Synthesis and Single-Crystal X-ray Diffraction Studies of New Cyclometallated Phenylimidazole Palladium(II) Compounds

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Cyclometallation of 1,4,5-trimethyl-2-phenylimidazole, **L**, with $Pd(OAc)_2$ gave exclusively the dinuclear *anti* isomer with bridging acetate ligands, **1**. Subsequent treatment of **1** with sodium chloride gave the corresponding dinuclear compound with bridging chloride ligands, **2**. Treatment of **2** with mono or diphosphanes led to partial or total bridge-splitting reactions, yielding mono or polynuclear compounds, **3–9**, depending on the palladium/phosphane ratio and the nature of the phosphane. The structure of **7** has been determined by X-ray diffraction analysis. Compounds **1** and **2** react with triphos to give the mononuclear compound, **10**, in which the phosphane acts as a terdentate ligand. The crystal structure of **10** confirms the pentacoordination of the palladium(II) centre, involving a long Pd–N interaction.

Introduction

Intramolecular activation of aromatic C−H bonds of coordinated ligands by transition metals, i.e. the cyclometallation reaction, has been widely investigated.[1−7] It has proved useful in numerous applications, such as the synthesis of new organometallic and organic compounds, many of which are obtained through insertions of unsaturated species into the metal−carbon bond,[8,9] the isolation of enantiomerically pure planar chiral compounds,[10] the design of complexes with interesting photochemical and electrochemical properties,[11] and their use as efficient catalytic materials[12−14] or liquid crystals.[15,16] The most abundant examples of cyclometallated compounds are those in which the metallated carbon atom is part of a phenyl ring.[4,5,17]

Cyclometallation reactions of heterocyclic derivatives have, in contrast, been less extensively studied, although such compounds can be expected to exhibit unique properties, not shown by their phenyl analogues, in applied fields of chemistry, biology, and pharmacy.[18] In recent years, the characterization of luminescent transition metal ions coordinated to heterocyclic organic ligands has attracted great interest; these systems exhibit new properties not seen for the pure organic molecules or transition metal compounds, which show only dd* transitions.[19] Other important aspects are the design of new liquid crystals,[20,21] as well as studies on cyclometallated palladium and platinum complexes that show remarkable and specific antitumor activity toward some forms of cancer[22,23] or other interesting biological properties.[24,25]

We have been interested in cyclometallation reactions of Schiff-base ligands derived from amines, diamines, and dialdehydes[26] and we have also reported five-membered metallacycles derived from substituted imidazoles with palladium(II)[27,28] and manganese(I).[29] In the present paper, we report the synthesis and characterization of a new series of mono- and polynuclear cyclometallated compounds of palladium(II) derived from a substituted imidazole ligand in conjunction with mono- and polyphosphanes

Results and Discussion

For the convenience of the reader, the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterized by elemental analysis (C, H, N), IR spectroscopy, and mass spectrometry (data in the Experimental Section), as well as by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see Table 1).

The ligand was synthesized according to the method described by Lettau,[30] through reduction of the imidazole *N*-oxide derivative (see Scheme 1). Treatment of 1,4,5-trimethyl-2-phenylimidazole (**L**) with $Pd(OAc)_2$ in glacial acetic acid under argon at 50 °C gave the dimeric acetate-bridged *ortho*-palladated complex $[\{Pd[o\text{-}C_6H_4C{=}NC(Me){=}C(Me)NMe]\}(\mu\text{-}O_2CMe)]_2$, **1**. The FAB mass spectrum of **1** shows peaks at m/z = 701, 642, and 583 attributable to $[M^+]$, $[M^+ - OAc]$, and $[M^+ - 2OAc]$, respectively, taking into account the distribution of palladium isotopes.[31] The IR spectrum of **1** features two strong bands at 1580 cm^{-1} and 1420 cm^{-1}, attributable to the $\nu_{as}(COO)$ and $\nu_s(COO)$ stretching vibrations of the acetate ligand, respectively.[32] The methyl groups of the acetate ligands give rise to just one singlet in the ^1H NMR spectrum at $\delta = 2.13$ (Table 1), indicating that they are equivalent. This is consistent with

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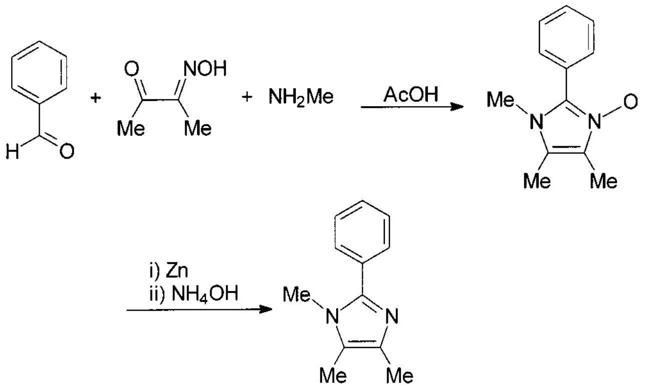
Table 1. ^{1}H and $^{31}P\{^{1}H\}$ NMR data

	δ(H2)[a]	δ(H3)	δ(H4)	δ(H5)	δ(NMe)	δ(Me)	δ(P)[b]	Others
L	7.58 dd[c] ^{3}J(H2H3) = 8.0[d] ^{4}J(H2H4) = 1.7	7.42 m	7.42 m	7.42 m	3.55 s	2.23 s 2.20 s		δ(H_6) = 7.58 dd ^{3}J(H6H5) = 8.0 ^{4}J(H6H4) = 1.7
1	6.96 d ^{3}J(H2H3) = 7.6	6.68 m	6.68 m	6.68 m	3.34 s	1.73 s 1.71 s		δ(O_2CMe) = 2.13 s
2	7.74 d ^{3}J(H2H3) = 7.8	7.08 m	7.08 m	7.08 m	3.76 s	2.13 s 2.12 s		
3[e]		6.87 td ^{3}J(H2H3) = 7.4 ^{3}J(H3H4) = 7.4 ^{4}J(H3H5) = 1.2	6.73 td ^{3}J(H4H5) = 7.4 ^{4}J(H4H2) = 1.2	6.65 m ^{4}J(PH5) = 6.5	3.83 s	2.54 s 2.18 s	43.00 s	
4[e]		6.84 t ^{3}J(H2H3) = 7.3 ^{3}J(H3H4) = 7.3	6.25 m	6.25 m	3.86 s	2.39 s 2.25 s	29.44 s	δ(C=CH_2) = 4.40 m
5[e]		6.84 t ^{3}J(H2H3) = 7.2 ^{3}J(H3H4) = 7.2	6.45 m	6.45 m	3.80 s	2.55 s 2.20 s	32.64 s	
6[e]		6.75 t ^{3}J(H2H3) = 7.3 ^{3}J(H3H4) = 7.3	6.40 m	6.40 m	3.80 s	2.54 s 2.18 s	31.64 s	δ(C_5H_5) = 4.97 b, 4.50 b
7[e]		7.12 t ^{3}J(H2H3) = 7.5 ^{3}J(H3H4) = 7.5	6.75 t ^{3}J(H4H5) = 7.5	6.90 m ^{4}J(PH5) = 9.4, 7.1	3.98 s	2.18 s 1.69 s	12.72 d −8.57 d J(PP) = 12.7	δ(C=CH_2) = 6.16 m
8[e]		7.05 t ^{3}J(H2H3) = 7.3 ^{3}J(H3H4) = 7.3	6.51 t ^{3}J(H4H5) = 7.3	6.71 m ^{4}J(PH5) = 9.3, 7.2	3.83 s	2.09 s 1.65 s	25.98 d −4.82 d J(PP) = 59.4	
9[e]		6.96 t ^{3}J(H2H3) = 7.4 ^{3}J(H3H4) = 7.4	6.45 t ^{3}J(H4H5) = 7.4	6.71 m ^{4}J(PH5) = 9.5, 7.0	3.94 s	2.08 s 1.62 s	35.70 d 8.58 d J(PP) = 42.3	δ(C_5H_5) = 4.69 m, 4.43 m
10[e]		6.78 t ^{3}J(H2H3) = 7.3 ^{3}J(H3H4) = 7.3	5.93 t ^{3}J(H4H5) = 7.3	6.26 t ^{4}J(PH5) = 7.3	3.27 s	2.02 s 1.56 s	82.56 t 41.48 d J(PP) = 28.0	

[a] ^{1}H NMR in $CDCl_3$, except for compound **2**, which was studied in [D_6]DMSO; measured at 200 MHz (ca. 20 °C), chemical shifts (δ) in ppm (±0.01) downfield from $SiMe_4$. – [b] $^{31}P\{^{1}H\}$ NMR in $CDCl_3$; measured at 81 MHz (ca. 20 °C), chemical shifts (δ) in ppm (±0.01) downfield from 85% H_3PO_4; *trans*-^{4}J(PH5) > *cis*-^{4}J(PH5); δ($P_{trans\text{-}N}$) > δ($P_{trans\text{-}C}$). – [c] s, singlet; d, doublet, dd, doublet of doublets, m, multiplet, b, broad. – [d] Coupling constants in Hz. – [e] Not assigned; obscured by the phosphane resonance.



Scheme 1

a *trans* geometry of the cyclometallated moieties in the *anti* isomer.[33–35] Some cyclopalladation reactions of substituted imidazoles lead to a mixture of the two possible geometrical isomers, *anti* and *syn*, but the reasons for this difference in behaviour are not clear.[28,36,37]

A doublet at δ = 6.96 can be assigned to the H2 proton, whilst the H3, H4, and H5 resonances appear as a multiplet centred at δ = 6.68. The shift towards lower frequency of these signals, as well as of those of the imidazole ring methyl groups, as compared with the signals of the free ligand, may be attributed to a shielding effect that arises as a result of the "open-book" configuration of the complex. The cyclometallated ligands are nearly face-to-face, similar to the situation observed in the related dimers.[38,39]

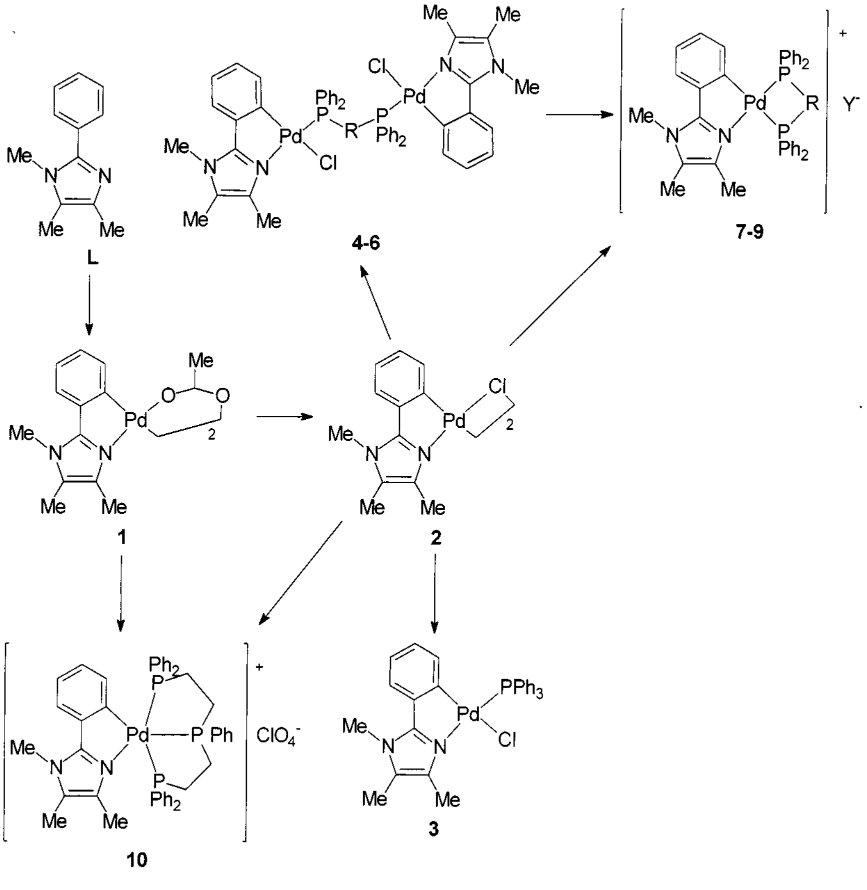
A metathesis reaction of **1** with aqueous sodium chloride afforded the chloride-bridged complex [{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe]}(μ-Cl)]$_2$, **2**. The IR spectrum of the product shows two ν(Pd–Cl) bands at 321 and 289 cm^{-1}, consistent with an asymmetric Pd_2Cl_2 bridging unit.[40] Complex **2** was found to be poorly soluble in the common organic solvents, but its full characterization by ^{1}H NMR was possible in [D_6]DMSO. The phenyl proton signals were seen to be shifted to higher frequencies as compared with the corresponding signals for compound **1**. This can be rationalized in terms of the planar arrangement in **2**, as opposed to the "open-book" geometry of **1**, in agreement with previously reported structural data.[41,42] Whereas in the free ligand the resonance of the NMe group of the imidazole ring is close to the value found in 1-methylimidazole,[43] suggesting that the imidazole and phenyl rings are mutually tilted by ca. 45°, in compound **2** the N–Me resonance is seen to be shifted to higher frequency by 0.21 ppm. This shift may be caused by the deshielding effect of the metallated phenyl ring and shows that the two rings have an almost coplanar disposition.

In view of the importance of palladium-assisted synthesis of heterocycles, some reactions of compounds **1** and **2** with unsaturated molecules were examined. Thus, **1** and **2** were treated with, e.g. phenylacetylenes, in order to ascertain the ability of the complexes to undergo insertion of organic molecules into the Pd−C bond. Unfortunately, our attempts did not meet with success and only intractable mixtures were obtained. Nevertheless, more recent results from our laboratory show that when these reactions are carried out with cyclomanganated phenylimidazole ligands, successful insertion of unsaturated organic molecules, e.g. 1-phenyl-1-propyne, into the Mn−C bond is observed with formation of a stable seven-membered ring containing the metal atom. We are currently engaged in developing this work further.

Chloride-bridge cleavage reactions were observed when $[\{Pd[o\text{-}C_6H_4C{=}NC(Me){=}C(Me)NMe]\}(\mu\text{-}Cl)]_2$ (**2**) was treated with triphenylphosphane in a 1:2 molar ratio, giving the mononuclear cyclometallated complex **3**. Likewise, treatment of **2** with the diphosphanes 1,1-bis(diphenylphosphanyl)ethene (vdpp), 1,3-bis(diphenylphosphanyl)propane (dppp), or 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) in a 1:1 molar ratio was found to give the dinuclear cyclometallated complexes **4**, **5**, and **6**, respectively (see Scheme 2). The $^{31}P\{^1H\}$ NMR spectra feature a singlet in all cases, shifted to higher frequency compared with the free phosphane, consistent with phosphorus coordination to the metal centre.[44] The δP values suggest that the phosphane is *trans* to the nitrogen atom and, in the case of the dinuclear compounds with the diphosphane acting as a bridging ligand, indicate that the two phosphorus nuclei are equivalent. The ^1H NMR spectra show the H4 and H5 proton signals shifted to lower frequencies by 0.3−0.8 ppm, as a result of the shielding effect of the phosphane phenyl rings. These signals are overlapped for compounds **4−6**, but can be clearly distinguished in the case of compound **3**. The H5 resonance shows coupling to the phosphorus atom [^4J(PH5) = 6.5 Hz], confirming the *cis* geometry of the phosphane and the metallated phenyl group.

For complexes **3−6**, the IR spectra show a band at ca. 275 cm^{-1} attributable to the ν_{as}(Pd−Cl) *trans* to the C_{phenyl} atom,[45] confirming that only a single isomer is present in each case. The FAB mass spectra show, among others, peaks attributable to [M$^+$] (**3**, **5**), [M$^+$ − CH$_2$] (**4**), and [M$^+$ − Cl] (**6**) ions, thereby confirming the dinuclear nature of these complexes (see Experimental Section). We have recently reported that complexes similar to **4** are subject to an interconversion between two conformations in solution, leading either to electrolyte species or to molecular compounds.[46,47]

Treatment of the chloride-bridged complex (**2**) with vdpp, dppp, or dppf in a 1:2 molar ratio in the presence of silver trifluoromethanesulfonate, ammonium hexafluorophosphate, or sodium perchlorate in acetone at room temperature yielded the mononuclear cyclometallated compounds **7**, **8**, and **9**, respectively. The products no longer contain Pd−Cl bonds and the diphosphane is chelated to the metal



Scheme 2

centre through the two phosphorus atoms. These compounds could also be prepared by reaction of the corresponding dinuclear species with the diphosphane in a 1:1 molar ratio in the presence of the ionic salt. The FAB mass spectra show similar fragmentation patterns, featuring peaks attributable to [M^+] and [M^+ − diphosphane] ions (see data in the Experimental Section). The conductivity data for complexes **7−9** (125−150 Ω^{-1}cm^{2}mol^{-1} in 10^{-3} mol·dm^{-3} solutions in dry acetonitrile) show that they are 1:1 electrolytes.[48]

The $^{31}P\{^1H\}$ NMR spectra feature two doublets, suggesting that the two phosphorus atoms are non-equivalent. The assignment of the doublets was made on the assumption that a ligand of greater *trans* influence shifts the resonances of the phosphorus nuclei *trans* to it to lower frequency.[44] This was confirmed by means of selective decoupling experiments (see Table 1).

The H4 and H5 resonances are shifted to lower frequency in the ^{1}H NMR spectra (*cf.* compounds **3−6**), although the signal order is reversed in this case, with the H4 signal showing the largest shift. We suggest that this is due to the different spatial shielding of the phenyl rings on the phosphorus atom *trans* to nitrogen, i.e. whether the phosphane ligand is in a bridging or a chelating mode. The H5 resonance is seen to be coupled to both phosphorus nuclei [$^4J(P_{trans\text{-}C}H)$ ca. 11 Hz, $^4J(P_{trans\text{-}N}H)$ ca. 8 Hz]. The 4-Me signal is shifted downfield by ca. 0.5 ppm due to the shielding effect of the PPh_2 groups *trans* to carbon. This is most noticeable in compounds **8** and **9** due to the larger chelate ring size. These findings were confirmed by an X-ray crystal structure determination of compound **7** (see Experimental Section).

Reaction of **1** with bis(2-diphenylphosphanylethyl)phenylphosphane (triphos) and sodium perchlorate in a 1:2 molar ratio in acetone at room temperature yielded the mononuclear complex **10** (see Scheme 2). The compound could also be obtained by treatment of **2** with triphos under similar conditions. The IR spectrum revealed an absence of bands in the range 1600−1400 cm^{-1} characteristic of COO stretching vibrations of acetate groups. The microanalytical data were consistent with the empirical formula [(L−H)Pd(triphos)][ClO_4], while the FAB mass spectrum showed the appropriate peak attributable to the [M^+] ion.

The $^{31}P\{^1H\}$ NMR spectrum shows a triplet [δ = 82.56 ppm, 1 P, $^3J(PP)$ = 28.0 Hz] and a doublet (δ = 41.48, 2 P), shifted to higher frequencies with respect to the signals of the free phosphane, in agreement with phosphorus coordination to the metal centre. The ^{1}H NMR spectrum shows that the ligand proton signals appear at lower frequencies compared to the corresponding signals in compounds **7−9**, especially those attributable to H4, H5, N−Me, and 4-Me, which are shifted by ca. 0.4−0.6 ppm. This may be rationalized in terms of the remarkable shielding effect of the phenyl rings of the phosphane. The signal attributable to H5 only shows coupling to one phosphorus nucleus [$^4J(PH5)$ = 7.3 Hz]. The crystal structure of **10** has been determined by X-ray diffraction analysis (vide infra).

Crystal and Molecular Structures of 7 and 10

Suitable crystals were grown by slowly evaporating the solvent from chloroform solutions of complexes **7** and **10**. The labelling schemes for the complexes are shown in Figures 1 and 2. Both crystals consist of discrete molecules, separated by normal van der Waals distances. Crystallographic data and selected interatomic distances and angles are listed in Table 2 and 3.

Table 2. Crystal data and structure refinement for complexes **7** and **10**

	7	**10**
Formula	$C_{40}H_{36}N_2O_3F_3P_2SCl_3Pd$	$C_{47}H_{47}N_2O_4Cl_4P_3Pd$
M_r	956.46	1044.98
Temperature (°K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal syst.	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cell dimensions		
a (Å)	12.248(1)	11.195(1)
b (Å)	14.203(1)	15.433(1)
c (Å)	22.287(1)	15.783(1)
α	114.870(1)	74.916(1)
β (°)	107.226(1)	72.017(1)
γ	90.586(1)	72.438(1)
V (Å^3)	2135.0(2)(8)	2430.5(2)
Z	2	2
μ (mm^{-1})	0.798	0.744
Crystal size (mm)	0.80 × 0.60 × 0.50	0.80 × 0.75 × 0.30
$2\theta_{max}$ (°)	52	52
Reflections:		
collected	12349	13933
unique	7938 (R_{int} = 0.060)	9054 (R_{int} = 0.087)
Transmissions	1.00, 0.57	1.00, 0.74
no. of parameters	496	561
S	1.079	1.001
R [F, $I > 2\sigma(I)$]	0.0699	0.0597
wR [F^2, all data]	0.2000	0.1981
max. Δ/σ	0.001	0.001
max. ρ (e Å^3)	1.456	0.901

Table 3. Selected bond distances (Å) and angles (°) in complexes **7** and **10**

7		**10**	
Pd(1)−C(1)	2.033(5)	Pd(1)−C(1)	2.087(4)
Pd(1)−N(1)	2.068(4)	Pd(1)−P(2)	2.2889(12)
Pd(1)−P(2)	2.2575(14)	Pd(1)−P(3)	2.3036(12)
Pd(1)−P(1)	2.3843(13)	Pd(1)−P(1)	2.3164(11)
P(1)−C(11)	1.816(6)	Pd(1)−N(2)	2.488(4)
P(2)−C(11)	1.830(5)	N(2)−C(7)	1.332(6)
C(11)−C(12)	1.308(9)	C(1)−C(6)	1.430(6)
N(1)−C(7)	1.352(7)	C(6)−C(7)	1.457(7)
C(1)−C(6)	1.383(8)		
C(6)−C(7)	1.462(9)		
C(1)−Pd(1)−N(1)	80.7(2)	P(3)−Pd(1)−P(1)	153.91(4)
C(1)−Pd(1)−P(2)	98.59(18)	P(3)−Pd(1)−N(2)	117.98(10)
P(2)−Pd(1)−P(1)	72.75(5)	P(1)−Pd(1)−N(2)	88.06(9)
N(1)−Pd(1)−P(1)	107.95(13)	C(1)−Pd(1)−P(1)	92.90(12)
C(11)−P(1)−Pd(1)	89.54(17)	C(1)−Pd(1)−P(3)	94.56(12)
C(11)−P(2)−Pd(1)	93.23(19)	C(1)−Pd(1)−N(2)	76.88(15)
P(1)−C(11)−P(2)	98.1(3)	P(2)−Pd(1)−P(1)	84.88(4)
C(6)−C(1)−Pd(1)	115.3(4)	P(2)−Pd(1)−P(3)	84.13(5)
C(7)−N(1)−Pd(1)	112.1(4)	P(2)−Pd(1)−N(2)	111.05(10)
N(1)−C(7)−C(6)	118.8(5)	C(6)−C(1)−Pd(1)	116.5(3)
C(1)−C(6)−C(7)	113.0(5)	C(7)−N(2)−Pd(1)	104.5(3)
		C(1)−C(6)−C(7)	118.0(4)
		N(2)−C(7)−C(6)	122.4(4)

In compound **7**, the palladium(II) centre is bonded to four atoms: one adjacent *ortho*-carbon and one nitrogen of the 1,4,5-trimethyl-2-phenylimidazole ligand, and two phosphorus atoms of a chelating 1,1-bis(diphenylphosphanyl)ethene in a slightly distorted square-planar coordination environment (see Figure 1). The sum of the angles about palladium is 360.03°, with the distortions more noticeable in the somewhat reduced "bite" angles enforced by the chelation. The requirements of the five- and four-membered chelate rings dictate C(1)−Pd(1)−N(1) and P(1)−Pd(1)−P(2) bond angles of 80.7(2)° and 72.75(5)°, respectively. The latter value is considerably smaller value than that of the corresponding angle in free vdpp, i.e. 118.4°.[49] The geometry about the palladium atom is almost planar; displacements from the least-squares plane formed by the metal centre and the atoms bonded to it [Pd(1), C(1), N(1), P(1), and P(2)] are as follows: Pd(1): 0.0157 Å, C(1): −0.0231 Å, N(1): 0.0127 Å, P(1): −0.0202 Å, and P(2): 0.0149 Å.

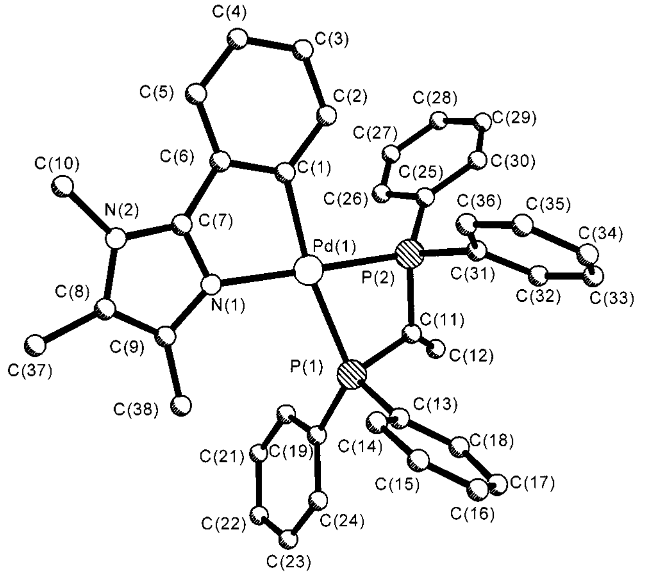


Figure 1. ORTEP projection of the [{Pd[o-$C_6H_4C{=}NC(Me){=}C(Me)NMe$]}{$Ph_2PC({=}CH_2)PPh_2$-*P,P'*}]$^+$ cation, corresponding to complex **7**

The palladium−nitrogen bond length, 2.068(4) Å, is longer than the predicted single-bond value of 2.011 Å, based on the sum of the covalent radii for sp^2 nitrogen and palladium, i.e. 0.701 and 1.31 Å, respectively,[50] reflecting the *trans* influence of the phosphorus atom.[51] The palladium−carbon bond length, 2.033(5) Å, is slightly shorter than the expected value of 2.081 Å (based on the sum of covalent radii for sp^2 carbon and palladium, i.e. 0.771 and 1.31 Å, respectively), but is longer than in related complexes for which partial multiple-bond character of the Pd−C bond has been proposed.[27,52,53] This suggests some degree of multiple-bond character in the Pd−C(aryl) linkage, and also reflects the *trans* influence of the phosphorus atom responsible for the observed lengthening. The palladium−phosphorus bond lengths are shorter than the sum of the single bond radii for the relevant atoms, 2.41 Å, suggesting some partial double-bond character, as has also been observed in some related examples.[27,54] The differing *trans* influence is clearly illustrated by the palladium−phosphorus distances *trans* to carbon, Pd(1)−P(1), and *trans* to nitrogen, Pd(1)−P(2), i.e. Pd(1)−P(1) = 2.3843(13) Å vs. Pd(1)−P(2) = 2.2575(14) Å. In complex **7**, the C(11)−C(12) bond length is 1.308(9) Å, which is within the range expected for a carbon−carbon double bond and is shorter than the value of 1.34 Å found in free vdpp.

Apart from the phenyl phosphane rings and the methyl groups, the compound is approximately planar. The mean deviations from the least-squares planes determined for the metallated phenyl ring (C1, C2, C3, C4, C5, C6; plane 1), the imidazole ring (N1, C7, N2, C8, C9; plane 2), and the metallacycle (Pd1, C1, C6, C7, N1; plane 3) are 0.0025, 0.0022, and 0.0150 Å, respectively. The angles between the planes are as follows: plane 1/plane 2: 4.2°, plane 1/plane 3: 2.0°, and plane 2/plane 3: 3.1°. The chelate phosphane ring is not planar, showing a mean deviation from the ideal plane of 0.1619 Å. The vinylidene carbon atoms, C(11) and C(12), are displaced from the plane formed by the metal centre and the phosphorus atoms [Pd(1), P(1), P(2), plane 4] by 0.5323 and 1.3178 Å, respectively. The angles between plane 4 and the other planes are: plane 1/plane 4: 1.3°, plane 2/plane 4: 5.3°, and plane 3/plane 4: 2.5°.

In compound **10**, the palladium(II) centre is bonded to four atoms: the adjacent *ortho*-carbon and three phosphorus atoms of the bis(diphenylphosphanylethyl)phenylphosphane. An additional fifth linkage results from a weak interaction between the palladium and one nitrogen of the imidazole ligand, giving an overall distorted bipyramidal-trigonal coordination (see Figure 2). The equatorial plane is formed by the palladium, the nitrogen, and the terminal phosphorus atoms of the phosphane ligand. The metallated carbon and the central phosphorus complete the coordination sphere at the apical positions. The geometry about the palladium centre is almost planar; displacements from the least-squares plane formed by Pd(1), N(2), P(1), and P(3) are as follows: Pd(1): −0.186 Å, N(2): 0.0033 Å, P(1): 0.0071 Å, and P(3): 0.0081 Å. The main distortions in this plane are seen in the widened P(3)−Pd(1)−P(1) bond angle, 153.91(4)°, and the reduced P(1)−Pd(1)−N(2) bond angle, 88.06(9)°, although the sum of the angles at the palladium in the equatorial plane is 359.95°. On coordination, the donor atoms of the chelating imidazole occupy *cis* sites with a reduced bond angle [C(1)−Pd(1)−N(2)] of 76.88(15)°.

The palladium−nitrogen bond length, 2.488(4) Å, is longer than the predicted single bond value of 2.011 Å, and is slightly longer than the Pd−N bond length of 2.23(2) Å characteristic of an authentic trigonal-bipyramidal Pd^{II} complex.[55] Nevertheless, it is much shorter than the range of values, i.e. 2.71−2.80 Å and 2.576(4) Å,[55] hitherto reported for cyclopalladated compounds in which a weak Pd···N interaction has been assumed to be present.[56−59] More recently, we have found very short Pd−N bond lengths in palladium(II) cyclometallated compounds incorporating the triphos ligand.[60] We have reasoned that this is due to a change from the more common square-

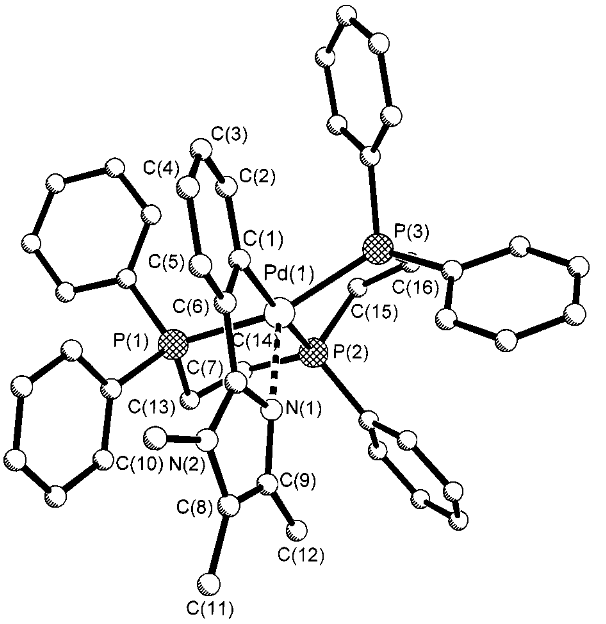


Figure 2. ORTEP projection of the [{Pd[*o*-$C_6H_4C{=}NC(Me){=}C(Me)NMe$]}{$(Ph_2PCH_2CH_2)_2PPh$-*P,P′-P′′*}]$^+$ cation, corresponding to complex **10**

planar geometry of Pd^{II} towards a trigonal-bipyramidal arrangement, which brings the nitrogen atom sufficiently close to the palladium such that a true bonding interaction may be postulated. In the light of this result, we changed the organic metallated moiety in order to verify that it was indeed mainly the triphos ligand that was responsible for this new situation in the palladium coordination sphere. Thus, bidentate Schiff-bases, azobenzenes,[61] and phenylimidazoles were used. Compound **10** represents an example of the latter type of ligand, the results for which we describe in the present paper. Thus, the data presented here seem to confirm that with triphos as a terdentate chelating ligand, unusually short Pd−N distances may be obtained, allowing a new insight into the chemistry of cyclopalladated compounds.

The Pd(1)−C(1) bond length, 2.087(4) Å, is longer than is usually found in related complexes bearing a phosphane ligand in the *trans* position. The Pd−P bond lengths, Pd(1)−P(1): 2.3164(11), Pd(1)−P(2): 2.2889(12), and Pd(1)−P(3): 2.3036(12) Å, are suggestive of slight double-bond character of the palladium−phosphorus linkages.

The cyclometallated moiety is somewhat distorted from planarity, mainly due to the imidazole ring. The mean deviations from the least-squares planes determined for the metallated phenyl ring (C1, C2, C3, C4, C5, C6; plane 1), the imidazole ring (N1, C7, N2, C11, C12; plane 2), and the metallacycle (Pd1, C1, C6, C7, N2; plane 3) amount to 0.0099, 0.0035, and 0.0471 Å, respectively. The angles between planes are as follows: plane 1/plane 2: 17.6°, plane 1/plane 3: 4.7°, and plane 2/plane 3: 15.1°. The angles between the equatorial plane formed by Pd(1), P(1), P(3), and N(2) (plane 4) are as follows: plane 1/plane 4: 83.4°, plane 2/plane 4: 90.8°, and plane 3/plane 4: 87.9°. Thus, the compound is clearly pentacoordinated, even though the imidazole ring is slightly tilted with respect to the phenyl and cyclometallated rings, and the Pd−N distance is rather long. These distortions can be rationalized taking into account the low tendency of palladium(II) to generate pentacoordinated complexes.

Experimental Section

General Remarks: All solvents were dried according to standard methods.[62] The following compounds were used as received from commercial sources: palladium(II) acetate from Strem Chemicals, diacetylmonooxime from Carlo Erba, zinc, aqueous methylamine, PPh_3, and $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp) from Acros, and silver trifluoromethanesulfonate, benzaldehyde, and $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) from Aldrich. $Ph_2PC(=CH_2)PPh_2$ (vdpp) was prepared according to procedures described elsewhere.[63] − Elemental analyses were carried out by the Servicios Generales de la Universidad de La Coruña using a Carlo Erba Model 1108 elemental analyzer. − IR spectra were recorded from samples in Nujol mulls or polythene discs on a Perkin−Elmer 1330 spectrophotometer. − NMR spectra were recorded from samples in $CDCl_3$ or [D$_6$]DMSO solutions on a Bruker AC 200F spectrometer and were referenced to internal $SiMe_4$ (^1H) or external 85% H_3PO_4 ($^{31}P\{^1H\}$). − Mass spectra were measured on a QUATRO mass spectrometer with a Cs ion-gun and NOBA or 3-NBA as the matrix.

Synthesis of 1,4,5-Trimethyl-2-phenylimidazole, $C_6H_5C{=}NC(Me){=}C(Me)NMe$ (L): Benzaldehyde (5.3 g, 0.049 mol), 40% aq. methylamine (3.87 g, 0.049 mol), and diacetylmonooxime (4.95 g, 0.049 mol) were added to glacial acetic acid (60 mL). After refluxing for 2 h, the solution was cooled, zinc (10 g, 0.152 mol) was added, and the resulting mixture was refluxed for a further 1 h and then kept overnight at room temperature. The zinc acetate formed was filtered off. Treatment of the filtrate with ammonium hydroxide resulted in the separation of a yellow oil, which was extracted with toluene (3 × 30 mL). The combined organic extracts were dried with anhydrous sodium sulfate, filtered, and then concentrated in vacuo to give a yellow solid, which was recrystallized from toluene. Yield: 55.9%. − $C_{12}H_{14}N_2$ (186.2): calcd. C 77.4, H 7.6, N 15.0; found C 77.0, H 7.4, N 15.2. − FAB-MS: *m*/*z* = 186 [M$^+$], 171 [M$^+$ − Me].

Synthesis of [{Pd[*o*-$C_6H_4C{=}NC(Me){=}C(Me)NMe$]}(μ-$O_2CMe$)]$_2$ (1): 1,4,5-Trimethyl-2-phenylimidazole (0.432 g, 2.322 mmol) and palladium(II) acetate (0.500 g, 2.228 mmol) were added to glacial acetic acid (50 mL) to give a yellow solution. After heating at 50 °C for 10 min. under argon, the solution was cooled and filtered. The collected solid was washed with glacial acetic acid and cold ethanol, and dried in vacuo. Yield: 75.1%. − $C_{28}H_{32}N_4O_4Pd_2$ (701.4): calcd. C 48.0, H 4.6, N 8.0; found C 48.3, H 4.7, N 8.0. − IR: $\tilde{\nu}$ = 1580 [s, ν_{as}(COO)], 1420 [s, ν_s(COO)]. − FAB-MS: *m*/*z* = 701 [M$^+$], 642 [M$^+$ − OAc], 583 [M$^+$ − 2AcO], 476 [(L−H)$_2$Pd$^+$], 291 [(L−H)Pd$^+$].

Synthesis of [{Pd[*o*-$C_6H_4C{=}NC(Me){=}C(Me)NMe$]}(μ-Cl)]$_2$ (2): An aqueous solution of NaCl (ca. 10^{-2} M) was added dropwise to a solution of **1** (0.252 g, 0.360 mmol) in acetone (ca. 20 mL). The resulting mixture was stirred for 4 days, after which a yellow solid had precipitated. This was filtered off, washed with water and cold acetone, and dried in vacuo. Yield: >95%. − $C_{24}H_{26}Cl_2N_4Pd_2$ (654.2): calcd. C 44.1, H 4.0, N 8.6; found C 44.2, H 3.9, N 8.5. − IR: $\tilde{\nu}$ = 321 [m, ν(Pd−Cl$_{trans\text{-}N}$)], 289 [m, ν(Pd−Cl$_{trans\text{-}C}$)].

Synthesis of [Pd{*o*-C_6H_4C=NC(Me)=C(Me)NMe}(PPh_3)(Cl)] (3): To a solution of **2** (32 mg, 0.049 mmol) in acetone (ca. 15 mL) was added PPh_3 (26 mg, 0.098 mmol). The resulting mixture was stirred for 3 h at room temperature, after which a precipitate had formed. This was filtered off, washed with cold acetone, and dried in vacuo. Yield: 74.5%. − $C_{30}H_{28}ClN_2PPd$ (589.4): calcd. C 61.1, H 4.8, N 4.7; found C 61.4, H 4.7, N 4.8. − IR: $\tilde{\nu}$ = 277 [m, ν(Pd−Cl)]. − FAB-MS: *m*/*z* = 589 [M^+], 553 [M^+ − Cl], 291 [(L−H)Pd^+].

Synthesis of [{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe]}$_2$[μ-Ph_2PC(=CH_2)PPh_2](μ-Cl)]Cl (4): To a solution of **2** (34 mg, 0.052 mmol) in acetone (ca. 15 mL) was added vdpp (20 mg, 0.052 mmol). The resulting mixture was stirred for 12 h at room temperature, after which a precipitate had formed. This was filtered off, washed with cold acetone, dried in vacuo, and recrystallized from dichloromethane/*n*-hexane. Yield: 90.9%. − $C_{50}H_{48}Cl_2N_4P_2Pd_2$ (1050.6): calcd. C 57.1, H 4.6, N 5.3; found C 57.1, H 4.6, N 5.2. − IR: $\tilde{\nu}$ = 282 [m, ν(Pd−Cl)]. − FAB-MS: *m*/*z* = 1001 [M^+ − Cl − CH_2].

Compounds **5** and **6** were similarly prepared and were isolated as solids.

[{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe](Cl)}$_2$(μ-$Ph_2PCH_2CH_2CH_2PPh_2$)] (5): Yield: 62.5%. − $C_{51}H_{52}Cl_2N_4P_2Pd_2$ (1066.6): calcd. C 57.4, H 4.9, N 5.2; found C 57.6, H 5.1, N 5.0. − IR: $\tilde{\nu}$ = 275 [m, ν(Pd−Cl)]. − FAB-MS: *m*/*z* = 1067 [M^+], 1031 [M^+ − Cl], 739 [(L−H)PdCl(PP)$^+$], 704 [(L−H)Pd(PP)$^+$], 291 [(L−H)Pd^+].

[{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe](Cl)}$_2$(μ-$Ph_2PC_5H_4FeC_5H_4PPh_2$)] (6): Yield: 78.1%. − $C_{58}H_{54}Cl_2FeN_4P_2Pd_2$ (1208.5): calcd. C 57.6, H 4.5, N 4.6; found C 57.6, H 4.3, N 4.7. − IR: $\tilde{\nu}$ = 285 [m, ν(Pd−Cl)]. − FAB-MS: *m*/*z* = 1173 [M^+ − Cl], 846 [(L−H)Pd(PP)$^+$], 291 [(L−H)Pd^+].

Synthesis of [{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe]}{Ph_2PC(=CH_2)PPh_2-*P*,*P*′}](CF_3SO_3) (7): To a solution of **2** (32 mg, 0.049 mmol) in acetone (ca. 15 mL) was added silver trifluoromethanesulfonate (25 mg, 0.098 mmol). The resulting mixture was stirred for 30 min. at room temperature, and then filtered through Celite to eliminate the silver chloride precipitate. To the filtrate was added vdpp (38 mg, 0.098 mmol) and the resulting solution was stirred for 2 days. The precipitate formed was filtered off, washed with cold acetone, dried in vacuo, and recrystallized from chloroform/*n*-hexane. Yield: 74.6%. − $C_{39}H_{35}F_3N_2O_3P_2PdS$ (837.1): calcd. C 55.9, H 4.2, N 3.3; found C 55.9, H 4.0, N 3.3.

Synthesis of [{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe]}($Ph_2PCH_2CH_2CH_2PPh_2$-*P*,*P*′)](PF_6) (8): To a solution of **2** (32 mg, 0.049 mmol) in acetone (ca. 15 mL) was added dppp (40 mg, 0.098 mmol). The mixture was stirred for 2 h at room temperature, and then an excess of ammonium hexafluorophosphate was added. The resulting mixture was stirred for 1 h, and then water was added dropwise until a precipitate formed. This was filtered off, washed with water, cold acetone, and ethanol, and dried in vacuo. Yield: 87.5%. − $C_{39}H_{41}F_6N_2P_3Pd$ (851.0): calcd. C 55.2, H 4.6, N 3.3; found C 55.5, H 4.4, N 3.2. − FAB-MS: *m*/*z* = 704 [M^+], 518 [Pd(PP)$^+$], 291 [(L−H)Pd^+].

Compound **9** was similarly prepared using dppf and sodium perchlorate as appropriate and was isolated as a solid.

[{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe]}($Ph_2PC_5H_4FeC_5H_4PPh_2$-*P*,*P*′)](ClO_4) (9): Yield: 94.8%. − $C_{46}H_{41}ClFeN_2O_4P_2Pd$ (945.5): calcd. C 58.4, H 4.4, N 3.0; found C 58.1, H 4.2, N 3.0. − FAB-MS: *m*/*z* = 846 [M^+], 660 [Pd(PP)$^+$], 291 [(L−H)Pd^+].

Synthesis of [{Pd[*o*-C_6H_4C=NC(Me)=C(Me)NMe]}{($Ph_2PCH_2CH_2$)$_2$PPh-*P*,*P*′-*P*′′}](ClO_4) (10): To a solution of **1** (27 mg, 0.038 mmol) in acetone (ca. 10 mL) was added triphos (41 mg, 0.077 mmol). The mixture was stirred for 2 h at room temperature, and then excess sodium perchlorate was added. The resulting mixture was stirred for a further 1 h and then water was added dropwise until a precipitate formed. This was filtered off, washed with water and ethanol, dried in vacuo, and recrystallized from chloroform/*n*-hexane. Yield: 84.0%. − $C_{46}H_{46}ClN_2O_4P_3Pd$ (925.6): calcd. C 60.0, H 5.0, N 3.0; found C 59.9, H 5.1, N 3.1. − FAB-MS: *m*/*z* = 826 [M^+], 640 [Pd(PP)$^+$], 291 [(L−H)Pd^+].

X-ray Crystallographic Study:[64] Three-dimensional X-ray data were collected for **7** and **10** at room temperature in the θ range 2.67 to 26.00° on a Siemens Smart CCD diffractometer by the ω-scan method. Reflections were measured from a hemisphere of data made up of frames each covering 0.3° in ω. Of the 12349 (**7**) and 13933 (**10**) reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections [minimum and maximum transmission coefficients 0.57 (**7**), 0.74 (**10**), and 1.00 (**7**, **10**)]; 7081 (**7**) and 8028 (**10**) independent reflections exceeded the significance level $|F| > 4.0\,\sigma|F|$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R_1 = 0.0699 (**7**) 0.0597 (**10**) [wR_2 = 0.2000 (**7**), 0.1981 (**10**) for all data] with allowance for thermal anisotropy of all non-hydrogen atoms. Geometrical constrains were used in the trifluoromethanesulfonate (**7**) and perchlorate (**10**) ions. The structure solution and refinement were carried out using the program package SHELX-97.[65]

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