, 1987.
29 M. Witt and H. W. Roesky, *Chem. Rev.*, 1994, **94**, 1163.
30 J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2893.
31 T. Q. Ly and J. D. Woollins, *Coord. Chem. Rev.*, 1998, **176**, 451.
32 R. Vogt, P. G. Jones, A. Kolbe and R. Schmutzler, *Chem. Ber.*, 1991, **124**, 2705.
33 J. Ellermann, M. Lietz and K. Geibel, *Z. Anorg. Allg. Chem.*, 1982, **492**, 122.
34 J. Andrieu, P. Braunstein, F. Naud, R. D. Adams and R. Layland, *Bull. Soc. Chim. Fr.*, 1996, **133**, 669.
35 P. Braunstein, M. D. Fryzuk, M. Le Dall, F. Naud, S. J. Rettig and F. Speiser, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1067.
36 A. Sen, *Acc. Chem. Res.*, 1993, **26**, 303.
37 E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663.
38 R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.
39 J. A. Davies and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79.
40 J. Vicente, A. Arcas, D. Bautista and P. G. Jones, *Organometallics*, 1997, **16**, 2127.
41 F. T. Lapido and G. K. Anderson, *Organometallics*, 1994, **13**, 303.
42 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.
43 M. N. Burnett and C. K. Johnson, ORTEP 3, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.