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Cyclo-palladated aryloxazolines: preparation and carbonylation reactions. Molecular and crystal structure of di-μ-acetato-bis-[2-(4′,4′-dimethyl-2-oxazolinyl)phenyl-1-*C*,3′-*N*]dipalladium(II)

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Abstract

Aryloxazolines, with various substituents on the aromatic ring, have given dimeric cyclo-palladated complexes by reaction with palladium acetate. Steric interaction between ligands causes opening of the molecular structure, as reflected in a long Pd · · · Pd distance. This structural feature and the fluxionality in solution may be responsible for an unexpected carbonylation reaction which gave diarylketones in good yields.

Introduction

Hetero-atom directed *ortho*-metallation reactions provide the basis of numerous methods for regio-controlled introduction of substituents in aromatic compounds [1]. Among the various *ortho*-directing groups, oxazolines are especially useful in organic synthesis [2]. Thus, the reaction of butyllithium with aryloxazolines generates *ortho*-lithiated species, which react with a large variety of electrophiles. Subsequently, the oxazoline ring can be converted into ester, amide, or ketone species. However, the organolithium reagents are poorly selective towards electrophiles, and lengthy protection/deprotection sequences are sometimes needed, particularly in total syntheses [3].

Cyclo-metallation transition metal complexes of aromatic substrates which bear a nitrogen atom in a benzylic position is well established [4]. In the case of palladium

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there is a rich variety of *ortho*-metallated species that undergo useful organic transformations [5]. We report here the preparation and the reactions with carbon monoxide of a series of cyclo-palladated aryloxazolines.

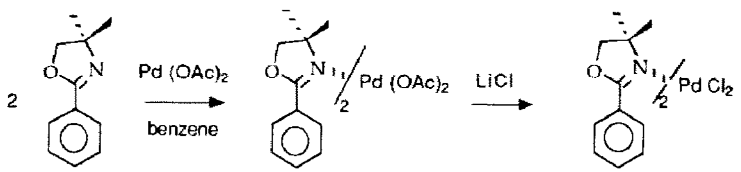
Results and discussion

The reaction of the 4,4-dimethyl-2-phenyloxazoline **1a** (Scheme 1) with palladium acetate in benzene (12 h, r.t.) gives complex **2a**. Its ^1H NMR spectrum shows the presence of ten aromatic protons and a 1/1 ligand/acetate ratio, indicating a non-metallated species. The signals from the four protons *ortho* to the heterocyclic rings are shifted downfield by 1.2 ppm from those from the parent oxazoline **1a**. The structure of **2a** was further confirmed by metathesis with lithium chloride to give the known **3a** [6]. The signals from the *ortho*-aromatic protons of **3a** are also significantly downfield shifted (by 0.8 ppm compared with **1a**). These shifts can be accounted for in terms of an agostic interaction [7] between these protons and the palladium centre, as previously suggested for related complexes [8]. Attemps for complex **2a** to undergo cyclometallation by refluxing its solutions in various solvents ($CHCl_3$, toluene, etc.) resulted only to extensive decomposition. No carbon–metal bond was formed even when the more electrophilic palladium trifluoroacetate was used.

However, the reaction of **1a** (X, Y, Z = H, Scheme 2) with one equivalent of palladium acetate as a concentrated solution in acetic acid (95 °C, 30 min) gave the cyclo-palladated complex **4a**. A single (vide-infra) product, a yellow microcrystalline solid, was isolated in 90% yield. Complex **4a** has been previously prepared (46% yield) as a 4/1 mixture of *anti*/*syn* isomers under different conditions [6].

In order to extend the scope of this reaction, a series of substituted aromatic oxazolines, **1a**–**i** (Table 1) were prepared [2] and treated with palladium acetate as before (Scheme 2). The resulting complex **4a**–**i** were isolated as yellow solids in good yields (> 80%), irrespective of the electro-donating (**4b**–**e**) or -withdrawing (**4f**–**h**) nature of the ring substituents. When formation of regio-isomers is feasible, the isomer arising from palladation at the less hindered carbon atom is always preferred. Steric hindrance around the amine group is not essential for this cyclometallation [9], since moving the *gem*-dimethyl moiety from the 4 to the 5 position of the heterocyclic ring (**1i**, Scheme 2) does not significantly change the yield (compare **4a** and **4i** in Table 1).

Several points are noteworthy. First, it can be seen that the regioselectivity of the palladation reaction can be different from that observed for the related lithiation. Thus, aryloxazoline **1e**, bearing two methoxy groups at the 3 and 4 positions of the



(1a) (2a) (3a)

Scheme 1

aromatic ring, is lithiated at the more acidic 2 position [2] but is palladated exclusively at the less hindered 6 position. Palladation of the oxazolines **1b** (2-methyl) and **1c** (2-methoxy) occurs as expected, at the 6 position, whereas the lithation of **1b** occurs at the benzylic site, and reaction of **1c** with lithio-reagents produces substituted aryloxazolines [2]. Finally, the substrates **1f** and **1g** (3- or 4-nitro) cannot be lithiated normally owing to side-reactions involving the nitro group [10].

Oxidative addition of aromatic halides to palladium(0) complexes has been shown to provide an alternative pathway to cyclo-pallated compounds [5]. Thus reaction of the bromooxazoline **1j** (Scheme 3) with one equivalent of $Pd(dba)_2$ in benzene was found to give the bromo-bridging dimer **5** in a 92% yield.

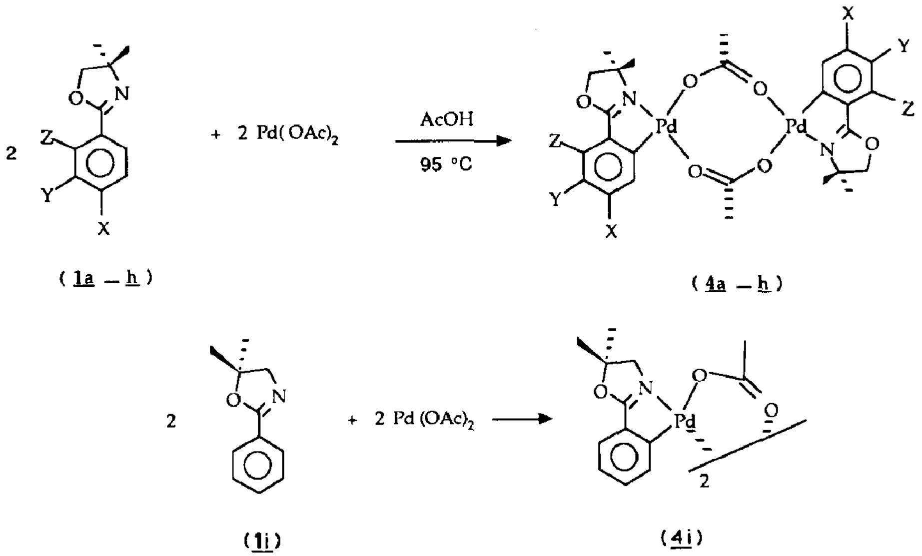
The proposed structures of the complexes **4** are in good agreement with their IR, MS, and NMR (^1H and ^{13}C) data. Relevant features are listed in Tables 1, 2 and 3.

The IR spectra of the cyclo-palladated species **4** display two strong bands, at 1570 and 1420 cm^{-1}, typical of an acetato-bridging ligand [11]. The $\nu_{asym.}$ C=N band appears between 1625 and 1615 cm^{-1}, shifted by 20 cm^{-1} towards the low frequencies relative to that for the parent oxazolines. This is an indication of a decrease in the bond-order of the carbon–nitrogen bond upon complexation [12].

The mass spectra of **4a–i** show a series of peaks corresponding to the ions $M^{+\cdot}$, $M^{+\cdot}$ – OAc, $M^{+\cdot}/2$ (monomer), $M^{+\cdot}/2$ – OAc, when account is taken of the distribution of palladium isotopes.

NMR spectroscopy

The ^1H NMR data for complexes **4a–i** are shown in Table 2. For these species stereo-isomerism is possible (Fig. 1), involving *anti*(A) and *syn*(B) isomers. In every case, however, there is only one sharp singlet attributable to the acetato-ligands, ruling out the presence of the *syn* isomer(B), in which the two acetato-groups are non-equivalent. Consequently, the *anti*-geometry is assigned to all the complexes **4a–i**. This was confirmed by a crystal structure determination in the case of **4a** (vide-infra).



Scheme 2

Table 1

Analytical data for complexes **4a–i**

	X	Y	Z	Yield (%)	M.p. [a] (°C)	Elemental analysis (Found (calcd.)(%))				
						C	H	N	O	Other
4a	H	H	H	90	> 260	45.97 (45.97)	4.51 (4.45)	4.03 (4.12)	14.20 (14.12)	–
4b	H	H	CH_3	96	218	47.70 (47.54)	4.92 (4.84)	4.04 (3.96)	13.48 (13.54)	–
4c	H	H	OCH_3	94	210	45.54 (45.48)	4.48 (4.63)	3.78 (3.79)	17.50 (17.31)	–
4d	OCH_3	H	H	88	> 260	45.60 (45.48)	4.69 (4.63)	4.02 (3.79)	17.26 (17.31)	–
4e	OCH_3	OCH_3	H	87	235	45.07 (44.90)	4.79 (4.79)	3.50 (3.68)	20.01 (19.81)	–
4f	NO_2	H	H	95	> 260	40.20 (40.59)	3.65 (3.67)	7.18 (7.28)	21.01 (20.80)	–
4g	H	NO_2	H	98	> 260	40.39 (40.59)	3.59 (3.67)	7.31 (7.28)	20.57 (20.80)	–
4h	Cl	H	H	82	> 260	41.64 (41.74)	3.68 (3.77)	3.96 (3.74)	12.67 (12.83)	Cl 9.58 (9.48)
4i [b]	H	H	H	96	> 260	45.73 (45.93)	4.39 (4.45)	4.19 (4.12)	14.29 (14.12)	–

[a] With decomposition. [b] 5,5-Dimethyl isomer.

The signals from the protons of the aromatic ring are shifted towards higher field upon cyclo-palladation, the magnitude of the shifts being related to the proximity of the proton to the metallic center [12]. Analysis of the aromatic part of the spectra allowed an unambiguous assigment for all signals (Table 2), and throw light on the regioselectivity of the palladation reaction.

The temperature dependence of ^1H NMR (250 MHz) spectra of **4a–i** reveals fluxional behaviour. Thus, at 25 °C the oxazoline ring pattern appears as two broad singlets near 0.8 ppm (6H) and 1.4 ppm (6H) for the *gem*-dimethyl groups and the AB system (4.1 ppm: d, 8 Hz, 2H; 4.3 ppm: d, 8 Hz, 2H) assigned to the methylene moieties. A variable temperature experiment (for **4a**) indicates that there is exchange, with a coalescence temperature of 323 K (at 60 MHz) for the *gem*-methyl groups. Estimation of the activation barrier for this process, $\Delta G^{\star} = 15.1 \pm 0.8$ kcal/mol, was calculated from the Eyring equation. Exchange was further confirmed by a Soft Pulse Transfer experiment (200 MHz) [13]. On the assumption that

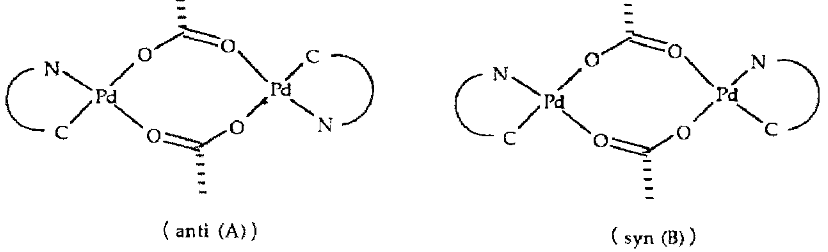
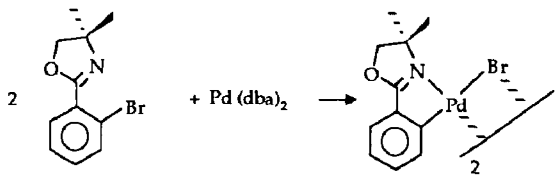


Fig. 1.



(1j) (5)

dba = dibenzylideneacetone

Scheme 3

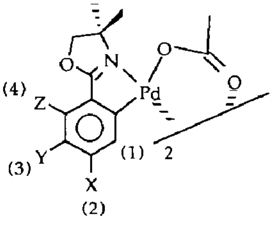
the transverse relaxation times for the protons of the two methyl groups involved in the exchange are identical, an average life time, $t = 0.11$ s, was derived, corresponding to a Gibbs Free Energy, $\Delta G^{\star}$, of 15.9 ± 0.5 kcal/mol at 298 K. Analysis of the variation of the constant $k_{\text{inv.}}$ with temperature [17], gave the following values for the activation parameters of this dynamic process: $\Delta H^{\star} = 5.7 \pm 1.1$ kcal/mol and $\Delta S^{\star} = -33 \pm 4$ cal K^{-1} mol^{-1}. This dynamic process is observed for all the complexes **4a–i** (Table 2).

A single-crystal X-ray structure determination was carried out for **4a**. The molecular structure is depicted in Fig. 2. The non-equivalence of the methyl groups

(continued on p. 266)

Table 2

^{1}H NMR spectra of complexes **4a–i** ($CDCl_3$, 250 MHz, 25 °C)



(4)

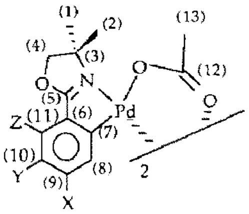
	Aromatic proton signals				
	H(1)	H(2)	H(3)	H(4)	Substituent
4a	6.98(m) [a]	7.03(m)	7.03(m)	7.10(m)	–
4b	6.75(m)	6.90(m)	6.90(m)	–	2.35(s)
4c	6.53(d,8 Hz)	6.66(d,8 Hz)	6.95(t,8 Hz)	–	3.85(s)
4d	6.50(d,8 Hz)	–	6.55(d,2 Hz)	7.02(dd,8/2 Hz)	3.75(s)
4e	6.60(s)	–	–	6.70(s)	3.77(s),3.85(s)
4f	7.27(d,8 Hz)	–	7.83(d,2 Hz)	7.88(dd,8/2 Hz)	–
4g	7.24(d,8 Hz)	7.90(dd,8/2 Hz)	–	7.96(d,2 Hz)	–
4h	6.93 to 7.05(m)	6.93 to 7.05(m)	–	6.93 to 7.05(m)	–
4i	6.97 to 7.15(m)	6.97 to 7.15(m)	6.97 to 7.15(m)	6.97 to 7.15(m)	–

Oxazoline rings pattern:
4a to **4h**: 0.78...0.95 ppm (s,6H); 1.40...1.50 ppm (s,6H); 4.03...4.18 ppm (d,8 Hz,2H) 4.22...4.43 ppm (d,8 Hz,2H); **4i**: 0.75 ppm (s,6H); 1.20 ppm (s,6H); 2.75 (d,8 Hz,2H);3.37 (d,8 Hz,2H)
Acetate ligand: 2.12...2.25 ppm (s,6H)

[a] Chemical shift in ppm (ref. TMS).

Table 3

^{13}C NMR data for complexes **4** ($CDCl_3$, 64.9 MHz, δ ppm/TMS) [a]



(**4**)

	C(1)/C(2)	C(3)	C(4)	C(5)	C(7)	C(12)	C(13)	Others carbons
4a	27.16	81.14	64.84	172.34	146.25	181.14	24.50	123.43, 124.64, 129.36, 134.13, 132.32
4b	27.24	81.00	64.07	173.51	147.96	180.98	24.60	18.94, 126.40, 129.04, 129.33, 129.85, 136.73
4c	27.15	81.20	63.80	172.10	149.00	180.90	24.50	55.30, 106.40, 125.10 128.80, 130.40, 155.90
4d	27.70	81.00	64.50	172.10	148.20	181.10	24.50	54.90, 109.60, 116.90, 125.70, 125.80, 159,70
4e	27.20	80.90	64.40	172.20	148.96	180.80	24.10	55.30, 55.70, 107.10, 114.00, 122.00, 132.90
4h	27.02/27.67	81.33	65.14	172.13	147.29	181.72	24.56	123.88, 125.75, 129.64, 132.20, 135.50
4i	26.25/27.20	88.80	61.08	173.28	147.25	181.04	24.09	123.66, 125.18, 130.35, 131.30, 131.59

[a] Complexes **4f** and **4g** are too insoluble to allow recording of ^{13}C NMR data.

Table 4

Crystal data and details of data collection

Formula	$C_{26}H_{30}N_2O_6Pd_2$
F_w	679.34
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	12.932(2)
b (Å)	16.372(2)
c (Å)	24.761(5)
V (Å^3)	5245.6
Z	8
ρ_{calc} (g/cm^3)	1.72
$F(000)$	2720
Crystal dimensions (mm)	0.15 × 0.13 × 0.12
Radiation	Mo-K_α
Linear abs coef (cm^{-1})	13.94
Scan type	$\omega-2\theta$
Scan speed (deg/min)	variable
2θ limits (deg)	2–50
Reflections collected	5063
Unique reflections used	3455 ($I > 3\sigma(I)$)
$R = \Sigma(\lvert F_o \rvert - \lvert F_c \rvert)/\Sigma \lvert F_o \rvert$	0.026
$R_\omega = \{\Sigma\omega(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma\omega F_o^2\}^{1/2}$	0.044
$GOF = \{\Sigma\omega(\lvert F_o \rvert - \lvert F_c \rvert)^2/(N_o - N_p)\}^{1/2}$	1.135

Table 5

Positional parameters and equivalent temperature factors, with their e.s.d.'s in parentheses

Atom	x	y	z	B (Å^2) [a]
Pd(1)	0.01986(2)	0.19803(2)	0.67203(1)	2.450(6)
Pd(2)	−0.11718(2)	0.20411(2)	0.56648(1)	2.521(6)
O(1)	0.0358(2)	0.3169(2)	0.6386(1)	3.33(6)
O(2)	−0.1187(2)	0.2286(2)	0.7066(1)	3.30(6)
O(3)	0.2751(2)	0.0561(2)	0.6495(1)	3.95(6)
O(4)	−0.0394(2)	0.3128(2)	0.5570(1)	3.32(6)
O(5)	−0.2073(2)	0.2538(2)	0.6305(1)	3.53(6)
O(6)	−0.2196(2)	−0.0163(2)	0.5128(1)	4.12(6)
N(1)	0.1614(2)	0.1592(2)	0.6475(1)	2.86(6)
N(2)	−0.1920(2)	0.0953(2)	0.5626(1)	3.00(6)
C(1)	0.0224(3)	0.0907(2)	0.7078(2)	2.82(7)
C(2)	−0.0516(3)	0.0568(3)	0.7425(2)	3.59(9)
C(3)	−0.0390(4)	−0.0203(3)	0.7628(2)	4.2(1)
C(4)	0.0487(4)	−0.0668(3)	0.7507(2)	4.3(1)
C(5)	0.1244(3)	−0.0340(3)	0.7159(2)	3.82(9)
C(6)	0.1104(3)	0.0440(2)	0.6977(2)	2.91(8)
C(7)	0.1834(3)	0.0872(2)	0.6639(2)	2.85(7)
C(8)	0.3251(3)	0.1193(3)	0.6175(2)	5.0(1)
C(9)	0.2490(3)	0.1913(2)	0.6147(2)	3.15(8)
C(10)	0.2147(4)	0.2076(3)	0.5577(2)	4.1(1)
C(11)	0.2932(3)	0.2678(3)	0.6402(2)	4.7(1)
C(12)	0.0159(3)	0.3447(2)	0.5932(2)	3.02(8)
C(13)	0.0679(4)	0.4250(3)	0.5784(2)	4.4(1)
C(14)	−0.1972(3)	0.2528(2)	0.6806(2)	3.05(8)
C(15)	−0.2867(3)	0.2833(3)	0.7136(2)	4.6(1)
C(16)	−0.0541(3)	0.1615(2)	0.4999(2)	2.68(7)
C(17)	0.0173(3)	0.1990(2)	0.4671(2)	3.23(8)
C(18)	0.0515(4)	0.1598(3)	0.4199(2)	3.93(9)
C(19)	0.0123(3)	0.0853(3)	0.4046(2)	4.2(1)
C(20)	−0.0592(4)	0.0458(3)	0.4369(2)	3.87(9)
C(21)	−0.0920(3)	0.0841(2)	0.4835(2)	3.00(8)
C(22)	−0.1684(3)	0.0568(2)	0.5208(2)	3.11(8)
C(23)	−0.2843(3)	−0.0272(3)	0.5599(2)	4.5(1)
C(24)	−0.2783(3)	0.0539(2)	0.5917(2)	3.45(8)
C(25)	−0.3745(4)	0.1061(3)	0.5853(3)	5.4(1)
C(26)	−0.2536(4)	0.0402(3)	0.6496(2)	4.9(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma + B_{13}ac\cos\beta + B_{23}bc\cos\alpha)$.

Table 6

Selected interatomic distances (Å) and angles (°).

Pd(1)–O(1)	2.125(3)	Pd(2)–O(5)	2.130(3)
Pd(1)–O(2)	2.049(3)	Pd(2)–O(4)	2.058(3)
Pd(1)–N(1)	2.032(3)	Pd(2)–N(2)	2.030(3)
Pd(1)–C(1)	1.967(4)	Pd(2)–C(16)	1.967(4)
O(1)–Pd(1)–O(2)	91.4(1)	O(4)–Pd(2)–O(5)	91.3(1)
O(1)–Pd(1)–N(1)	94.7(1)	O(5)–Pd(2)–N(2)	96.3(1)
O(1)–Pd(1)–C(1)	172.5(1)	O(5)–Pd(2)–C(16)	170.6(1)
O(2)–Pd(1)–N(1)	172.0(1)	O(4)–Pd(2)–N(2)	170.6(1)
O(2)–Pd(1)–C(1)	92.6(1)	O(4)–Pd(2)–C(16)	90.5(1)
N(1)–Pd(1)–C(1)	80.8(1)	N(2)–Pd(2)–C(16)	81.1(1)

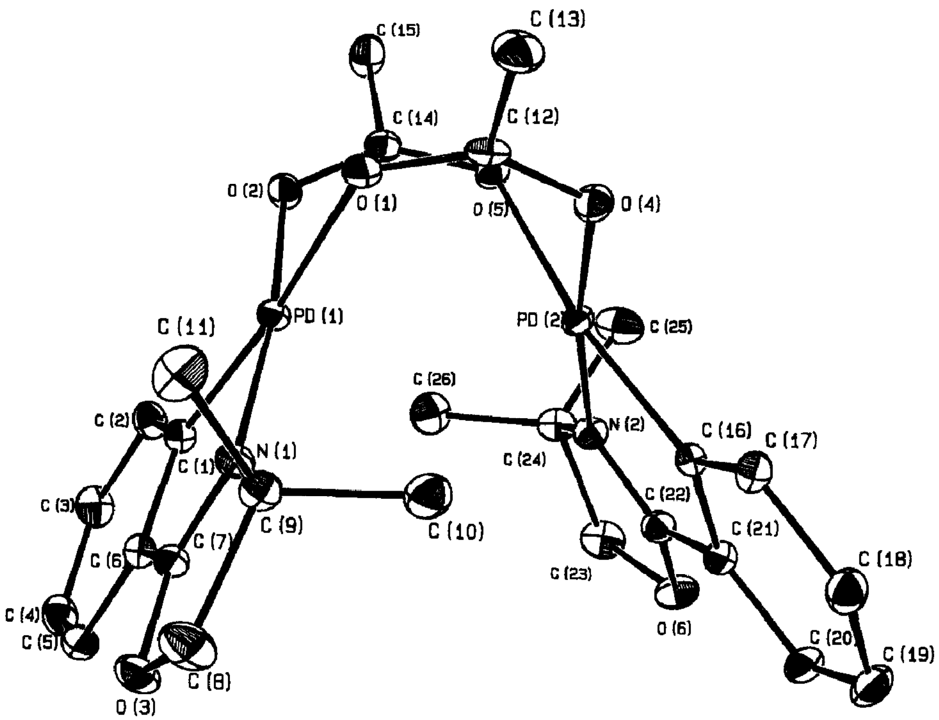


Fig. 2.

of each heterocycle (as well as the methylene protons) is clearly revealed. The dimeric complex presents an "open book" type of structure [14]. One methyl group of each oxazoline cycle is directed inwards and the other outwards, and so the molecule lacks symmetry elements other than a C_2 axis and is therefore chiral. The exchange between diastereotopic protons on the ^1H NMR time scale is associated with an interconversion between the two enantiomeric forms of the complex **4a**. A similar process has been reported by Powell [15] for complexes of the type $[(Me_2PhP)ClPd(OCOCH_3)]$, and by Deeming [16] and Ryabov [17] for cyclo-palla-

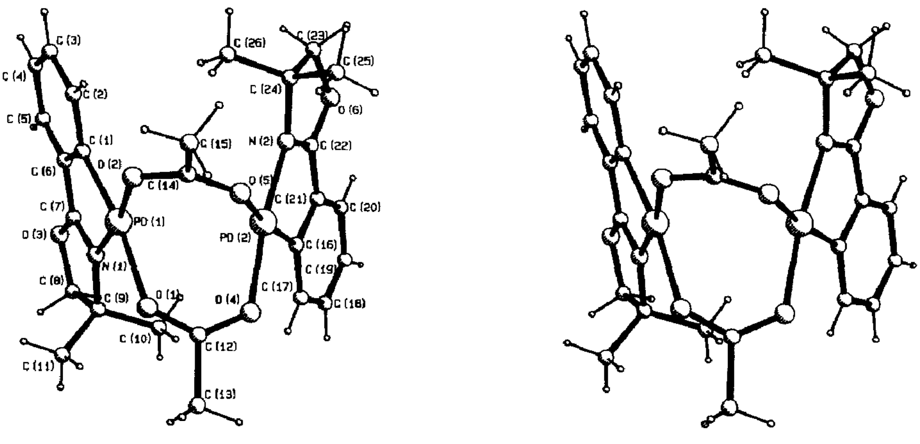


Fig. 3.

Table 7

Least-squares planes with distances (Å × 10^3) of atoms from the means plane in parentheses

Atoms defining planes					*Equation of plane expressed as* A × X + B × Y + C × Z + D = 0			
1 Pd(1)(78)	O(1)(−31)	O(2)(−9)	N(1)(−6)	C(1)(−33)	−0.4436	−0.3581	−0.8216	−15.0249
2 Pd(2)(−100)	O(4)(−12)	O(5)(60)	N(2)(−15)	C(16)(67)	−0.7048	0.3680	−0.6064	−6.1077
3 Pd(1)(85)	Pd(2)(−85)	O(1)(+120)	O(4)(−120)		0.7835	−0.3926	−0.4817	−9.1716
4 Pd(1)(86)	Pd(2)(−85)	O(2)(−121)	O(5)(120)		0.3209	0.9399	−0.1166	1.1043

Dihedral angles between the planes (°)

Plane	Angle	Plane	Angle
1–2	47.2(1)	3–4	93.5(1)

dated complexes; from the magnitude of $\Delta S^{\star}$, -21 cal K^{-1} mol^{-1}, a mechanism involving a partial rupture of the acetate bridge was suggested [17]. The value of $\Delta S^{\star}$ derived for **4a** (-33 ± 4 cal K^{-1} mol^{-1}) is not very different suggesting that the same mechanism operates.

Relevant data on the complexes **4a**–**i** ^{13}C NMR spectra are listed in Table 3. The signals from the palladated carbon atoms (C-7) always appear between 145 and 150 ppm, corresponding to a 20–30 ppm downfield shift from the signal form the parent oxazolines. The carbon atoms C(1) and C(2) (*gem*-dimethyl groups) give only one signal in all cases exept **4b**,**i**, implying that the dynamic process is rapid on the ^{13}C NMR time scale.

Crystal sructure of ***4a***

The molecular structure of **4a** is depicted in an ORTEP diagram in Fig. 2), which also shows the atom numbering. The estimated bond lengths and angles and their estimated standard deviations are listed in Table 6. Several mean planes have been calculated and the dihedral angles and the distances of relevant atoms from these place are listed in Table 7. A stereoscopic view of **4a** is presented in Fig. 3.

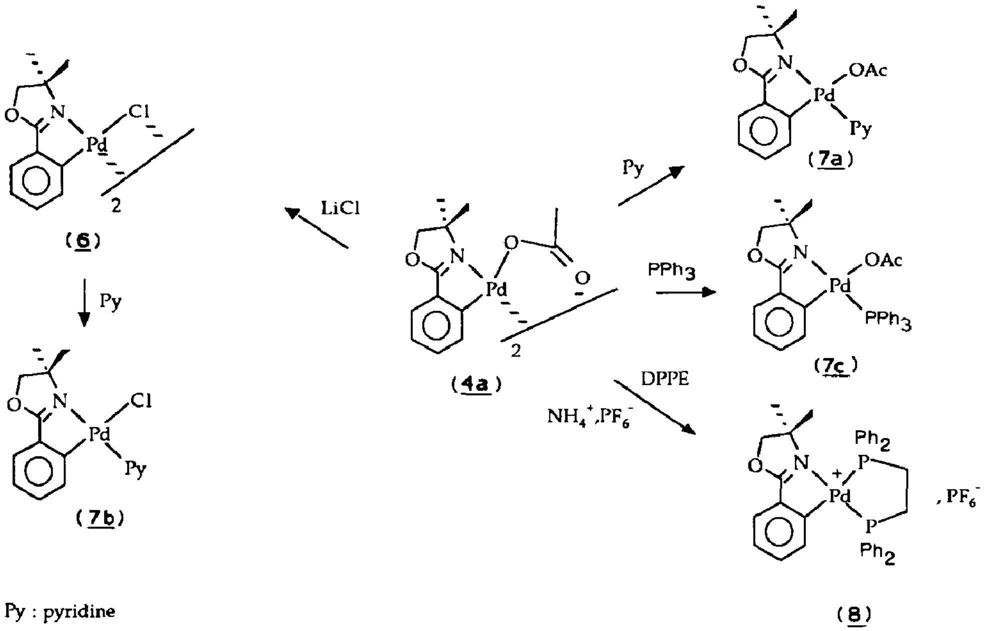
The overall molecular geometry of complex **4a** is closely related to that of other *cis*-bis(μ-carboxylato)dipalladium complexes [18–20]. The dimeric molecule possesses an approximate C_2 symmetry axis (non-crystallographic). As a result of Pd(1) and Pd(2) being bridged by two mutually *cis*-μ-acetato ligands, the chelating *N*,*C*-bonded 2-phenyloxazoline ligands are forced to lie above one another in the dimeric molecules. This brings interligand repulsions between the aromatic rings and the two methyl groups pointing inside the molecular structure which results in the coordination planes of the palladium atoms * being tilted at an angle of 47.2(1)°. This is significantly larger than the tilt angles [18] reported for the related benzoxazole (23.96°) and benzothiazole (24.46°) cyclopalladated complexes. As a consequence, the non-bonding distance Pd(1)–Pd(2) is 3.160 Å, and falls outside the range (2.84 to 2.96 Å) observed for related complexes [18,19]. We note, however, that a large Pd $\cdots$ Pd distance (3.413(1) Å) and tilt angle (48°) have been reported by Gainsford [20] for the bulky cyclo-palladated phosphine [PdOAc{CH_2-C_6H_4-P-^{t}Bu(*o*-tolyl)}]$_2$.

The coordination geometry around each palladium atom is approximately square-planar. The deviations of the palladium atoms from the coordination planes (nitrogen atom, carbon atom *ortho* to the heterocycle, one oxygen atom of each acetato ligand) are 0.098 Å (Pd(1)) and 0.125 Å (Pd(2)). The C(1)–Pd(1) and Pd(2)–C(16) distances (1.967(4) Å) are slightly shorter than would be expected for a covalent Pd–C(sp_2) bond (2.05 Å) [21], indicating a significant degree of the metal to ligand back-bonding. The *trans*-lengthening influence of a σ-bonded carbon is illustrated by the lengthening of the palladium oxygen distances *trans* to carbon (2.125(3) Å for Pd(1); 2.130(3) Å for Pd(2)) relative to those *trans* to nitrogen atoms (Pd(1): 2.049(3) Å; Pd(2): 2.058(3) Å).

Reactivity

Metathesis of the complex **4a** with lithium chloride in acetone allowed isolation of the chloro-bridging complex **6** in a nearly quantitative yield [6]. The reactions of

* Pd(1)–O(1)–O(2)–N(1)–C(1) and Pd(2)–O(4)–O(5)–N(2)–C(16).



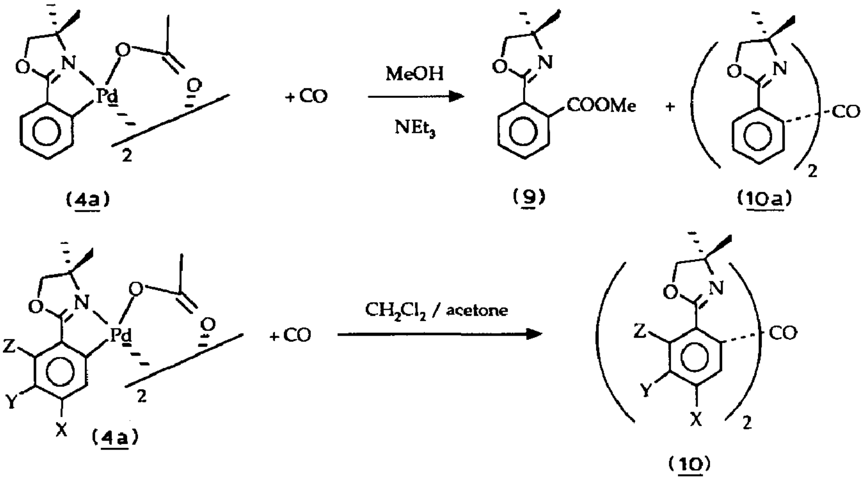
Py : pyridine

DPPE : diphenylphosphinoethane

Scheme 4

4a and **6** with triphenylphosphine or pyridine gave the monomers **7a–c**. The pyridine adducts **7a** and **7b** (Scheme 4) were fully characterized, but are only moderately stable and revert to the dimers **4a** and **6** during a few weeks at −20 °C. The cationic complex **8** was isolated quantitatively after treatment of **4a** with a stoechiometric amount of 1,2-bisdiphenylphosphinoethane followed by aqueous ammonium hexafluorophosphate.

The reactions of cyclo-palladated complexes with carbon monoxide have been investigated in detail [5,22]. Depending on the substrates and conditions, various



Scheme 5

Table 8

Yields and physical data for ketones **10**

	X	*Y*	*Z*	Yield (%)	M.p. (°C)	IR [a]
10a	H	H	H	85	123–125	1675, 1650
10b	H	H	CH_3	81	172–174	1675, 1660
10c	H	H	OCH_3	64	172–174	1700, 1660
10d	OCH_3	H	H	55	95– 97	1660, 1650
10e	OCH_3	OCH_3	H	73	143–145	1660, 1650
10f	NO_2	H	H	56	195–197	1700, 1650
10h	Cl	H	H	87	143–145	1690, 1650

[a] ν(C=N), ν(C=O) (cm^{-1}).

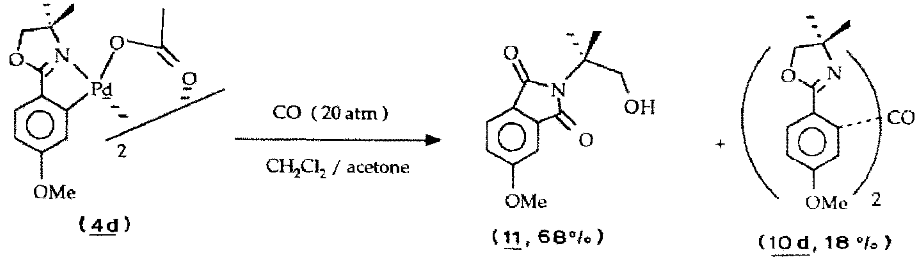
organic products (esters, heterocycles) as well as palladium complexes have been isolated. Complex **4a** was found to react with CO (1 atm, 25°C) in methanol to give the methyl ester **9** in a 72% yield, and ketone **10a** (Scheme 5) was isolated as a by-product (18%). The preparation of diarylketones by carbonylation of dimeric cyclo-palladated complexes has not, to the best of our knowledge, been previously reported. When the carbonylation was conducted in an aprotic solvent (CH_2Cl_2/acetone) the ketone **10a** was the sole product of the reaction. The structure of **10a** was confirmed by an alternative synthesis (see Experimental Section). A series of diarylketones was similarly obtained from complexes **4b–h** in fair to good yields (Table 8).

We suggest that the ketones **10** are formed by an intramolecular coupling between an acylpalladium moiety Ar–CO–Pd (formed by insertion of a molecule of carbon monoxide in one C–Pd bond) with the other Ar–Pd moiety of the dimeric molecule.

It is noteworthy that during the carbonylation (P_{CO} = 1 atm) of **4d** (*p*-methoxy) a small amount of the phtalimide **11** (Scheme 6) was formed, and this was isolated and characterized. Under higher CO pressure (20 atm) **11** becomes the major product (68% yield).

Experimental

$Pd(OAc_2)$ was obtained from Johnson-Matthey and was purified before use by dissolving it in hot benzene, filtering the solution, and removing the solvent. The substituted aryloxazolines **1a–j** were prepared by a published procedure [2]. Acetic acid was refluxed for several hours over potassium permanganate then distilled.



Scheme 6

IR spectra were recorded on a Perkin Elmer 880 spectrometer in the range 4000–200 cm^{-1}; solid samples were examined as Nujol mulls and oils as neat samples. ^{1}H NMR spectra were recorded on Varian EM360 L, EM 390 L, Bruker AC-200 and Buker WM-250 spectrometers, and ^{13}C NMR spectra on the latter spectrometer. All NMR samples were dissolved in $CDCl_3$ (unless otherwise stated) with TMS as internal reference. Chemical shift values are in ppm, with TMS taken as zero. $^{1}H-^{1}H$ coupling constants are in Hz. Microanalyses were carried out by the "Centre de Microanalyses du C.N.R.S., Gif/Yvette, France".

*X-ray data collection and structure determination of **4a***

Cell constants and other pertinent data are presented in Table 4. A yellow crystal of the compound was mounted on a glass fibre and centered on an Enraf-Nonius CAD4 diffractometer. Cell dimensions and their estimated standard deviations were determined by least-squares fit of 25 reflections with $15.6 < 2\theta < 20.4°$. The crystal was orthorhombic, and the observed systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) indicated unambiguously the space group *Pbca* (D_{2h}, No. 61). All intensity data were collected at room temperature by use of graphite monochromatized Mo-K_α radiation ($\lambda = 0.7103$ Å) and the ω–2θ scan technique, with a variable scan width $(1.00 + 0.35\text{tg}\theta)°$ extended 25% on each side for background measurements, and a variable horizontal aperture $(2.0 + 0.5\text{tg}\theta)$mm. All reflections (5063) with $h,k,l > 0$ with $1° < \theta < 25°$ were measured in this manner. During the data collection three standard reflections checked after every hour of X-ray exposure time and showed slight changes (2% in 68 h), and correction was made for this. Corrections were made for Lorentz and polarization effects but not for absorption. Of the 4545 unique data, 3455 were considered observed ($I > 3\sigma(I)$) and used in subsequent calculations. The structure was solved by use of the direct methods MULTAN 11/82 series of programs [23] and a Patterson map from which the two Pd atoms were located. Subsequent difference Fourier maps revealed the location of all non-hydrogen atoms. Refinements by full-matrix least squares (all non-hydrogen atoms with anisotropic temperature factors) gave the final R factors values shown in Table 4. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, where the weighting is $1/[\sigma^2(F_o) + (0.07F_o)^2]$. Hydrogen atoms were located on difference maps but were placed at calculated position (C–H = 1.0Å, C–C–H = 120 or 109.5°) with fixed isotropic temperature factor and not refined. The final difference map displayed no significant residual peaks (the largest peak of 0.52 e/A^3 was in the vicinity of the Pd(2) atom). All calculations were performed by use of the Enraf-Nonius Structure Determination Package SDP [24] on a PDP 11/60 computer. The neutral-atom scattering factors and anomalous dispersion corrections were taken from ref. 25. Tables of hydrogen atom coordinates, anisotropic thermal parameters for the non-hydrogen atoms, least-squares planes and torsional angles calculations, a list of the observed and calculated structure amplitudes, and a complete list of bond distances and angles are available from the authors.

*Preparation of the diacetatobis(2-phenyl-4,4-dimethyl-2-oxazoline)palladium(II) (**2a**)*

A solution of 2-phenyl-4,4-dimethyl-2-oxazoline **1a** [2] (1.90 g, 11 mmol) in benzene (10 ml) was added to one of palladium acetate (1.1 g, 5 mmol) in 100 ml of benzene at room temperature and stirred for 24 h. The resulting yellow solution was filtered through a small pad of Celite and evaporated. The yellow residue was washed with hexane, then recrystallized from methylene chloride/hexane to yield complex **2a** (2.7 g, 95%).

M.p. ca. 120 °C (decomp.). IR: 1625 cm^{-1} (ν(C=N)asym.).

^{1}H NMR (250 MHz): 1.50 (s,6H); 1.67 (s,12H); 4.20 (s,4H); 7.60 (m,6H); 9.23 (m,4H).

Anal. Found C, 54.10; H, 5.70; N, 4.82. $C_{22}H_{32}N_2O_6Pd$ (M = 574.96) calc.: C, 54.31; H, 5.61; N, 4.87%.

*Preparation of the dichlorobis(2-phenyl-4,4-dimethyl-2-oxazoline)palladium(II) (**3a**)*

Complex **2a** (1.15 g, 2 mmol) was added to a solution of lithium chloride (0.17 g, 4 mmol) in 20 ml of anhydrous methanol. The yellow suspension was stirred 12 h (25 °C) and the solid then filtered off, successively washed with water, methanol, and ether, then dried under high vacuum; 1.01 g (96%).

M.p. ca. 245 °C (decomp.). IR: 1630 cm^{-1}.

Anal. Found. C, 49.81; H, 4.82; N, 5.31. $C_{22}H_{26}Cl_2N_2O_2Pd$ (M = 527.78) calc.: C, 49.97; H, 4.95; N, 5.29%.

These values are in good agreement with those previously reported [6].

^{1}H NMR (DMSO-d_6, 250 MHz): 1.72 (s,12H,72%); 1.90 (s,12H,28%); 4.27 (s,4H); 7.36 to 7.72 (m,6H); 8.66 (m,4H,28%); 8.92 (m,4H,72%).

*Preparation of the cyclopalladated complexes **4a–i**: general procedure.*

A mixture of palladium acetate (1.1 g, 5 mmol) and the aromatic oxazoline (5 mmol) in 5 ml acetic acid was stirred for 30 min at 95 °C, during which the colour changed from dark brown to yellow and a solid precipitated. The mixture was cooled and kept 12 h at room temperature then the precipitate was filtered off, washed with cold acetic acid then water, dried and dissolved in chloroform. The solution was filtered through Celite then evaporated, and residue recrystallysed from $CHCl_3$/hexane at −20 °C).

Yields and data are listed in Tables 1, 2 and 3.

*Preparation of di-μ-bromobis[2-(4′,4′-dimethyl-2′oxazolinyl)phenyl,1-C,3′-N]dipalladium(II) (**5**)*

A brown solution of the *ortho*-bromooxazoline **1j** (0.254 g, 1 mmol) and palladium bisdibenzilidenacetone (0.681 g, 1 mmol) in 10 ml of dry degassed benzene was kept at 60 °C under argon, and after a few minutes the solution turned yellow and a solid separated. The mixture was kept for 15 min at 60 °C, then cooled and filtered. The precipitate was washed with hexane and recrystallized ($CHCl_3$/hexane) to yield 0.332 g of **5** (92%). It was found to be identical with a sample obtained by an alternative pathway [6].

*Preparation of the di-μ-chlorobis[2-(4′,4′-dimethyl-2′oxazolinyl)phenyl,1-C,3′-N]dipalladium (II) (**6**)*

A literature process was followed [6].

*Preparation of the acetato[2-(4′,4′-dimethyl-2′-dimethyl-2′-oxazolinyl)phenyl,1-C,3′-N](pyridine)palladium(II) (**7a**)*

A solution of the complex **4a** (0.34 g, 0.5 mmol) in 5 ml of dry degassed pyridine was kept for 3 h at 50 °C under argon then cooled and filtered through Celite. The residual pyridine was evaporated off under high vacuum and the light yellow residue was recrystallized from CH_2Cl_2/MeOH at −20 °C. Yield 0.402 g; 96%.

M.p. ca. 260 °C. IR: 1620 cm^{-1}.

Anal. Found: C, 51.55; H, 4.80; N, 16.49. $C_{18}H_{20}N_2O_3Pd$ (M = 418.77) calc.: C, 51.63; H, 4.81; N, 6.69%.

^1H NMR (250 MHz): 1.50 (s,6H); 1.88 (s,3H); 4.38 (s,2H); 6.13 (d,7.5,1H); 6.96 (ddd,7.5–7.5–1.5,1H); 7.02 (dd, 7.5–7.5, 1H); 7.22 (dd,7.5–1.5,1H); 7.45 (dd,8.0–7.0,2H); 7.87 (td,8.0–7.5,1H); 9.10 (td,7.0–1.5,2H).

The complex **7a** was found to be only weakly stable even at −20 °C, and decomposes to its precursors (**4a** and pyridine) within a few days. The observed melting point is probably that of **4a**.

The chloro complex **7b** was obtained by the same route from **6a** in 83% yield. Again the stability was poor.

M.p. ca. 175 °C. IR: 1625 cm^{-1}.

^1H NMR (250 MHz): 1.70 (s,6H); 4.38 (s,2H); 6.13 (d,8.0,1H); 7.02 (ddd, 1.0–8.0–8.0,1H); 7.06 (dd,8.0–8.0,1H); 7.27 (dd,8.0–1.0,1H); 7.48 (dd,6.0–8.0,1H); 7.90 (tt,8.0–1.0,1H); 8.97 (dd,6.0–1.0,1H).

Preparation of the acetato[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl,1-C,3′-N](triphenylphosphine)palladium (II) (7c)

A solution of the complex **4a** (0.34 g, 0.5 mmol) and triphenylphosphine (0.262 g; 1 mmol) in 20 ml CH_2Cl_2 was refluxed for 2 h under argon. The solution was then filtered (Celite) and evaporated. The yellow solid was crystallized from CH_2Cl_2/hexane at −20 °C (yield 0.581 g, 96,5%).

M.p. 190–193 °C (decomp.), IR: 1625 cm^{-1}.

Anal. Found: C, 61.73; H, 5.42; N, 2.50; P, 5.38. $C_{31}H_{30}NO_3PPd$ (M = 601.96) calc.: C, 61.86; H, 5.02; N, 2.33; P, 5.15%.

Preparation of [2-(4′,4′-dimethyl)-2′-oxazolinyl)phenyl,1-C,3′-N](1,2-bisdiphenylphosphinoethane)palladium(II) hexafluorophosphate (8)

A solution of the complex **4a** (0.34 g, 0.5 mmol) and 1,2-bis-diphenylphosphinoethane in 10 ml of methylene chloride was stirred overnight (25 °C), then a solution of ammonium hexafluorophosphate (0.85 g, 5 mmol) in 10 ml H_2O was added. The organic phase was separated, dried ($MgSO_4$), and evaporated. The resulting white solid was recrystallized from CH_2Cl_2/ether at −20 °C to give **8** in 98% yield.

M.p. ca. 250 °C (decomp.), IR: 1620 cm^{-1}.

^1H NMR (250 MHz): 0.70 (s,6H); 2.35 (m,4H); 4.32 (s,2H); 6.80 (m,2H); 7.04 (ddd, 7.5–7.5–1.0,1H); 7.44 (dd,7.5–1.0,1H); 7.5 to 7.65 (m,12H); 7.70 to 7.90 (m,6H).

Preparation of the 2-(2′-carbomethoxy)phenyl-4,4-dimethyl-oxazoline (9)

To a solution of complex **4a** (0.34 g, 0.5 mmol) in 20 ml of anhydrous methanol were added 0.5 g (5 mmol) of dry triethylamine. The mixture was stirred for 24 h under CO (1 atm) then filtered through Celite (to remove palladium metal) and evaporated. The oily residue was subjected to flash-chromatography (90/10 $CHCl_3$/AcOEt) to give the ester **9** as a colourless oil (yield 0.168 g, 72%).

IR: 1720, 1650 cm^{-1}.

^1H NMR (250 MHz): 1.40 (s,6H); 3.75 (s,3H); 3.90 (s,2H); 7.10 to 7.30 (m,2H); 7.80 to 8.00 (m,2H).

Further elution (75/25 $CHCl_3$/AcOEt) gave of the ketone **10a** (0.040 g, 18%) as a white solid (after crystallization from hexane).

M.p. = 123–125 °C.

Anal. Found: C, 72.73; H, 6.41; N, 7.58; O, 12.86. $C_{23}H_{24}N_2O_3$ (M = 376,45) calc.: C, 73.47; H, 6.43; N, 7.45; O, 12.77%.

^1H NMR (90 MHz): 1.20 (s, 12H, 3.85 (s,4H); 7.50 (m,6H); 7.80 (m,2H).

*Preparation of the ketones **10** by carbonylation of the complexes **4**: general procedure*

A solution of the complex **4** (0.5 mmol) in CH_2Cl_2 (10 ml) and acetone (10 ml) was treated with CO (1 atm) for 24 h at r.t. The resulting dark suspension was filtered through Celite to remove Pd(metal) and then concentrated on a rotary evaporator. The residue was purified by flash-chromatography (3/1 ($CHCl_3$/AcOEt) then recrystallized (hexane). Data for ketones **10** are listed in Table 8 or below.

10b: ^1H NMR (90 MHz): 1.22 (s,12H); 2.45 (s,6H); 3.90 (s,4H); 7.30 (m,6H).

Anal. Found: C, 73.34; H, 6.71; N, 6.72; O, 11.89. $C_{25}H_{28}N_2O_3$ (M = 404,50) calc.: C, 74.33; H, 6.99; N, 6.93; O, 11.88%.

10c: ^1H NMR (90 MHz): 1.25 (s,18H); 3.90 (s,6H); 4.00 (s,4H); 7.15 (m,4H); 7.40 (m,2H).

Anal. Found: C, 67.81; H, 6.36; N, 6.55; O, 18.53. $C_{25}H_{28}N_2O_5$ (M = 436,50) calc.: C, 68.78; H, 6.47; N, 6.42; O, 18.33%.

10d: ^1H NMR (90 MHz): 1.20 (s,12H); 3.80 (s,10H); 7.00 (m,4H); 7.70 (m,2H).

Anal. Found: C, 68.22; H, 6.51; N, 6.47; O, 18.80. $C_{25}H_{28}N_2O_5$ (M = 436.50) calc.: C, 68.78; H, 6.47; N, 6.42; O, 18.33%.

10e: ^1H NMR (90 MHz): 1.25 (s,12H); 3.75 (s,4H); 3.90 (s,6H); 4.00 (s,6H); 7.10 (s,2H); 7.25 (s,2H).

Anal. Found: C, 65.23; H. 6.49; N, 5.73; O, 22.43. $C_{27}H_{32}N_2O_7$ (M = 496,55) calc.: C, 65.31; H, 6.50; N, 5.64; O, 22.56%.

10f: ^1H NMR (90 MHz): 1.20 (s,12H); 3.95 (s,4H); 8.00 (m,2H); 8.35 (m,4H).

Anal. Found: C, 58.81; H, 4.79; N, 11.53; O, 23.67. $C_{23}H_{22}N_2O_7$ (M = 466,45) calc.: C, 59.22; H, 4.75; N, 12.01; O, 24.01%.

10h: ^1H NMR (90 MHz): 1.25 (s,12H); 3.90 (s,4H); 7.50 (m,4H); 7.75 (d,6Hz, 2H).

Anal. Found: C, 61.49; H, 5.12; N, 6.34; O, 10.99; Cl, 16.39. $C_{23}H_{22}N_2O_3Cl_2$ (M = 445,34) calc.: C, 62.02; H, 4.98; N, 6.29; O, 10.78; Cl, 15.94%.

*Preparation of the phtalimide **11***

A solution of 0.353 g of complex **4d** in 20 ml of CH_2Cl_2 was exposed to CO (20 atm) in a glass lined stainless steel autoclave for 48 h. After removal of the palladium metal (Celite), the oily residue was purified by flash-chromatography (3/1 ($CHCl_3$/AcOEt) to give 3 products; the oxazoline **1d** (0.02 g), the ketone **10d** (vide supra) (0.04 g, 18.4%), and the phtalimide **11** (0.170 g, 68.3%).

Analytical data for **11**:

M.p. = 133–135 °C. IR: 3600, 1760, 1700 cm^{-1}.

^1H NMR (200 MHz): 1.58 (s,6H); 3.67 (t,8 Hz, 1H); 3.89 (d,8 Hz,1H); 3.92 (d, 8 Hz,1H); 3.92 (s,3H); 7.15 (d.d,8–2 Hz,1H); 7.26 (d,2 Hz, 1H); 7.70 (d, 8 Hz,1H).

^{13}C NMR (64.9 MHz): 23.32; 56.17; 62.13; 69.70; 107.57; 120.24; 124.08; 124.77; 134.66; 165.02; 169.98.

Anal. Found: C, 62.30; H, 6.07; N, 5.63; O, 25.20. $C_{13}H_{15}NO_4$ ($M = 249.26$) calc.: C, 62.64; H, 6.07; N, 5.62; O, 25.68%.

Alternative preparation of ***10a***

A solution of oxazoline **1a** (3.5 g, 20 mmol) in 40 ml of anhydrous THF under argon was cooled to −78 °C (acetone-dry ice bath) and 1.01 equivalents of t-butyllithium in pentane (1.4 *N*, 14.5 ml) were added dropwise from a syringe. The solution was then stirred for 2 h at −78 °C then *N,N,O*-trimethylcarbamate (1.03 g, 10 mmol) was added. The solution mixture was allowed to warm to room temperature during 2 h, then worked up to give a colorless oil which was purified by flash-chromatography (3/1 $CHCl_3$/AcOEt). The white solid (1.0 g, 27%) obtained was identical (m.p., spectra) with that described above.

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