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The σ-Bonded Palladium(II) Complexes of 2-Aryl-4,4-dimethyl-2-oxazolines

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Reactions of 2-phenyl-4,4-dimethyl-2-oxazoline with lithium tetrachloropalladate(II) and palladium(II) acetate give dichlorobis(2-phenyl-4,4-dimethyl-2-oxazoline,3-*N*)palladium(II) and a cyclopalladated binuclear complex, di-μ-acetato-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl,1-*C*,3′-*N*]dipalladium(II), respectively. The latter complex is readily converted by a metathetical reaction with lithium chloride into its chloro-bridged analogue. The chloro-bridged complex reacts with triphenylphosphine to give the corresponding mononuclear σ-bonding palladium complex. All the complexes prepared in this study were characterized by means of IR and NMR spectroscopies.

Following the first report of the intramolecular cyclopalladation of azobenzene and *N*,*N*-dimethylbenzylamine,[1] there has been considerable interest in the intramolecular cyclometalation of nitrogen, phosphorus, and sulfur donor ligands by transition metals.[2] The cyclometalation reaction of 2-aryloxazolines with butyllithium proceeds regiospecifically and nearly quantitatively to the formation of an ortho-lithiation product.[3,4] One might, therefore, expect 2-aryloxazolines to undergo cyclopalladation. In this paper, we wish to report on the intramolecular cyclopalladation reaction of 2-phenyl-4,4-dimethyl-2-oxazoline (**1**) and 2-(3,4-dimethoxyphenyl)-4,4-dimethyl-2-oxazoline (**2**) in the formation of acetato-bridged binuclear complexes.

Results and Discussion

In the presence of sodium acetate, the reaction of **1** with lithium tetrachloropalladate(II) in methanol at room temperature gave dichloro-bis(2-phenyl-4,4-dimethyl-2-oxazoline)palladium(II) (**3**), which has no palladium-carbon σ-bonding. The NMR spectrum could not be measured because of the low solubility of **3** in all common solvents. However, the structure of **3** was consistent with the results of the elemental analysis and the IR spectrum of the compound. The IR bands of the aromatic ring C–H out-of-plane deformation vibrations suggest the modes of ring substitution.[5] The bands of the starting material **1** are observed at 745 and 695 cm^{-1}, corresponding to five adjacent ring hydrogens. The bands of complex **3** are observed at 750 and 690 cm^{-1}. This indicates the presence of monosubstituted benzene ring. Furthermore, complex **3** also shows ν(Pd–Cl) at 350 cm^{-1}, the position characteristic of *trans*-[PdCl$_2$L$_2$],[6] and ν(C=N) was shifted to lower frequencies (1630 cm^{-1}) compared with **1** (ν(C=N) = 1650 cm^{-1}). Judging from these results, complex **3** contains two moles of **1** as ligands coordinated only with

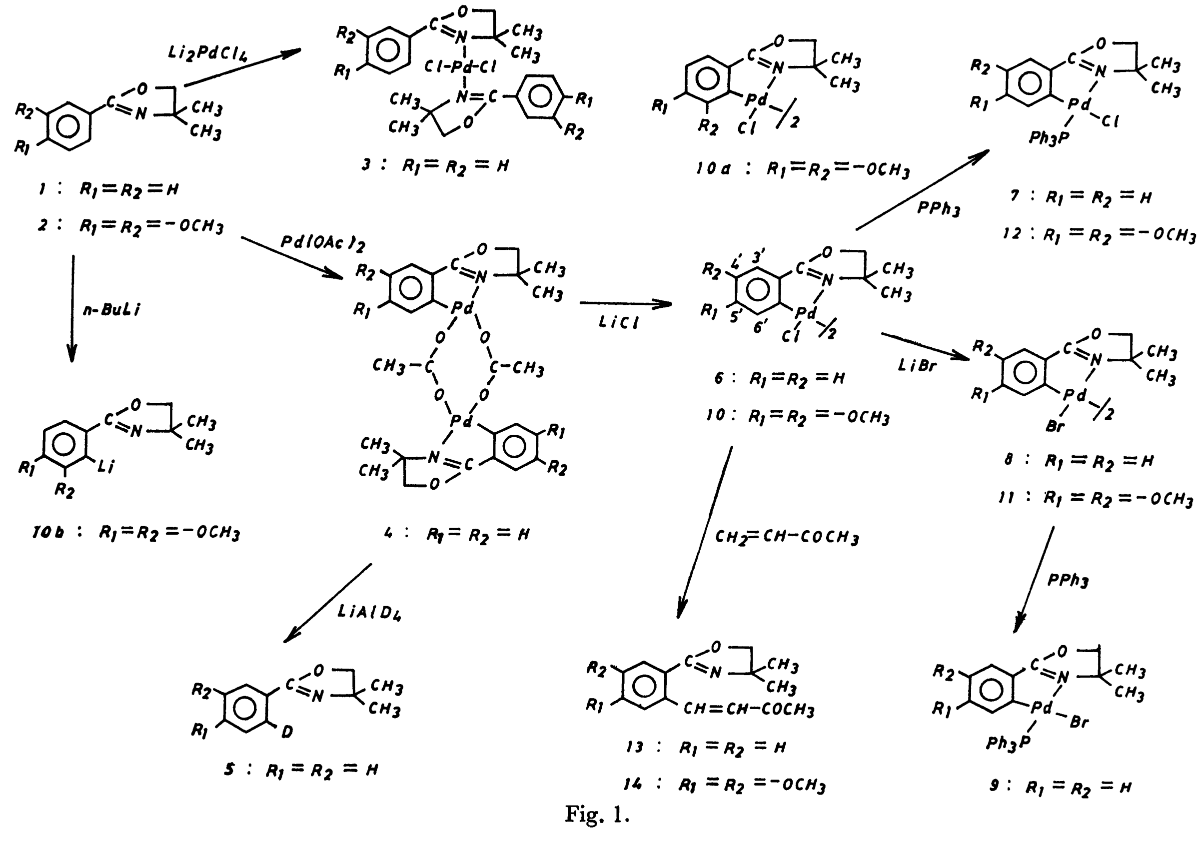
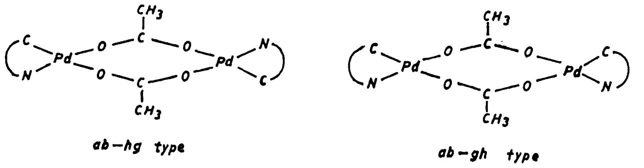


Fig. 1.

a nitrogen donor site, but does not contain a cyclopalladation moiety, and may have a trans-configuration with **1** as a N-donor.

On the other hand, the reaction of **1** with equimolar quantities of palladium(II) acetate in acetic acid at reflux produced the desired σ-bonded palladium complex (**4**), whose IR spectrum exhibited two strong absorption bands due to bridging acetato ligand at 1570 and 1410 cm^{-1}.⁷⁾ Moreover, the IR spectrum in **4** exhibits a band about 725 cm^{-1} which is characteristic of ortho-disubstituted benzene ring. The lithium aluminum hydride reduction of **4** gave **1**, whose mass spectrum was identical with that of an authentic sample, while the lithium aluminum deuteride reduction of **4** gave 2-(phenyl-2-*d*)-4,4-dimethyl-2-oxazoline (**5**). On the basis of elementary analysis and the characterization of the derivatives from **4**, the complex was assigned to a binuclear cyclopalladated complex, di-μ-acetato-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl, 1-*C*, 3′-*N*]-dipalladium(II). It is noteworthy that even in the presence of acetate ion, **1** reacted with tetrachloropalladate(II) ion to give only the addition product **3** and with palladium(II) acetate to produce the cyclopalladated complex **4**, similar to the case of 1-ethyl-2-phenylimidazole.⁸⁾ The NMR spectrum of **4** was also in good agreement with the proposed structure, and the methyl resonance of bridging acetato ligand showed a sharp singlet at δ 2.22 together with two weak resonances at 2.15 and 2.28 ppm. These resonances were ascribed to two geometrical isomers, as shown in Fig. 2;⁹⁾ the former was due to two magnetically equivalent methyl protons in an ab-hg type and the latter were due to non-equivalent methyl protons in an ab-gh type (the isomer ratio ab-hg : ab-gh=4 : 1, approximately).



C/N =2-[4′,4′-Dimethyl-2′-oxazolinyl]phenyl,1-*C*, 3′-*N*-

Fig. 2. Geometrical isomers of **4**.

The complex **4** was smoothly converted by metathetical reaction with lithium chloride in acetone into its chloro-bridged analogue, di-μ-chloro-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl,1-*C*,3′-*N*]dipalladium(II) (**6**). The IR spectrum in **6** exhibits a band at 730 cm^{-1} which can be assigned to the C–H deformation mode of an ortho-disubstituted benzene derivative. In the far-IR spectrum of **6**, there are two bridged Pd–Cl stretching absorptions at 270 and 245 cm^{-1}. The NMR spectrum of the complex was also in agreement with the proposed structure. The singlet at 1.51 ppm corresponds to the methyl group, the singlet at 4.36 ppm corresponds to the methylene group, and a typical ABCD system at 6.86—7.56 ppm corresponds to the *o*-phenyl group in 2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl moiety. The 4′- or 5′-H was observed at δ 6.98 (2H) and 7.31 ppm (2H) as a double triplet due to coupling with other ring protons. The 6′-H and 3′-H appeared at 6.86 (2H) and 7.56 ppm (2H) as a double doublet due to coupling with 4′- and 5′-H, respectively. The coupling constants were $3'J_{\text{HH}}=7.0$ Hz and $4'J_{\text{HH}}=1.5$ Hz. Moreover, the complex **6** underwent a typical bridge-splitting reaction with triphenylphosphine to give a monomeric triphenylphosphine derivative (**7**). These results indicate unambiguously that the complex **4** has the cyclopalladated structure of **1**. In the far-IR spectrum of **7**, a band at 295 cm^{-1} was assigned as the ν(Pd–Cl) frequency, by comparison with the corresponding bromo derivative (**9**) which was derived from the bromo-bridged complex (**8**). Crociani *et al.* reported that the ν(Pd–Cl) frequencies trans to an aromatic nitrogen atom and an ary-carbon one fell in the range of 353—321 and 299—280 cm^{-1}, respectively.¹⁰⁾ The chloride ligands in **7**, therefore, are located trans to a carbon donor.

On the other hand, the reaction of **2** with equimolar amounts of palladium(II) acetate in acetic acid at reflux, followed by treatment with lithium chloride, gave di-μ-chloro-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)-4, 5-dimethoxyphenyl, 1-*C*, 3′-*N*]dipalladium(II) (**10**). The IR spectrum in the complex **10** exhibits a band near 860 cm^{-1} which is characteristic of 1,2,4,5-tetrasubstituted benzene ring. In addition, the NMR spectrum in the region of aromatic absorption displays two singlets at 6.73 and 6.98 ppm. The infrared frequencies and the coupling constants in the NMR spectrum are all in agreement with the proposed structure **10** rather than with **10**$_{\text{a}}$. Meyers and Mihelich⁴⁾ had reported that ortho-lithiation of **2** with butyllithium led to the formation of 1,2,3,4-tetrasubstituted phenyllithium derivative (**10**$_{\text{b}}$). It is noteworthy that **2** reacted with palladium(II) acetate to produce the 1,2,4,5-tetrasubstituted benzene derivative (**10**). The complex **10** also shows a quite low ν(Pd–Cl) frequency at 240 cm^{-1}; this band disappears on metathesis with lithium bromide, and yields the bromo analogue product (**11**). Furthermore, the complex **10** underwent the typical bridge-splitting reaction with triphenylphosphine to afford **12**.

The reactions of cyclopalladation products from σ-aryl-nitrogen derivatives with numerous reagents have been reported.²⁾ In the presence of triethylamine, complexes **6** and **10** reacted with methyl vinyl ketone in toluene at 100 °C, leading to the formation of 1-(2-acetylvinyl)-2-(4,4-dimethyl-2-oxazolin-2-yl)benzene (**13**) and 1-(2-acetylvinyl)-2-(4,4-dimethyl-2-oxazolin-2-yl)-4,5-dimethoxybenzene (**14**), respectively.

Experimental

Materials. All the melting points are uncorrected. 2-Phenyl-4,4-dimethyl-2-oxazoline (**1**) and 2-(3,4-dimethoxyphenyl)-4,4-dimethyl-2-oxazoline (**2**) were prepared according to the method described by A. I. Meyers *et al.*¹¹⁾

Measurements. The IR spectra were measured on KBr disks (4000—650 cm^{-1}) and nujol mulls mounted on thin polyethene windows (700—200 cm^{-1}) with Hitachi 215 and EPI-L spectrometers. The NMR spectra were determined in CDCl_3 with a Hitachi R-22 spectrometer (90 MHz), using TMS as the internal standard (δ, ppm). The mass spectra were obtained on a Hitachi RMU-6M mass spectrometer, using a direct insertion probe at an ionization energy of 70 eV.

The molecular weight was determined in $CHCl_3$ with a Hitachi 115 vapor pressure osmometer.

Dichlorobis(2-phenyl-4,4-dimethyl-2-oxazoline)palladium(II) (3). A solution of **1** (2.0 g, 11.4 mmol) in 50 cm^3 of methanol was added to a solution of lithium tetrachloropalladate (II) (1.31 g, 5 mmol) in 50 cm^3 of methanol at room temperature for 15 h. The yellow precipitate which formed immediately was filtered and washed with several portions of methanol. The solid (2.3 g, 88% yield based on Li_2PdCl_4) was insoluble in all common solvents: mp 245—248 °C (dec). IR: 1630 (coordinated C=N), 750, 690 (monosubstituted benzene ring), and 350 cm^{-1} (νPd–Cl). Found: C, 49.75; H, 4.79; N, 5.16%. Calcd for $C_{22}H_{26}Cl_2N_2O_2Pd$: C, 49.97; H, 4.95:; N, 5.29%.

*Di-μ-acetato-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl, 1-*C*, 3′-*N*]dipalladium(II) (4).* To a solution of palladium(II) acetate (1.3 g, 5.7 mmol) in acetic acid (30 cm^3) was added **1** (1.0 g, 5.1 mmol) in acetic acid (30 cm^3) at room temperature. After refluxing for 1.5 h, the resulting mixture was diluted with water and extracted with chloroform. The chloroform extracts were concentrated and chromatographed on silica gel. A yellow band eluted by chloroform was collected and the solvent was evaporated. Recrystallization from benzene gave 0.8 g of **4** as yellow crystals: yield 46% based on **1**, mp 135—137 °C (dec). IR: 1625 (coordinated C=N), 1570, 1410 (bridging acetate), and 720 cm^{-1} (*o*-disubstituted benzene ring). NMR: δ 1.55 (s, 12H, CH_3–C), 2.15, 2.22, and 2.28 (each s, 6H, CH_3 of acetato group), 4.38 (s, 4H, –CH_2–), 6.96—7.55 ppm (m, 8H, Ar–H). Found: C, 45.74; H, 4.34; N, 3.97%; mol wt (in $CHCl_3$), 665. Calcd for $C_{26}H_{30}N_2O_6Pd_2$: C, 45.82; H, 4.43; N, 4.12%; mol wt 679.

Reduction of 4 with Lithium Aluminium Hydride. Lithium aluminium hydride (0.02 g, 0.5 mmol) in anhydrous ether (50 cm^3) was slowly added to a suspended solution of **4** (0.66 g, 1 mmol) in anhydrous ether (100 cm^3). The resulting black mixture was stirred at room temperature for 6 h; then water (10 cm^3) was added with cooling. The ether layer was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent, **1** was obtained as a pale yellow oil and the IR, NMR, and MS spectra were identical with those of the authentic sample.[12] IR: 1650 cm^{-1} (C=N). NMR: δ 1.24 (s, 6H, CH_3–), 3.95 (s, 2H, –CH_2–), 7.31 (m, 3H, Ar–H), and 7.89 ppm (m, 2H, Ar–H). MS: 175 (M^+). Calcd for $C_{11}H_{13}NO$: M, 175.

Reduction of 4 with Lithium Aluminium Deuteride. The reduction of **4** (0.66 g) in anhydrous ether with lithium aluminium deuteride (0.02 g) was carried out as in the preceding experiment; this gave a pale yellow oily product which can be identified as 2-(phenyl-2-d)-4,4-dimethyl-2-oxazoline (**5**) on the basis on the following evidence: IR: 1650 cm^{-1} (C=N). NMR: δ 1.24 (s, 6H, CH_3–), 3.95 (s, 2H, –CH_2–), 7.31 (m, 3H, Ar–H). 7.89 ppm (m 1H, Ar–H). Found: C, 74.31; H, 7.94; N, 7.88%; M^+, 176. Calcd for $C_{11}H_{12}DNO$: C, 74.40; H, 7.99; N, 7.94%; M, 176.

*Di-μ-chloro-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl, 1-*C*, 3′-*N*]dipalladium(II) (6).* A mixture of lithium chloride (0.10 g, 2.4 mmol) and **4** (0.78 g, 1.16 mmol) in acetone (50 cm^3) was stirred at room temperature for 10 h. The evaporation of the solvent gave a pale yellow solid, which was washed with water and diethyl ether. The solid was purified by passing through a short silica gel column with chloroform, and 0.72 g of **6** was obtained as pale yellow crystals; yield 98% based on **4**, mp 175—178 °C (dec.) IR: 1620 (coordinated C=N), 730 (*o*-disubstituted benzene ring), 270, and 245 cm^{-1} (bridged Pd–Cl). NMR: δ 1.51 (s, 12H, CH_3–), 4.36 (s, 4H, –CH_2–), 6.86 (d-d, 2H, 6′-H), 6.98 (d-t, 2H, 4′- or 5′-H), 7.31 (d-t, 2H, 5′- or 4′-H), and 7.56 ppm (d-d, 2H, 3′-H). Found: C, 41.69; H, 3.73; N, 4.27%; mol wt (in $CHCl_3$), 624. Calcd for $C_{22}H_{24}Cl_2N_2O_2Pd_2$: C, 41.80; H, 3.82; N, 4.43%; M, 632.

Reaction of 6 with Triphenylphosphine. Triphenylphosphine (0.24 g, 0.92 mmol) was added to a suspension of **6** (0.29 g, 0.46 mmol) in 30 cm^3 of benzene. A clear solution formed immediately; this was concentrated after stirring for 10 h at room temperature. The evaporation of the solvent gave a pale yellow solid, which was purified by passing through a silica gel column with chloroform. 0.52 g of chloro-[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl, 1-*C*, 3′-*N*](triphenylphosphine)palladium(II) (**7**) was obtained as pale yellow crystals: yield 98%, mp 181—183 °C (dec). IR: 1630 (coordinated C=N), 740 (*o*-disubstituted benzene ring), 750, 690 (mono-substituted benzene ring), and 295 cm^{-1} (terminal Pd–Cl). NMR: δ 1.67 (s, 6H, CH_3–), 4.34 (s, 2H, –CH_2–), 6.72—7.11 (m, 4H, Ar–H), and 7.24—7.75 ppm (m, 15H, Ar–H). Found: C, 60.11; H, 4.57; N, 2.33%; mol wt (in $CHCl_3$), 565. Calcd for $C_{29}H_{27}ClNOPPd$: C, 60.22; H, 4.70; N, 2.42%; M, 578.

*Di-μ-bromo-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl, 1-*C*, 3′-*N*]dipalladium(II) (8).* The complex **6** (0.2 g) suspended in acetone (50 cm^3) was treated with lithium bromide (0.2 g), and the mixture was warmed at reflux for 6 h. The resulting orange red solution was evaporated to dryness under reduced pressure. After silica gel column chromatography with chloroform, recrystallization from benzene–hexane gave pale yellow crystals of **8**; yield 60% based on **6**, mp 186—188 °C (dec). IR: 1620 (coordinated C=N) and 730 cm^{-1} (*o*-disubstituted benzene ring). NMR: δ 1.52 (s, 12H, CH_3–), 4.36 (s, 4H, –CH_2–), and 6.90—7.54 ppm (m, 8H, Ar–H). Found: C, 36.89; H, 3.31; N, 3.85%; mol wt (in $CHCl_3$), 695. Calcd for $C_{22}H_{24}Br_2N_2O_2Pd_2$: C, 37.05; H, 3.39; N, 3.92%; M, 713.

*Bromo[2-(4′,4′-dimethyl-2′-oxazolinyl)phenyl, 1-*C*, 3′-*N*](triphenylphosphine)palladium(II) (9).* The reaction of **8** with triphenylphosphine was carried out in the same way as described for **7**, and pale yellow crystals of **9**, mp 198—200 °C (dec), were produced in 57% yield. IR: 1625 (coordinated C=N), 740 (*o*-disubstituted benzene ring), 750, and 690 cm^{-1} (mono-substituted benzene ring). NMR: δ 1.67 (s, 6H, –CH_3), 4.35 (s, 2H, –CH_2–), 6.75—7.13 (m, 4H, Ar–H), and 7.26—7.73 ppm (m, 15H, Ar–H). Found: C, 55.81; H, 4.30; N, 2.17%; mol wt (in $CHCl_3$), 615. Calcd for $C_{29}H_{27}BrNOPPd$: C, 55.92; H, 4.36; N, 2.24; M, 622.

*Di-μ-chloro-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)-4,5-dimethoxyphenyl, 1-*C*, 3′-*N*]dipalladium(II) (10).* To a solution of palladium(II) acetate (1.23 g, 5.5 mmol) in acetic acid (20 cm^3) was added the compound **2** (1.15 g, 5.0 mmol) in acetic acid (15 cm^3) at room temperature. After refluxing for 1 h, the resulting mixture was treated with an aqueous solution of lithium chloride (5.0 g) in water (20 cm^3) for 10 h at room temperature. The reaction mixture was diluted with water and extracted with several portions of chloroform. The combined extracts were washed with water, dried over anhydrous $MgSO_4$, concentrated, and chromatographed on silica gel. The product **10** (0.90 g, 45% yield based on **2**) was obtained as pale yellow crystals from benzene–hexane: mp 245—248 °C (dec). IR: 1620 (coordinated C=N), 860 (1,2,4,5-tetra-substituted benzene ring), 270, and 240 cm^{-1} (bridged Pd–Cl). NMR: δ 1.62 (s, 12H, –CH_3), 3.82 (s, 6H, –OCH_3), 3.91 (s, 6H, –OCH_3), 4.37 (s, 4H, –CH_2–), 6.73 (s, 2H, Ar–H), and 6.98 ppm (s, 2H, Ar–H), Found: C, 41.44; H, 4.21; N, 3.63%; mol wt (in $CHCl_3$), 746. Calcd for $C_{26}H_{32}Cl_2N_2O_6Pd_2$: C, 41.51; H, 4.28; N, 3.72%; M, 752.

*Di-μ-bromo-bis[2-(4′,4′-dimethyl-2′-oxazolinyl)-4,5-dimethoxyphenyl, 1-*C*, 3′-*N*]dipalladium(II) (11).* The reaction of **10** with lithium bromide in acetone was carried out in the same way as described for **8**, and pale yellow crystals of **11**, mp

242—245 °C (dec), were produced in 65% yield. IR: 1620 (coordinated C=N) and 860 cm^{-1} (1,2,3,5-tetra-substituted benzene ring). NMR: δ 1.64 (s, 12H, –CH$_3$), 3.82 (s, 6H, –OCH$_3$), 3.93 (s, 6H, –OCH$_3$), 4.38 (s, 4H, –CH$_2$–), 6.75 (s, 2H, Ar–H), and 6.99 ppm (s, 2H, Ar–H), Found: C, 37.06; H, 3.77; N, 3.28%; mol (in CHCl$_3$), 810. Calcd for $C_{26}H_{32}Br_2N_2O_6Pd_2$: C, 37.12; H, 3.83; N, 3.33%; M, 821.

*Chloro[2-(4′,4′-dimethyl-2′-oxazolinyl)-4,5-dimethoxyphenyl, 1-*C*, 3′-*N*](triphenylphosphine)palladium(II) (**12**).* The reaction of **10** with triphenylphosphine was carried out in the same way as described for **7**, and pale yellow crystals of **12** were obtained; mp 225—227 °C (dec). IR: 1620 (coordinated C=N), 860 (1,2,4,5-tetrasubstituted benzene ring), 750, 690 (monosubstituted benzene ring), and 290 cm^{-1} (terminal Pd–Cl). NMR: δ 1.65 (s, 6H, –CH$_3$), 3.80 (s, 3H, –OCH$_3$), 3.89 (s, 3H, –OCH$_3$), 4.36 (s, 2H, –CH$_2$–), 6.75 (s, 1H, Ar–H), 7.01 (s, 1H, Ar–H), and 7.25—7.73 ppm (m, 15H, Ar–H). Found: C, 58.19; H, 4.81; N, 2.05%; mol wt (in CHCl$_3$) 626. Calcd for $C_{31}H_{31}ClNO_3PPd$: C, 58.32; H, 4.89; N, 2.19; M, 638.

*Reaction of **6** with Methyl Vinyl Ketone.* In a closed vessel, a mixture of the complex **6** (1.26 g, 2 mmol) and methyl vinyl ketone (6 mmol) and triethylamine (0.60 g, 6 mmol) in toluene (50 cm^3) was stirred for 5 h at 80 °C under a nitrogen atomsphere. The reaction mixture was cooled and filtered to remove precipitated palladium, and the filtrate was evaporated *in vacuo*. The residue was dissolved in ether, which had been washed with water and dried over anhydrous MgSO$_4$. After removal of the solvent, purification of the crude product by column chromatography (silica gel–hexane) gave 1-(2-acetylvinyl)-2-(4,4-dimethyl-2-oxazolin-2-yl)benzene (**13**), a pale yellow oil, in 45% yield based on **6**. IR (oil film): 1680 (C=O), 1650 (C=N), 1620 and 950 cm^{-1} (trans –CH=CH–). NMR: δ 1.33 (s, 9H, –CH$_3$), 4.10 (s, 2H, –CH$_2$–), 6.94—7.40 (m, 5H, Ar–H+–C=CH–CO–), and 7.55 ppm (d, 1H, –CH=C–CO–). Found: C, 74.96; H, 6.91; N, 5.70%; M$^+$, 243. Calcd for $C_{15}H_{17}NO_2$: C, 75.05; H, 7.04; N, 5.76%; M, 243.

*Reaction of **10** with Methyl Vinyl Ketone.* The reaction of **10** with methyl vinyl ketone was carried out in the same way as above, and 1-(2-acetylvinyl)2-(4,4-dimethyl-2-oxazolin-2-yl)-4,5-dimethoxybenzene (**14**), a pale yellow oil, was obtained in 38% yield. IR (oil film): 1675 (–C=O), 1650 (–C=N), 1620, and 950 cm^{-1} (trans –CH=CH–). NMR: δ 1.31 (s, 9H, –CH$_3$), 3.89 (s, 3H, –OCH$_3$), 3.91 (s, 3H, –OCH$_3$), 4.07 (s, 2H, –CH$_2$–), 6.85 (d, 1H, –C=CH–CO–), 7.27 (s, 1H, Ar–H), 7.47 (s, 1H, Ar–H), and 7.53 ppm (d, 1H, –CH=C–CO–). Found: C, 67.19; H, 6.88; N, 4.53; M$^+$, 303 Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62%; M, 303.

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