A Simple Route to Novel Palladium(II) Catalysts with Oxazolin-2-ylidene Ligands

Cristina Tubaro,[†] Andrea Biffis,*[,†] Marino Basato,[†] Franco Benetollo,[‡] Kingsley J. Cavell,*[,§] and Li-ling Ooi[§]

Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131, Padova, Italy, ICIS-CNR, Corso Stati Uniti 4, I-35127, Padova, Italy, and Department of Chemistry, Cardiff University, PO Box 912, Cardiff CF10 3TB, UK

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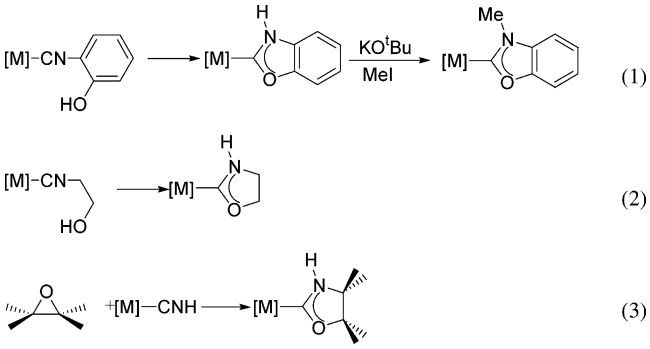
Novel palladium(II) complexes with oxazolin-2-ylidene ligands have been synthesized via direct reaction of palladium acetate and oxazolium salts, prepared in turn by alkylation of oxazole with methyl iodide or benzylic bromides. The resulting complexes have been characterized and used as catalysts in Heck coupling reactions of aryl bromides, where they exhibit remarkable catalytic activity, higher than that of the closely related bis-imidazolin-2-ylidene and bis-benzothiazolin-2-ylidene complexes.

Introduction

Since Arduengo et al. first isolated stable imidazolin-2-ylidenes in 1991,[1] much interest has developed in the chemistry of *N*-heterocyclic carbenes (NHCs) and their metal complexes.[2] NHCs behave like typical strong σ-donor ligands with negligible π-acceptor abilities. In particular, the donor/acceptor character of imidazolin-2-ylidene ligands has been experimentally measured as well as theoretically simulated and found to be similar to trialkylphosphanes.[3] However, the reactivity of NHC-stabilized organometallic compounds may be quite different from that of the corresponding phosphane complexes. For example, it has been recently established that the coordinated carbene moiety can undergo reductive elimination processes with hydrocarbyl ligands.[4] On the other hand, the high dissociation energy of the metal−carbene bond as opposed to the metal−phosphane bond[5] implies a much more limited dissociation of ligand in solution, which in turn accounts for the often observed superior stability of NHC-metal complexes under harsh reaction conditions (high temperature, oxidative environment) and in the absence of excess ligand.

Phosphanes represent a broad class of ligands that enjoy great diversity, so that the steric and electronic features of a phosphane ligand can be, in principle, readily varied and therefore optimized for a given purpose. Such diversity is at present not available for NHCs, although changing the degree of unsaturation of the heterocyclic ring, the substituents at the nitrogen atoms, or the nature of the heteroatoms can significantly modify the properties of these ligands. In particular, whereas metal complexes of imidazolin-2-ylidenes are known for almost all the metals of the periodic table, few examples are reported in which one of the two heteroatoms is different from nitrogen; these examples involve more frequently substitution by a sulfur atom (thiazolin-2-ylidene ligands)[6] or more rarely by an oxygen (oxazolin-2-ylidene ligands).[7] The paucity of examples of oxazolin-2-ylidene metal complexes is undoubtedly related to the fact that such complexes have been previously obtained only via two indirect synthetic methods, namely, through intramolecular cyclization of a functionalized hydroxyisocyanide (eqs 1 and 2)[7] or by reaction of an epoxide with a hydrogen-isocyanide complex (eq 3).[8] The electronic properties of oxazolin-2-yildene ligands are expected to be quite different from those of the related imidazolin-2-yilidene species, due

Chart 1



* To whom correspondence should be addressed. E-mail: andrea.biffis@unipd.it. Phone: +39-049-8275216. Fax: +39-049-8275223. E-mail: cavellkj@cf.ac.uk. Phone/Fax: +44 (0)29 2087 5899.
† Università di Padova.
‡ ICIS-CNR.
§ Cardiff University.

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to the higher electronegativity of the oxygen atom. Consequently, it can also be expected that the catalytic performance of the corresponding metal complexes will be influenced by the heteroatom change. In this contribution we report for the first time on the direct synthesis of oxazolin-2-ylidene carbene complexes by reaction of oxazolium salts with palladium acetate and on the reactivity of the resulting complexes in C−C coupling reactions.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox. All solvents were dried by standard procedures and distilled under nitrogen immediately prior to use. NMR spectra were recorded on a Bruker Avance 400 MHz or on a Bruker Avance 250 MHz spectrometer; chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals. GC analyses were performed on a Shimadzu GC-8A gas chromatograph equipped with a 25 m OV-1701 capillary column. Elemental analyses were carried out by the Warwick Analytical Service Ltd, University of Warwick Science Park.

3-Methyloxazolium Iodide.[9] A solution of oxazole (0.52 g, 7.6 mmol) and MeI (0.94 g, 8.1 mmol) in DMSO (3 mL) was stirred at room temperature for 48 h, to give an orange solution. Dichloromethane (20 mL) was added to precipitate the product, which was filtered, washed with dichloromethane (5 mL) and THF (2 × 5 mL), and dried in vacuo, giving the product as a pale yellow powder (yield 57%). ^{1}H NMR (DMSO-d_6): δ 3.92 (s, 3H, CH_3), 8.24 (s, 1H, CH=CH), 8.75 (s, 1H, CH=CH), 10.21 (s, 1H, NCHO). ^{13}C NMR (DMSO-d_6): δ 36.1 (CH_3), 123.4 and 144.0 (CH=CH), 155.8 (NCHO). MS (ESI, Da): m/z 83 ($M^+ - I$, 40%), 101 ($M^+ - I + H_2O$, 100%). Anal. Calcd for C_4H_6INO (M = 210.9): C, 22.78; H, 2.84; N, 6.63. Found: C, 22.17; H, 2.60; N, 6.14.

3-Benzyloxazolium Bromide (2). A solution of oxazole (0.52 g, 7.6 mmol) and benzyl bromide (1.56 g, 9.1 mmol) in THF (4 mL) was stirred at 120 °C for 24 h in a sealed tube, to give a white suspension. The supernatant was decanted off and the solid washed with THF (2 × 5 mL) and dried in vacuo, giving **2** as a white powder (yield 20%). ^{1}H NMR (DMSO-d_6): δ 5.49 (s, 2H, CH_2), 7.2−7.7 (m, 5H, Ph), 8.24 (s, 1H, CH=CH), 8.78 (s, 1H, CH=CH), 10.49 (s, 1H, NCHO). ^{13}C NMR (DMSO-d_6): δ 51.4 (CH_2), 121.0−144.0 (Ph and CH=CH), 155.4 (NCHO). MS (ESI, Da): m/z 160 ($M^+ - Br$, 100%). Anal. Calcd for $C_{10}H_{10}BrNO$ (M = 240.1): C, 50.02; H, 4.16; N, 5.83. Found: C, 49.87; H, 4.15; N, 5.78.

3-*o*-Bromobenzyloxazolium Bromide (3). A solution of oxazole (0.52 g, 7.6 mmol) and 2-bromobenzyl bromide (2.85 g, 11.4 mmol) in THF (4 mL) was stirred at 120 °C for 24 h in a sealed tube, to give a white suspension. The supernatant was decanted off and the solid washed with THF (2 × 5 mL) and dried in vacuo, giving **3** as a tan powder (yield 25%). ^{1}H NMR (DMSO-d_6): δ 5.74 (s, 2H, CH_2), 7.3−7.9 (m, 4H, Ph), 8.40 (s, 1H, CH=CH), 8.97 (s, 1H, CH=CH), 10.67 (s, 1H, NCHO). ^{13}C NMR (DMSO-d_6): δ 52.2 (CH_2), 122.0−145.0 (Ph and CH=CH), 156.5 (NCHO). MS (ESI, Da): m/z 238 ($M^+ - Br$, 100%). Anal. Calcd for $C_{10}H_9Br_2NO$ (M = 318.98): C, 37.65; H, 2.82; N, 4.39. Found: C, 37.50; H, 2.78; N, 4.29.

3-Picolyloxazolium Bromide (4). A solution of oxazole (0.26 g, 3.8 mmol) and picolyl bromide (4.5 mmol, prepared by adding $NaHCO_3$ to 1.15 g of picolyl bromide hydrobromide) in THF (4 mL) was stirred at 120 °C for 24 h in a sealed tube, to give an orange suspension. The supernatant was decanted off and the solid washed with THF (2 × 5 mL) and dried in vacuo, giving **4** as an orange powder (yield 25%). ^{1}H NMR (DMSO-d_6): δ 6.53 (s, 2H, CH_2), 8.2−9.5 (m, 6H, Ar and CH=CH), 10.60 (s, 1H, NCHO). Anal. Calcd for $C_9H_9BrN_2O$ (M = 241.1): C, 44.85; H, 3.73; N, 11.62. Found: C, 41.26; H, 3.94; N, 8.78.

3,3′-(*o*-Xylyl)-bis-oxazolium Dibromide (5). A solution of oxazole (0.26 g, 3.8 mmol) and α,α′-dibromo-*o*-xylene (0.5 g, 1.9 mmol) in THF (4 mL) was stirred at 120 °C for 24 h in a sealed tube, to give a white suspension. The supernatant was decanted off and the solid washed with THF (2 × 5 mL) and dried in vacuo, giving **5** as a white powder (yield 28%). ^{1}H NMR (DMSO-d_6): δ 5.84 (s, 2H, CH_2), 7.5−7.8 (m, 2H, Ph), 8.38 (s, 1H, CH=CH), 8.87 (s, 1H, CH=CH), 10.54 (s, 1H, NCHO). ^{13}C NMR (DMSO-d_6): δ 48.7 (CH_2), 121.0−145.0 (Ph and CH=CH), 155.7 (NCHO). Anal. Calcd for $C_{14}H_{14}Br_2N_2O_2$ (M = 402.0): C, 41.80; H, 3.48; N, 6.96. Found: C, 40.29; H, 3.58; N, 6.51.

3,3′-(*m*-Xylyl)-bis-oxazolium Dibromide (6). A solution of oxazole (0.26 g, 3.8 mmol) and α,α′-dibromo-*m*-xylene (0.5 g, 1.9 mmol) in THF (4 mL) was stirred at 120 °C for 24 h in a sealed tube, to give a white suspension. The supernatant was decanted off and the solid washed with THF (2 × 5 mL) and dried in vacuo, giving **6** as a white powder (yield 13%). ^{1}H NMR (DMSO-d_6): δ 5.70 (s, 2H, CH_2), 7.4−7.9 (m, 2H, Ph), 8.44 (s, 1H, CH=CH), 8.95 (s, 1H, CH=CH), 10.62 (s, 1H, NCHO). ^{13}C NMR (DMSO-d_6): δ 51.6 (CH_2), 121.0−156.0 (Ph and CH=CH), 163.5 (NCHO). Anal. Calcd for $C_{14}H_{14}Br_2N_2O_2$ (M = 402.0): C, 41.80; H, 3.48; N, 6.96. Found: C, 40.50; H, 3.85; N, 6.18.

[$PdI_2(C_4H_5NO)_2$] (1). A solution of *N*-methyloxazolium iodide (0.190 g, 0.90 mmol) and $Pd(OAc)_2$ (0.10 g, 0.45 mmol) in DMSO (4 mL) was heated at 100 °C for 2 h, and then the volatiles were removed in vacuo. The oily residue was washed with MeCN (2 × 1 mL) and dried in vacuo, giving **1** as a yellow powder (yield 78%). ^{1}H NMR (DMSO-d_6): δ 3.84 (s, 3H, CH_3), 7.79 (s, 1H, CH=CH), 8.46 (s, 1H, CH=CH). ^{13}C NMR (DMSO-d_6): δ 36.3 (CH_3), 122.4 and 145.7 (CH=CH), 190.3 (NCO). Anal. Calcd for $C_8H_{10}I_2N_2O_2Pd$ (M = 526.3): C, 18.25; H, 1.91; N, 5.32. Found: C, 18.02; H, 1.53; N, 5.05. X-ray diffraction quality crystals were grown by slow evaporation of an acetone solution.

[$PdBr_2(C_{10}H_9NO)_2$] (7). A solution of **2** (50 mg, 0.20 mmol) and $Pd(OAc)_2$ (23 mg, 0.10 mmol) in DMSO (4 mL) was heated at 100 °C for 2 h, and then the volatiles were removed in vacuo. The oily residue was washed with MeCN (2 × 1 mL) and dried in vacuo, giving **7** as a pale yellow powder (yield 56%). ^{1}H NMR (DMSO-d_6): δ 5.63 (s, 2H, CH_2), 7.41 (m, 5H, Ph), 7.75 (s, 1H, CH=CH), 8.50 (s, 1H, CH=CH). ^{13}C NMR (DMSO-d_6): δ 50.5 (CH_2), 120.0−146.0 (CH=CH and Ph), 181.0 (NCO). Anal. Calcd for $C_{20}H_{18}Br_2N_2O_2Pd$ (M = 584.4): C, 41.10; H, 3.08; N, 4.80. Found: C, 41.18; H, 3.27; N, 4.52.

[$PdBr_2(C_{10}H_8BrNO)_2$] (8). A solution of **3** (60 mg, 0.20 mmol) and $Pd(OAc)_2$ (23 mg, 0.10 mmol) in DMSO (4 mL) was heated at 100 °C for 2 h, and then the volatiles were removed in vacuo. The oily residue was washed with MeCN (2 × 1 mL) and dried in vacuo, giving **8** as a white powder (yield 53%). ^{1}H NMR (DMSO-d_6): δ 5.72 (s, 2H, CH_2), 7.0−7.7 (m, 4H, Ph), 7.90 (s, 1H, CH=CH), 8.60 (s, 1H, CH=CH). ^{13}C NMR (DMSO-d_6): δ 52.2(CH_2), 120.0−146.0 (CH=CH and Ph); the carbene carbon resonance was not detected. Anal. Calcd for $C_{20}H_{16}Br_4N_2O_2Pd$ (M = 742.2): C, 32.36; H, 2.15; N, 3.77. Found: C, 32.26; H, 1.97; N, 3.52.

[$PdBr_2$(*o*-$C_{14}H_{12}N_2O_2$)] (9). A solution of **5** (54 mg, 0.13 mmol) and $Pd(OAc)_2$ (30 mg, 0.13 mmol) in DMSO (4 mL) was heated at 100 °C for 2 h, and then the volatiles were removed in vacuo, giving **9** as a orange powder (yield 48%). ^{1}H NMR (DMSO-d_6): δ 5.20 (d, 1H, CH_2, $^2J_{HH}$ = 14 Hz), 6.55 (d, 1H, CH_2, $^2J_{HH}$ = 14 Hz), 7.35 (m, 1H, Ar), 7.78 (m, 1H, Ar), 7.98 (s, 1H, CH=CH), 8.32 (s, 1H, CH=CH). ^{13}C NMR (DMSO-d_6): δ 49.1 (CH_2), 121.0−147.0 (CH=CH and C Ar), 183.0 (NCO). Anal. Calcd for $C_{14}H_{12}Br_2N_2O_2Pd\cdot C_2H_6SO$ (M = 584.4): C, 32.88; H, 3.07; N, 4.79; S, 5.47. Found: C, 32.41; H, 3.08; N,

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4.48; S, 6.04. X-ray diffraction quality crystals were grown by slow evaporation of a DMSO solution.

[$PdBr_2$(*m*-$C_{14}H_{12}N_2O_2$)] (10). A solution of **6** (54 mg, 0.13 mmol) and $Pd(OAc)_2$ (30 mg, 0.13 mmol) in DMSO (4 mL) was heated at 100 °C for 2 h, and then the volatiles were removed in vacuo, giving as a brown paste. Subsequent treatment with acetonitrile (3 mL) followed by filtration and solvent evaporation yielded **10** as a yellow powder (yield 10%). ^{1}H NMR (DMSO-d_6): δ 5.74 (s, 2H, CH_2), 7.4−8.7 (m, 4H, CH=CH and Ar). Anal. Calcd for $C_{14}H_{12}Br_2N_2O_2Pd$ C_2H_6SO (M = 584.4): C, 32.88; H, 3.07; N, 4.79; S, 5.47; Pd, 18.21. Found: C, 29.55; H, 2.71; N, 3.66; S, 4.96; Pd, 12.10.

X-ray Crystallography. Crystals of **1** suitable for X-ray crystal structure determination were grown by slow evaporation of an acetone solution, lodged in Lindemann glass capillary, and centered on a four-circle Philips PW1100 diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å), following standard procedures at room temperature. There were no significant fluctuations of intensities other than those expected from Poisson statistics. All intensities were corrected for Lorentz−polarization and absorption.[10] The structures were solved by standard direct methods.[11] Refinement was carried out by full-matrix least-squares procedures (based on F_0^2) using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were located and refined isotropically, except those of the methyl group, which were placed in calculated positions with fixed isotropic thermal parameters ($1.2U_{equiv}$) of the parent carbon atom. For a total of 79 parameters, $R_w' = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2} = 0.078$, S = 1.174, and conventional $R = 0.031$, based on the F values of 1892 reflections having $I \geq 2\sigma(I)$. Structure refinement and final geometrical calculations were carried out with the SHELXL-97[12] program, implemented in the WinGX package.[13]

Crystals of **9** suitable for X-ray diffraction were grown by slow evaporation of a DMSO solution and mounted in perfluoro-ether oil on a glass fiber. Data collection was then carried out at 150 K on a Bruker/Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation, equipped with an Oxford Cryostream cooling apparatus. The data were corrected for Lorentz and polarization effects and for absorption using SORTAV.[14] Structure solution was achieved by direct methods[11] and refined by full-matrix least-squares on F^2 with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealized positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme that gave a relatively flat analysis of variance was introduced, and refinement continued until convergence was reached. For a total of 455 parameters, $R_w' = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2} = 0.0825$, S = 1.046, and conventional $R = 0.0451$, based on the F values of 8833 reflections having $I \geq 2\sigma(I)$. Structure refinement and final geometrical calculations were carried out with the SHELXL-97[12] program, while further geometrical analyses were carried out using PARST,[15] both implemented in the WinGX package.[13]

General Procedure for Heck Coupling Reaction. In a Schlenk tube evacuated and filled with nitrogen were placed the aryl halide (2.0 mmol), sodium acetate (200 mg, 2.4 mmol), and a solution of the required amount of complex in 4 mL of *N*-methylpyrrolidone.The resulting mixture was heated to 120 °C, after which the olefin (2.4 mmol) was added. The reaction mixture was further heated to 135 °C and stirred for 5 h. Yields were determined by GC on 0.4 mL of the reaction solution to which 9 μL of hexadecane as internal standard was added. The resulting solution was partitioned between 1 mL of dichloromethane and 5 mL of a 5% w/w aqueous $KHCO_3$ solution. GC analysis was performed on the resulting dichloromethane phase using a temperature program based on a 140 °C isotherm for 150 s followed by heating at 32 °C/min to 270 °C. The GC system was previously calibrated by determining the retention times and the response factors of the aryl halide reagents and of the reaction products.

Scheme 1. Synthesis of *N*-Methyloxazolin-2-ylidene Complex 1

1

Results and Discussion

Our approach to the preparation of oxazolin-2-ylidene palladium complexes is an extension of a synthetic strategy that has already proved useful for the preparation of imidazolin- and thiazolin-2-ylidene complexes,[6,16] namely, the direct synthesis of the complexes by reaction of oxazolium salts with palladium acetate; in this reaction, the carbene ligands are generated in situ via deprotonation by the acetate ligands, yielding the corresponding neutral dicarbene-dihalide palladium complexes. Our initial results proved that this strategy was indeed applicable to oxazolium substrates as well: reaction of 1 equiv of palladium acetate with 2 equiv of *N*-methyloxazolium iodide[9] in DMSO at 100 °C under vacuum (Scheme 1) produced the parent *N*-methyloxazolin-2-ylidene palladium complex **1** in good yield. The product is obtained as a yellow solid that can be safely handled in air and is stable for long periods also in solution.

Interestingly, the *trans* isomer of **1** is almost exclusively obtained under the reaction conditions employed. A similar result was reported by Calò et al. with *N*-methylbenzothiazolin-2-ylidene ligand precursors.[6a] In contrast *N*,*N*′-dimethylimidazolin-2-ylidene ligand precursors form the *cis* product under the same reaction conditions,[16,17] the *trans* isomer being predominantly obtained only in the case of much larger *N*-substituents on the carbene ligand precursor.[18,19] The related 1,4-dimethyltriazolin-5-ylidene ligand precursors represent a somewhat intermediate case, since they form the *cis* product, which is however readily converted to the *trans* one upon treatment with water.[20] The preference for one of the two geometries can be tentatively rationalized in

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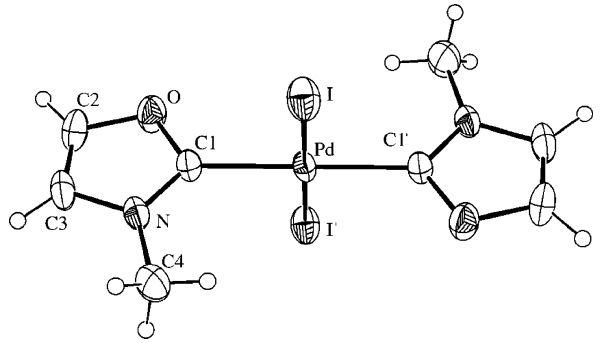
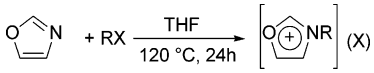


Figure 1. ORTEP view of the molecule *trans*-[$PdI_2(C_4H_5ON)_2$] (**1**) with the adopted numbering scheme. Relevant bond lengths (Å) and angles (deg): Pd−I 2.598(1), Pd−C(1) 2.012(4), C(1)−O 1.344(5), C(2)−O 1.387(5), C(1)−N 1.315(5), N−C(3), 1.405(5), C(2)−C(3) 1.301(8), N−C(4) 1.460(6), C(1)−Pd−I 90.4(1), O−C(1)−N 106.9(3), C(1)−O−C(2) 108.6(4), C(3)−N−C(1) 109.8(4).

Scheme 2. Synthesis of the *N*-Substituted Oxazolium Salts



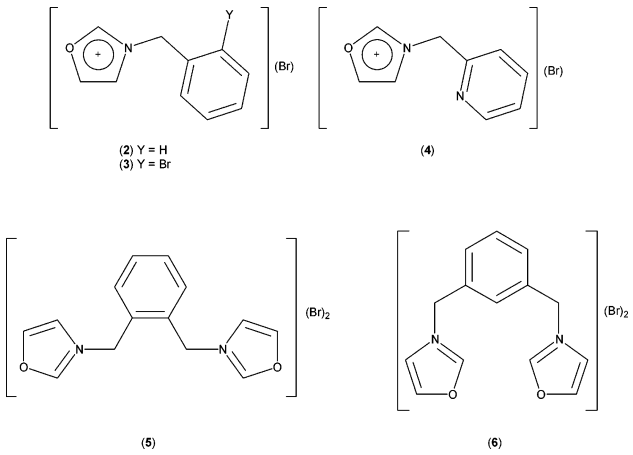
terms of differences in the antisymbiotic effect exerted by the carbene ligands on the ligand *trans* to them.[21] Although the *trans* isomer should be invariably preferred for steric reasons, the higher electron-donating ability of imidazolin-2-ylidene ligands, compared to oxazolin or benzothiazolin analogues, may end up favoring the *cis* product.

The ^{1}H NMR spectra of **1** exhibit signals that are mostly shifted slightly upfield from the values observed for the oxazolium salt reagent; furthermore, the $_{ox}C_2$−H signal is absent, as required. Correspondingly, the ^{13}C NMR spectrum shows the characteristic coordinated $_{ox}C_2$ signal at δ 190.3, well downfield from δ 155.8 in the oxazolium salt. The $_{ox}C_2$ signal lies at lower fields than the corresponding signal of the related *trans*-bis-imidazolin-2-ylidene-dialogeno palladium(II) complexes (δ 170−175),[18,19] probably as the consequence of the higher electronegativity of oxygen compared with nitrogen. On the other hand, in the corresponding benzothiazolin-2-ylidene complex the carbene carbon resonates at δ 210.5;[6a] in this case, weaker π donation from the third-row sulfur atom to the carbene carbon may explain the observed deshielding.

The solid state structure of **1** has been determined through standard X-ray diffraction analysis: the molecular structure shows a perfect *trans* orientation of the carbene ligands with the metal ion lying at an inversion center due to the crystallographic imposed C_i symmetry (Figure 1). The square planar coordination geometry around Pd is characterized by values of the Pd−C and Pd−I bond distances of 2.012(4) and 2.598(1) Å, respectively, consistent with literature data[18] for similar Pd(II) derivatives with coordinated carbene ligands. Interestingly, the C(2)−C(3) bond distance is found to be 1.301(8) Å, well below the value found in analogous imidazolin-2-ylidene complexes, which is about 1.33 Å.[18,19] This may indicate a lower degree of electronic delocalization in the oxazolin-2-ylidene ring as compared with the imidazoline one.

To widen the scope of our synthetic methodology, we set out to evaluate the range of oxazolium reagents that

Scheme 3. *N*-Benzyl Oxazolium Salts Prepared in the Present Work



can be efficiently prepared and used for the synthesis of the corresponding palladium complexes. We were unable to find in the literature examples of the preparation of simple *N*-substituted oxazolium salts apart from the *N*-methyl-substituted salt. Therefore, we prepared additional oxazolium salts through the alkylation of oxazole with alkyl halides (Scheme 2).

This preparation method presents some limitations, due to the low nucleophilicity of the oxazole nitrogen atom. For example, we have been unable to synthesize the *N*-propyl oxazolium salt starting from reagents such as bromopropane or 1-chloro-3-iodopropane, probably because of the relatively low electrophilicity of the employed reagents. On the other hand, the reaction appears to be relatively easy if sufficiently activated electrophilic reagents are used; in this way, we have succeeded in preparing a series of *N*-benzylic oxazolium and bis(oxazolium) salts by reaction of benzyl halides with oxazole (Scheme 3). The resulting salts are air and moisture stable except for **4**, whose proton NMR changes with time, indicating a progressive decomposition of the salt. Moreover, the bis(oxazolium) salts **5** and **6** are rather hygroscopic solids, and this leads to poor elemental analyses. Nevertheless, all products are spectroscopically pure in ^{1}H and ^{13}C NMR and exhibit the expected signals for the heterocyclic ring; the $_{ox}C_2$−H signal moves downfield upon benzylation, indicating a greater acidity of that proton.

The suitability of the *N*-benzyl oxazolium salts to serve as carbene ligand precursors was subsequently tested by reacting them with $Pd(OAc)_2$ under the same experimental conditions already employed in the synthesis of **1**. This synthetic methodology was found to proceed well with most of the *N*-benzyl oxazolium salts, the only exception being **4**, whose low stability in solution apparently prevented successful reaction. Thus, dicarbene palladium complexes **7**−**10** (Scheme 4) were prepared via this synthetic route. All complexes were obtained in about 50% yield and gave satisfactoy elementary analyses, with the exception of **10**, which was isolated in only 10% yield and, although appearing spectroscopically pure, did not yield satisfactory elemental analysis even by allowing for different amounts of

(21) See for example: Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Commun.* **2003**, 278.

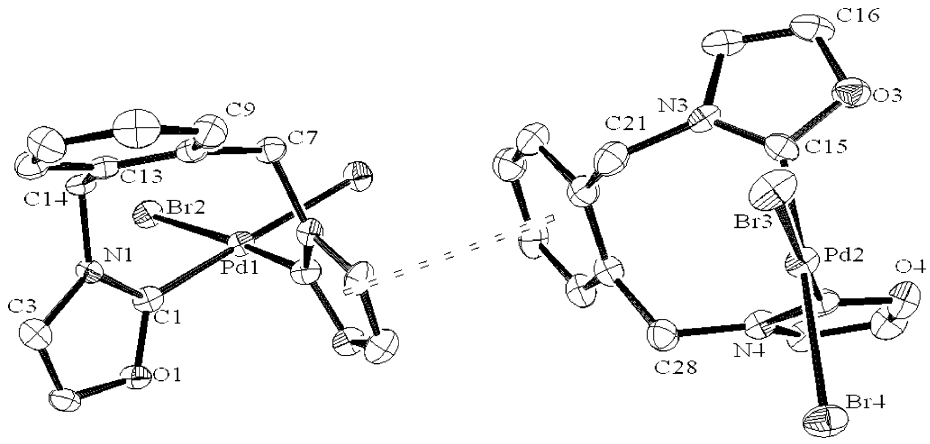
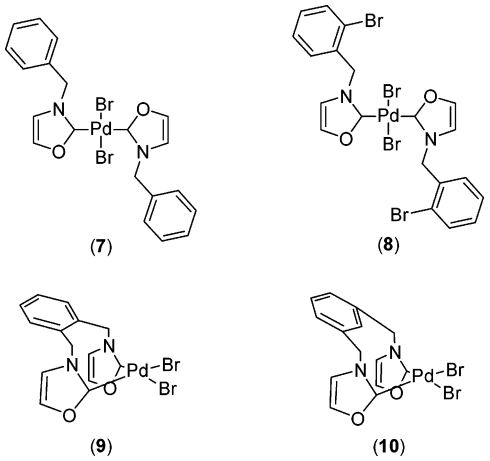


Figure 2. ORTEP view of the molecules *cis*-[$PdBr_2(C_{14}H_{12}N_2O_2)$] (**9**) with the adopted numbering scheme and the intermolecular $\pi-\pi$ interaction. Hydrogen atoms and the solvent molecules have been removed for clarity. Relevant bond lengths (Å) and angles (deg): C(1)−Pd(1) 1.964(5), C(1)−O(1) 1.337(6), C(1)−N(1) 1.315(6), Br(2)−Pd(1) 2.4743(6), C(15)−Pd(2) 1.961(5), C(15)−N(3) 1.325(6), C(15)−O(3) 1.342(6), Br(3)−Pd(2) 2.4794(7), Ctd−Ctd 3.689. C(4)−Pd(1)−C(1) 84.2-(2), Br(4)−Pd(2)−Br(3) 95.36(2), Br(2)−Pd(1)−Br(1) 95.13(2), C(18)−Pd(2)−C(15) 83.2(2).

Scheme 4. *N*-Benzyloxazolin-2-ylidene Complexes Prepared in the Present Work



DMSO as solvating molecules. Possibly the presence of some water can account also in this case for the observed results.

The ^1H NMR spectra of the complexes exhibit signals that are mostly shifted slightly upfield from the values observed for the oxazolium salt; furthermore, the $_{ox}C_2-H$ signal is absent as required. Correspondingly, the ^{13}C NMR spectra show the characteristic coordinated $_{ox}C_2$ signal at δ ca. 180, well downfield from δ ca. 150 in the oxazolium salt. The methylene protons in complex **9** are nonequivalent, with two doublets (5.20 and 6.56 ppm) exhibiting a geminal coupling costant of 14 Hz. In contrast to **9**, the ^1H NMR of **10** shows only very broad signals. Consequently, it was not possible to obtain ^{13}C NMR spectra. Cavell et al. have previously reported bis-imidazolin-2-ylidene complexes fully analogous to **9** and **10** and found exactly the same NMR features.[19] Unfortunately, the limited solubility of complexes **9** and **10** in most common solvents prevented further characterization by, for example, low-temperature NMR. No evidence of cyclometalation was noted for complex **10** despite the rather harsh reaction conditions employed.

The solid state structure of **9** (Figure 2) includes two complex molecules and two solvent (DMSO) molecules in the asymmetric unit. The structure shows the expected *cis* orientation of the chelating bis-carbene ligand about the metal center. The distorted square planar arrangement is illustrated by the small C−Pd−C bite angles, averaging 83.7°, and a concomitant opening out of the Br−Pd−Br bond angles to 93.67°. The Pd−C bond distances to the chelating ligand are significantly shorter, averaging 2.04 Å compared to the average Pd−Br bond of 2.43 Å. This shortening is most likely due to the *trans* influence of the bromides.[22] Although the backbone carbon−carbon distances within the oxazolin-2-ylidene rings for **9** are also shorter than average, ranging from 1.313(8) Å for C(16)−C(17) to 1.323(8) Å for C(2)−C(3), the slightly longer distances compared to **1** indicate greater electronic delocalization within the oxazolin-2-ylidene ring. Within the molecular structure, the benzyl ring of the chelating ligand lies almost perpendicular to the plane of the oxazolin-2-ylidene rings. For example, the dihedral angle of C(1)−N(1)−C(3)−C(7)−C(8)−C(13)−C(14) is 88.41(33)°. This angle is largely dictated by the intermolecular $\pi-\pi$ interactions between the benzyl ring and a neighboring oxazolin-2-ylidene ring with centroid−centroid distances of 3.689 Å (see Figure 2).

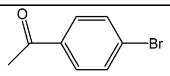
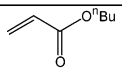
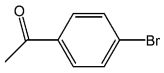
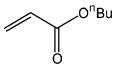
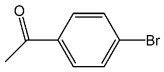
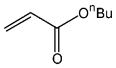
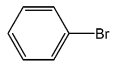
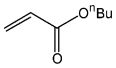
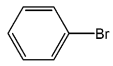
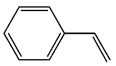
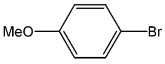
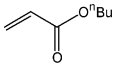
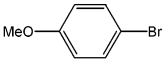
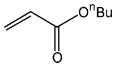
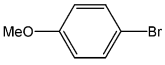
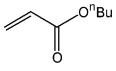
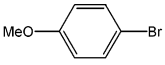
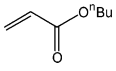
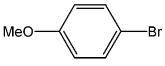
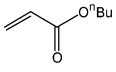
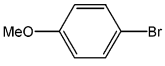
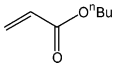
The NHC complexes prepared in this work have been employed as catalysts for the arylation of olefins with aryl halides (Heck reaction).[23] The Heck reaction was employed as a standard test reaction to probe the reactivity of these new palladium complexes; in fact, Pd-carbene complexes are among the most active catalysts for this reaction.[2b,c,19] The results obtained with our complexes are reported in Table 1.

Complex **1** diplays an excellent catalytic activity with activated aryl bromides, reaching TOF values up to 2×10^4 h^{-1} in the absence of any other promoter (Table 1, entry 3). The catalytic activity of the complex is lower but still significant with unactivated and deactivated aryl bromides; the catalytic activity can be further enhanced by addition of 1 equiv (with respect to the aryl halide) of tetrabutylammonium bromide to the reaction mixture (Table 1, entries 4−7). Further tests were

(22) Gründemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2163.

(23) (a) Bräse, S.; de Meijere, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederichs, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; pp 99−166. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

Table 1. Heck Reactions Catalyzed by Complexes 1 and 7−10[c]

Entry	Catalyst	Aryl halide	Olefin	mol% catalyst	Yield (%)	TON	TOF (h^{-1})
1	(**1**)			0.05	100	2000	400
2	(**1**)			0.005	100	20000	4000
3	(**1**)			0.001	97	97000	19400
4	(**1**)			0.05	14	280	56
5	(**1**)			0.05	20[a]	400	80
6	(**1**)			0.05	26	520	104
7	(**1**)			0.05	42[b]	840	168
8	(**7**)			0.05	38	760	152
9	(**8**)			0.05	87	1740	348
10	(**9**)			0.05	85	1700	340
11	(**10**)			0.05	100	2000	400

[a] Yield of *trans*-stilbene; 1% *cis*-stilbene is also formed as coproduct. [b] Reaction with 1 equiv of tetrabutylammonium bromide. [c] Reaction conditions: see the Experimental Section.

undertaken with complexes **7**−**10** in the reaction between the deactivated aryl bromide *p*-bromoanisole and *n*-butyl acrylate. Remarkably, these complexes, and in particular complexes **8**−**10**, display a greater activity than complex **1**. On the whole, the catalytic activity of bis-oxazolin-2-ylidene complexes appears higher than that of the closely related bis-imidazolin-2-ylidene complex reported by Herrmann[17] under similar reaction conditions and is comparable with that exhibited by Calò's bis-benzothiazolin-2-ylidene complex in molten tetrabutylammonium bromide.[6a]

We have also tested the reactivity of our complexes with activated aryl chlorides such as 4-chloroacetophenone; the recorded catalytic activity is however quite low (yield ca. 5% for all catalysts tested under the reaction conditions reported in Table 1).

In conclusion, we have developed a simple, direct method for the synthesis of *N*-benzylic oxazolium salts and for the related *N*-substituted-oxazolin-2-ylidene complexes of palladium. The resulting complexes exhibit high catalytic activity in the Heck reaction of aryl bromides. We are currently extending this synthetic strategy to different metal centers. The determination of the catalytic activity of such complexes in other synthetically useful reactions is also underway.

Supporting Information Available: Table of crystal data, collection, and refinement parameters for complexes **1** and **9**. Crystallographic data, in CIF format, for the structure analyses of **1** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050222B