High-Yield Syntheses of Sterically Demanding Bis(N-heterocyclic carbene) Complexes of Palladium†,‡

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The synthesis of bis(N-heterocyclic carbene) chelates of formula [*cis*-E{N(H)C=C(H)N-(R)C}$_2$PdX$_2$] (E = spacer linkage; R = alkyl, aryl; X = halide) is presented via improved high-yielding, air-stable procedures (for E = CH_2). A detailed study of the intermediates involved in the preparation of [*cis*-CH_2{N(H)C=C(H)N(t-Bu)C}$_2$PdX$_2$] (X = Br, I) provide evidence for the difficulty in extending our synthetic procedures to include chelates of different ring sizes and also in preparing the analogous nickel complexes.

1. Introduction

In recent publications we have established N-heterocycle-based carbene complexes[1] of palladium to be efficient catalysts for various C−C and C−N coupling reactions[2−4] and for the copolymerization of ethene and CO.[5] We have also attempted to prepare cationic chelating dicarbene palladium and nickel[6] complexes that were active in the polymerization of olefins. For this application, we felt it necessary to focus our efforts on preparing chelating bis(N-heterocyclic carbene) complexes featuring bulky N substituents for the seemingly established reasons which have become set in place over the previous 2 years in order to achieve success in this field.[7]

Herein we report a detailed study of the preparation of N-heterocyclic carbene chelates of formula [*cis*-CH_2-{N(H)C=C(H)N(t-Bu)C}$_2$PdX$_2$] (X = Br, I), which has led to a greatly improved, general synthetic method for the preparation of a large range of analogous complexes that were previously inaccessible. Complexes featuring primary, secondary, and tertiary alkyl substituents, as well as aryl substituents of minimal and intermediate steric requirements, can now be prepared. We have demonstrated the general synthetic applicability of this procedure by preparing analogous examples based on benzimidazolin-2-ylidene and triazolin-2-ylidene heterocyclic ring systems in addition to the examples based on the imidazolin-2-ylidene heterocyclic ring system. We also discuss the apparent limitations of our synthetic procedures based on a detailed study of the intermediates involved during the course of the reaction.

2. Experimental Section

2.1. General Procedures. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. Methanol was dried over Mg, and dichloromethane and acetonitrile were dried over CaH_2 and distilled prior to use using conventional procedures. Other solvents were used as received. All the described procedures herein do not require the use of dried solvents; yields quoted are for reactions in technical grade solvents which were used as received. $Pd(OAc)_2$ was obtained from Degussa AG. Other chemicals were obtained from Aldrich and used as received. 1-*tert*-Butylimidazole (**1**) (and other 1-alkylimidazoles) was prepared according to the literature.[8] 1,1′-disubstituted-3,3′-methylenediimidazolium dihalides were prepared by modifications of our existing literature procedures in either tetrahydrofuran or toluene.[5] ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX 400 spectrometer in $CDCl_3$, d_6-DMSO, and D_2O and referenced to the residual ^{1}H resonances of the solvents. Elemental analyses were performed by the microanalytical laboratory at our institute. Melting points were

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(1) Herrmann, W. A.; Köcher, C. *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(2) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem.* **1995**, *107*, 2602; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371. For a theoretical study on this system, see: Albert, K.; Gisdakis, P.; Rösch, N. *Organometallics* **1998**, *17*, 1608.

(3) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93.

(4) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23.

(5) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239.

(6) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *575*, 80.

(7) For initial papers in the field, see: (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (c) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. For theoretical interpretations relating to this matter, see: (d) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177. (e) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581.

(8) Gridnev, A. A.; Mihaltseva, I. M. *Synth. Commun.* **1994**, *24*, 1547.

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determined in glass capillaries under air. IR spectra were recorded on a FT-IR Perkin-Elmer 1680 spectrometer. Mass spectra were recorded on a Varian MAT 311a spectrometer using FAB ionization (xenon/*p*-nitrobenzyl alcohol matrix). GC/MS spectra were obtained on a Hewlett-Packard 5890 instrument. The typical procedure for conducting in situ NMR experiments to follow the course of the carbene complex syntheses involved sampling (ca. 10 mg) a freshly prepared, homogeneously mixed larger portion of the appropriate diimidazolium dihalide salt and $Pd(OAc)_2$ to ensure the correct stoichiometric ratio of the reagents was obtained, which was then dissolved in the deuterated solvent immediately prior to obtaining the spectra.

2.2. Synthesis of 1,1′-Di-*tert*-butyl-3,3′-methylenediimidazolium Dibromide (2a). A stirred THF solution (10 mL) of 1-*tert*-butylimidazole (**1**; 2.00 g, 16.1 mmol) and CH_2Br_2 (1.74 g, 10.0 mmol) was heated at 150 °C for 2 days in a sealed tube to yield a white powder of the product, which was collected, washed with THF, and dried in vacuo (2.65 g, 78%). Mp: >300 °C. ^{1}H NMR (400 MHz, D_2O): δ 1.55 (18 H, s, Me), 6.47 (2 H, s, CH_2), 7.62 (2 H, s, CH(imid)), 7.68 (2 H, s, CH(imid)) (remaining N−CH−N imid proton exchanged with D).

2.3. Synthesis of 1,1′-Di-*tert*-butyl-3,3′-methylenediimidazolium Diiodide (2b). This compound was prepared by following the above procedure (section 2.2) using CH_2I_2. Yield: 73%. Mp: >300 °C. ^{1}H NMR (400 MHz, D_2O): δ 1.43 (18 H, s, Me), 6.34 (2 H, s, CH_2), 7.51 (2 H, s, CH(imid)), 7.52 (2 H, s, CH(imid)), (remaining N−CH−N imid proton exchanged with D).

2.4. Synthesis of [1,1′-Di-*tert*-butyl-3,3′-methylene(imidazolin-2-ylidene)imidazolium]palladium(II) Acetate Dibromide (3a). A stirred DMSO solution (5.0 mL) of 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium dibromide (**2a**; 188 mg, 0.45 mmol) and $Pd(OAc)_2$ (100 mg, 0.45 mmol) was heated at 50 °C for 4 h, during which time the reaction solution had bleached to a paler orange. The remaining DMSO was then removed in vacuo at 50 °C to give a yellow solid, which was washed with DCM to give the product as a pale yellow solid that could be recrystallized from acetonitrile (218 mg, 92%). Mp: 230 °C dec. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.63 (9 H, s, Me), 1.93 (9 H, s, Me), 1.72 (3 H, s, OAc), 7.14 (2 H, s, CH_2), 7.86 (1 H, s, CH(imid)), 7.97 (1 H, s, CH(imid)), 8.01 (1 H, s, CH(imid)), 8.12 (1 H, s, CH(imid)), 11.41 (1 H, s, CH(imid)).

2.5. Synthesis of [1,1′-Di-*tert*-butyl-3,3′-methylene(imidazolin-2-ylidene)imidazolium]palladium(II) Acetate Diiodide (3b). This complex was prepared by following the above procedure (section 2.4) using 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium diiodide (**2b**). Yield: 87%. Mp: 210 °C dec. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.63 (9 H, s, Me), 1.88 (9 H, s, Me), 1.70 (3 H, s, OAc), 7.01 (2 H, s, CH_2), 7.73 (1 H, s, CH(imid)), 7.98 (1 H, s, CH(imid)), 7.98 (1 H, s, CH(imid)), 8.05 (1 H, s, CH(imid)), 11.16 (1 H, s, CH(imid)).

2.6. Synthesis of [1,1′-Di-*tert*-butyl-3,3′-methylene(imidazolin-2-ylidene)imidazolium]palladium(II) Triiodide (4b). A stirred DMSO solution (5.0 mL) of 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium dibromide (**2a**; 188 mg, 0.45 mmol) and $Pd(OAc)_2$ (100 mg, 0.45 mmol) was heated at 50 °C for 4 h, during which time the reaction solution had bleached to a paler orange. At this point an excess of NaI (5 g, 33 mmol) was added and heating continued for a further 1 h. The remaining DMSO was then removed in vacuo at 50 °C to give an orange solid, which was dissolved in an acetonitrile/water mixture (20 mL/20 mL). The solution was heated at 80 °C for 10 min followed by removal of the acetonitrile in vacuo to precipitate the complex as a brown solid, which was washed with DCM to give the product as a red solid which could be recrystallized from acetonitrile (280 mg, 84%). Mp: 226 °C dec. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.63 (9 H, s, Me), 1.87 (9 H, s, Me), 6.79 (2 H, s, CH_2), 7.97 (1 H, m, CH(imid)), 7.97 (1 H, m, CH(imid)), 8.01 (1 H, m, CH(imid)), 8.13 (1 H, m, CH(imid)), 9.64 (1 H, m, CH(imid)). ^{13}C NMR (100.53 MHz, d_6-DMSO): δ 29.3 (Me), 31.5 (Me), 59.9 (*C*Me$_3$), 60.5 (*C*Me$_3$), 62.7 (CH_2), 121.6, 122.5, 123.7, 124.7, 136.7 (4 × CH(imid) (carbene C not visible). Anal. Found: C, 25.87; H, 3.58; N, 9.00. Calcd for $C_{15}H_{25}N_4I_3Pd{\cdot}CH_3CN$: C, 25.86; H, 3.57; N, 8.87.

2.7. Synthesis of (1,1′-Di-*tert*-butyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) Dibromide (5a). A stirred DMSO solution (5.0 mL) of 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium dibromide (**2a**; 188 mg, 0.45 mmol) and $Pd(OAc)_2$ (100 mg, 0.45 mmol) was heated at 50 °C for 4 h, after which the reaction mixture was heated at reflux for a further 20 min to yield a pale yellow solution. The remaining DMSO was then removed in vacuo at 80 °C to give an orange solid, which was washed with DCM to give the product as a pale yellow solid that could be recrystallized from acetonitrile (211 mg, 90%). Mp: 270 °C dec. ^{1}H NMR (400 MHz, 100 °C, d_6-DMSO): δ 1.83 (18 H, br s, Me), 6.20, 6.60 (2 H, br AB, CH_2), 7.50−7.70 (4 H, br, CH(imid)). Anal. Found: C, 36.26; H, 4.88; N, 12.62. Calcd for $C_{15}H_{24}N_4Br_2Pd{\cdot}CH_3CN$: C, 35.97; H, 4.79; N, 12.34.

2.8. Synthesis of (1,1′-Di-*tert*-butyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) Diiodide (5b). This complex was prepared by following the above procedure (section 2.7) using 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium diiodide (**2b**). Yield: 92%. Mp: 270 °C dec. ^{1}H NMR (400 MHz, 100 °C, d_6-DMSO): δ 1.83 (18 H, s, Me), 6.30, 6.60 (2 H, AB, $^2J_{HH}$ = 12.8 Hz, CH_2), 7.56 (2 H, br s, CH(imid)), 7.68 (2 H, br. s, CH(imid)). Anal. Found: C, 31.22; H, 4.19; N, 10.86. Calcd for $C_{15}H_{24}N_4I_2Pd{\cdot}CH_3CN$: C, 30.86; H, 4.11; N, 10.58.

Method B. A stirred DMSO solution (5.0 mL) of 1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium dibromide (**2a**; 188 mg, 0.45 mmol) and $Pd(OAc)_2$ (100 mg, 0.45 mmol) was heated at 50 °C for 4 h, after which the reaction mixture was heated at reflux for a further 20 min to yield a pale yellow solution. At this point an excess of NaI (5 g, 33 mmol) was added and the solution heated at 50 °C for a further 1 h. The remaining DMSO was then removed in vacuo at 80 °C to give an orange solid, which was dissolved in an acetonitrile/water mixture (20 mL/20 mL). The solution was heated at 80 °C for 10 min followed by removal of the acetonitrile in vacuo to precipitate the complex as an orange solid, which was washed with DCM to give the product as a yellow solid that could be recrystallized from acetonitrile (246 mg, 89%). The physical, analytical, and spectroscopic properties of the complex were identical with those obtained above. Anal. Found: I, 48.61. Calcd for $C_{15}H_{24}N_4I_2Pd{\cdot}CH_3CN$: Br, 0.0; I, 48.22.

Method C. A stirred DMSO solution (5.0 mL) of [1,1′-di-*tert*-butyl-3,3′-methylene(imidazolin-2-ylidene)imidazolium]-palladium(II) triiodide (**4b**; 100 mg, 0.13 mmol) and anhydrous NaOAc (1 g, 12 mmol) was heated at reflux for 20 min. At this point an excess of NaI (5 g, 33 mmol) was added and the solution heated at 50 °C for a further 1 h. The remaining DMSO was then removed in vacuo at 80 °C to give an orange solid, which was dissolved in an acetonitrile/water mixture (20 mL/20 mL). The solution was heated at 80 °C for 10 min followed by removal of the acetonitrile in vacuo to precipitate the complex as an orange solid, which was washed with DCM to give the product as a yellow solid that could be recrystallized from acetonitrile (77 mg, 93%). The physical, analytical, and spectroscopic properties of the complex were identical with those obtained above.

2.9. Structure Determinations for Compounds 3b, 4b, and 5b. 3b: $C_{17}H_{28}N_4I_2O_2Pd$, M_r = 680.63, monoclinic, space group $P2_1/n$ (No. 14), a = 7.8058(3) Å, b = 30.126(2) Å, c = 9.906(6) Å, β = 103.543(3)°, U = 2264.8(14) Å^3, Z = 4, D_{calcd} = 1.996 g cm^{-3}, T = 100 K, F(000) = 1304, monochromated Mo Kα radiation, λ = 0.710 73 Å, μ = 3.563 mm^{-1}. **4b**: $C_{15}H_{25}N_4I_3Pd{\cdot}CH_3CN$, M_r = 789.54, monoclinic, space group $P2_1$ (No. 4), a = 9.8088(2) Å, b = 10.7198(4) Å, c = 12.7248(4) Å, β = 108.249(2)°, U = 1270.70(7) Å^3, Z = 2, D_{calcd} = 2.064 g cm^{-3}, T = 100 K, F(000) = 740, monochromated Mo Kα radiation, λ = 0.710 73 Å, μ = 4.385 mm^{-1}. **5b**: $C_{15}H_{24}N_4I_2Pd{\cdot}CH_3CN$, M_r =

661.64, orthorhombic, space group *Pnma* (No. 62), $a = 13.5508(2)$ Å, $b = 16.8104(2)$ Å, $c = 10.13580(10)$ Å, $U = 2308.88(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.903$ g cm^{-3}, $T = 100$ K, $F(000) = 1264$, monochromated Mo Kα radiation, $\lambda = 0.710\ 73$ Å, $\mu = 3.487$ mm^{-1}.

Crystals of **3b**, **4b**, and **5b** suitable for X-ray structure determination were grown by slow evaporation of acetonitrile solutions at room temperature and mounted in glass capillaries for data collection. Data were collected on a Nonius KappaCCD detection system at 100 K ($\theta_{min}-\theta_{max} = 2.4-26.4°$). A total of 3963 (**3b**), 2529 (5 suppressed) (**4b**), and 2422 (9 suppressed) (**5b**) unique reflections were measured, and 2865 (**3b**), 2515 (**4b**), and 2196 (**5b**) were considered observed ($F_o > 4\sigma(F_o)$) (R_{int} = 0.000 (**3b**), 0.000 (**4b**), 0.0131 (**5b**)) and used in the full-matrix least-squares refinement. Data were corrected for extinction in the case of complex **5b** (coefficient 0.0037(3)). Preliminary positions of heavy atoms were found by Patterson methods,[9] and the positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotopic least-squares refinement.[10] The PLATON program was used for the molecular projection diagrams.[11] Anisotropic thermal parameters were refined for all non-hydrogen atoms in the structure determinations. Hydrogen atom positions were calculated and constrained at estimated values (C−H = 0.93, 0.97, and 0.96 Å for the sp^2, methylene, and methyl hydrogens, respectively) for complexes **4b** and **5b**. Hydrogen atom positions for complex **3b** were located in successive Fourier difference maps and positionally refined. Temperature factors for hydrogen atoms of all three complexes were estimated at 1.2, 1.2, and 1.5 times the U_{ii}-(average) value of the attached carbon atom for sp^2, methylene, and methyl hydrogen atoms, respectively. The final residuals (for observed data, $F_o > 4\sigma(F_o)$) were R1 = 0.0356 (**3b**), 0.0371 (**4b**), and 0.0267 (**5b**) and wR2 = 0.0660 (**3b**), 0.1025 (**4b**), and 0.0735 (**5b**) for 320 (**3b**), 236 (**4b**, one restraint). and 123 (**5b**) parameters, with $s = 0.970$ (**3b**), 1.122 (**4b**), and 1.063 (**5b**), and a final difference map had extreme values of 0.755 and −0.827 (**3b**), 1.271 and −1.315 (**4b**), and 0.881 and −0.881 (**5b**) e Å^{-3}. The refined Flack parameter for complex **4b** was 0.07-(5). Non-hydrogen atom coordinates and isotropic thermal parameters are presented in the Supporting Information, and selected structural parameters are presented in Tables 1−3 . Further details of the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre.

Table 1. Selected Structural Parameters for [1,1′-di-*tert*-Butyl-3,3′-methylene(imidazolium)imidazolin-2-ylidene]palladium(II) Acetate *trans*-Diiodide (3b)

Bond Distances (Å)			
Pd(1)−C(1)	1.953(5)	C(10)−N(11)	1.457(7)
Pd(1)−O(1)	2.088(4)	N(11)−C(12)	1.326(6)
Pd(1)−I(1)	2.610(2)	N(11)−C(15)	1.387(6)
Pd(1)−I(2)	2.628(2)	C(12)−N(13)	1.319(6)
C(1)−N(2)	1.338(6)	C(12)−H(12)	0.89(5)
C(1)−N(5)	1.356(6)	N(13)−C(14)	1.378(6)
N(2)−C(3)	1.389(7)	N(13)−C(16)	1.510(6)
N(2)−C(6)	1.513(7)	C(14)−C(15)	1.338(8)
C(3)−C(4)	1.330(8)	C(14)−H(14)	0.89(5)
C(3)−H(3)	0.93(5)	C(15)−H(15)	0.87(5)
C(4)−N(5)	1.372(7)	C(20)−O(1)	1.183(5)
C(4)−H(4)	0.73(5)	C(20)−O(2)	1.285(5)
N(5)−C(10)	1.455(7)	C(20)−C(21)	1.568(7)

Bond Angles (deg)			
C(1)−Pd(1)−O(1)	173.6(2)	N(5)−C(10)−N(11)	112.6(5)
C(1)−Pd(1)−I(1)	86.1(2)	C(12)−N(11)−C(15)	108.8(4)
O(1)−Pd(1)−I(1)	89.18(11)	C(12)−N(11)−C(10)	126.2(4)
C(1)−Pd(1)−I(2)	90.0(2)	C(15)−N(11)−C(10)	125.0(5)
O(1)−Pd(1)−I(2)	95.04(11)	N(13)−C(12)−N(11)	108.7(5)
I(1)−Pd(1)−I(2)	174.51(2)	C(12)−N(13)−C(14)	108.3(5)
N(2)−C(1)−N(5)	105.2(4)	C(12)−N(13)−C(16)	128.0(4)
N(2)−C(1)−Pd(1)	135.5(4)	C(14)−N(13)−C(16)	123.6(4)
N(5)−C(1)−Pd(1)	118.9(4)	C(15)−C(14)−N(13)	108.0(5)
C(1)−N(2)−C(3)	110.5(4)	C(14)−C(15)−N(11)	106.1(5)
C(1)−N(2)−C(6)	128.9(4)	C(14)−C(15)−H(15)	134(4)
C(3)−N(2)−C(6)	120.6(4)	N(11)−C(15)−H(15)	119(4)
C(4)−C(3)−N(2)	106.6(5)	O(1)−C(20)−O(2)	130.1(4)
C(3)−C(4)−N(5)	107.5(5)	O(1)−C(20)−C(21)	116.4(4)
C(1)−N(5)−C(4)	110.2(5)	O(2)−C(20)−C(21)	113.3(5)
C(1)−N(5)−C(10)	125.6(4)	C(20)−O(1)−Pd(1)	113.7(3)
C(4)−N(5)−C(10)	124.2(5)		

Table 2. Selected Structural Parameters for [1,1′-Di-*tert*-butyl-3,3′-methylene(imidazolium)imidazolin-2-ylidene]palladium(II) Triiodide−Acetonitrile (4b)

Bond Distances (Å)			
Pd(1)−C(1)	1.990(9)	C(4)−N(5)	1.376(13)
Pd(1)−I(1)	2.6235(8)	N(5)−C(10)	1.438(12)
Pd(1)−I(2)	2.6258(8)	C(10)−N(11)	1.471(14)
Pd(1)−I(3)	2.6878(11)	N(11)−C(12)	1.329(11)
C(1)−N(2)	1.346(12)	N(11)−C(15)	1.405(13)
C(1)−N(5)	1.373(11)	C(12)−N(13)	1.324(13)
N(2)−C(3)	1.387(13)	N(13)−C(14)	1.374(12)
N(2)−C(6)	1.526(12)	N(13)−C(16)	1.531(11)
C(3)−C(4)	1.33(2)	C(14)−C(15)	1.34(2)

Bond Angles (deg)			
C(1)−Pd(1)−I(1)	86.7(3)	C(4)−N(5)−C(1)	110.6(8)
C(1)−Pd(1)−I(2)	86.6(3)	C(4)−N(5)−C(10)	125.1(8)
I(1)−Pd(1)−I(2)	173.13(3)	C(1)−N(5)−C(10)	124.3(8)
C(1)−Pd(1)−I(3)	178.6(2)	N(5)−C(10)−N(11)	110.6(8)
I(1)−Pd(1)−I(3)	93.09(3)	C(12)−N(11)−C(15)	108.6(8)
I(2)−Pd(1)−I(3)	93.51(3)	C(12)−N(11)−C(10)	124.9(8)
N(2)−C(1)−N(5)	104.6(8)	C(15)−N(11)−C(10)	126.3(7)
N(2)−C(1)−Pd(1)	133.1(7)	N(13)−C(12)−N(11)	108.5(8)
N(5)−C(1)−Pd(1)	122.2(6)	C(12)−N(13)−C(14)	108.6(8)
C(1)−N(2)−C(3)	110.4(8)	C(12)−N(13)−C(16)	125.7(8)
C(1)−N(2)−C(6)	129.8(8)	C(14)−N(13)−C(16)	125.7(8)
C(3)−N(2)−C(6)	119.8(8)	C(15)−C(14)−N(13)	108.5(9)
C(4)−C(3)−N(2)	107.6(8)	C(14)−C(15)−N(11)	105.8(8)
C(3)−C(4)−N(5)	106.8(9)		

3. Results and Discussion

3.1. Detailed Investigation of the Synthesis of *tert*-Butyl-Substituted Carbene Complexes. The optimized reaction conditions for the preparation of the palladium carbene complexes **5** are presented in Scheme 1. Initial attempts to prepare complexes **5a** and **5b** by utilizing our previously published procedure involving reaction in tetrahydrofuran solution[2] resulted in mixtures of complexes **3**−**5** in yields less than ca. 10%, the major product being material arising from unidentified decomposition pathways along with a substantial amount of palladium black formation.[12] To obtain near-quantitative preparations of complexes **5**, we found it necessary to use mild reaction conditions of 50 °C in DMSO solution for a period of 4 h to fully convert the diimidazolium dihalide salts into the intermediate palladium mono(carbene) complexes **3**. After this time, the complexes **3** can be heated to reflux in DMSO for a period of 20 min in order to deprotonate the remaining imidazolium pendant arm of complexes **3** in the 2′-position to yield the chelating bis(carbene)palladium dihalide

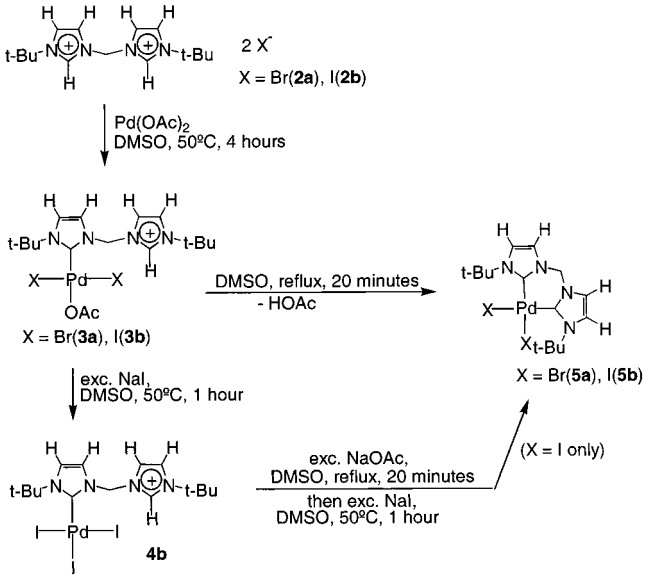
(9) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(10) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1993.
(11) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(12) A decomposition pathway for cationic (imidazolin-2-ylidene)-palladium methyl complexes has recently been recognized, whereby a 2-alkylimidazolium salt and reduced palladium(0) species are formed: McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165. We report no evidence for the formation of such species here during our synthetic procedure.

Table 3. Selected Structural Parameters for (1,1′-Di-*tert*-butyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) Diiodide−Acetonitrile (5b)

Bond Distances (Å)			
Pd(1)−C(1)	2.004(3)	C(3)−C(4)	1.325(5)
Pd(1)−I(1)	2.6694(3)	C(4)−N(5)	1.396(4)
C(1)−N(5)	1.350(3)	N(5)−C(7)	1.507(4)
C(1)−N(2)	1.364(3)	C(7)−C(10)	1.520(5)
N(2)−C(3)	1.376(4)	C(7)−C(9)	1.532(5)
N(2)−C(6)	1.456(3)	C(7)−C(8)	1.532(5)
Bond Angles (deg)[a]			
C(1)*−Pd(1)−C(1)	83.3(2)	C(1)−N(2)−C(6)	121.5(2)
C(1)*−Pd(1)−I(1)	91.65(7)	C(3)−N(2)−C(6)	126.7(3)
C(1)−Pd(1)−I(1)	167.27(8)	C(4)−C(3)−N(2)	106.2(3)
I(1)−Pd(1)−I(1)*	90.79(1)	C(3)−C(4)−N(5)	108.4(3)
N(5)−C(1)−N(2)	104.9(2)	C(1)−N(5)−C(4)	109.2(2)
N(5)−C(1)−Pd(1)	141.2(2)	C(1)−N(5)−C(7)	129.2(2)
N(2)−C(1)−Pd(1)	113.8(2)	C(4)−N(5)−C(7)	121.6(2)
C(1)−N(2)−C(3)	111.1(2)	N(2)*−C(6)−N(2)	108.6(3)

[a] The asterisk denotes the symmetry transformation $x, -y + 1/2, z$ used to generate equivalent atoms.

Scheme 1



complexes **5** without decomposition. When harsher initial temperature conditions are employed in this reaction using DMSO as solvent, as were reported for the successful synthesis of sterically less demanding analogues,[3] very low reaction yields were observed (vide infra, in situ NMR studies).

The acetato−mono(carbene) complexes **3** are somewhat unstable with respect to reaction, giving complexes **5** in solution at room temperature over a period of days, but can be converted to the thermally stable triiodo derivative **4b** by anion exchange with excess NaI. Complexes **3** and **5** were isolated as microcrystalline solids by removal of DMSO in vacuo followed by washing with DCM. Complex **4b** (and **5b** via the triiodo derivative **4b**) was isolated by dissolution in an acetonitrile/water solution after removal of DMSO in vacuo, followed by precipitation of the complex by removal of the acetonitrile in vacuo, and was then washed with water and DCM. Complexes **3**−**5** can be further purified by recrystallization from acetonitrile solutions, albeit with some contamination of complexes **3** by complexes **5** due to further reaction of the labile intermediate. The complexes have been fully characterized, where possible,[13] and exhibit characterization features similar to those of our previously reported analogues.[2,5] We have limited the characterization discussion of the complexes to features bearing on the reaction mechanism.

The reactions shown in Scheme 1 have been followed by in situ ^{1}H NMR studies in d_6-DMSO solution. Table 4 lists the ^{1}H NMR spectroscopic details of the species observed in the reaction. Also included for comparative purposes are the data for **2b** and the complex, presumably the palladate species [1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium]$^{2+}$[PdI$_4$]$^{2-}$, formed on mixing **2b** with PdI$_2$. Resonances which have been assigned as compounds **3b**−**5b** exhibit ^{1}H NMR spectra identical with those of the isolated samples.

Presumably the palladate species [1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium]$^{2+}$[PdI$_2$(OAc)$_2$]$^{2-}$ is formed on dissolution of **2b** and Pd(OAc)$_2$ in DMSO solution to give a deep red-purple solution. The ^{1}H NMR spectrum of this species is largely unchanged from that of **2b** or the palladate species [1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium]$^{2+}$[PdI$_4$]$^{2-}$ (deep purple in DMSO solution),[14] except for the downfield shift of 0.27 ppm observed for the resonances of the hydrogens in the 2- and 2′-positions of the diimidazolium dications. This may be due to exchanging H-bonds formed between those hydrogen atoms and the acetato moieties (vide infra). When the solution is heated to 50 °C, a second species is observed which is identical with isolated samples of **3b** and exhibits the expected resonances for such a mono(carbene)palladium complex bearing an unreacted imidazolium pendant arm. Continued heating for a period of 4 h at 50 °C gives compound **3b** as almost the sole product present in the orange solution (a trace of complex **5b** is already present). Heating the sample further at 150 °C for 1 h results in the quantitative conversion to complex **5b** to give a yellow solution. If the temperature is raised above ca. 60 °C prior to the complete formation of the intermediate species **3b**, reduced yields are observed, arising from substantial amounts of decomposition products being formed. In the event of this decomposition, scavenging of iodide by complex **3b** to yield complex **4b** by iodide−acetate exchange occurs, which is then thermally stable and does not react further to yield complex **5b** (this can be overcome by the addition of an approximately stoichiometric amount of NaOAc to the reaction mixture before the increased heating, but this is obviously best avoided).

Most notable about the ^{1}H NMR spectrum of **3b** is the downfield chemical shift observed for the proton in the 2′-position of the imidazolium functionality (11.16

(13) The ^{1}H NMR spectrum of complexes **5** in d_6-DMSO at room temperature are consistent with at least two species being present in slow fluxional exchange. ^{13}C NMR spectra of complexes **5** could not be obtained at any temperature. In the presence of NaI or NaOAc or in coordinating solvents (acetonitrile) only one species is present at room temperature. Similarly, at higher temperatures the species equilibrate. We cannot account for this behavior at present. The complexes exhibit mass fragments for both monomeric and dimeric forms in their FAB mass spectra, which we have previously noted for other analogues.[5] Thermal instability prevented us from obtaining ^{13}C NMR spectra for complexes **3**, and impurities of complexes **4** prevented accurate microanalyses of complexes **3**.

(14) A number of crystallographically authenticated diimidazolium palladate complexes have been prepared by this method. Recent examples include the following. (a) [4-BrC$_3$N$_2$H$_4$]$_2^+$[PdCl$_4$]$^{2-}$: Valle, G.; Ettorre, R. *Acta Crystallogr.* **1994**, *C50*, 1221. (b) [C$_3$N$_2$H$_4$]$_2^+$[PdCl$_4$]$^{2-}$: Valle, G.; Ettore, R. *Z. Kristallogr.* **1997**, *212*, 166. (c) [1-Me-3-Et-C$_3$N$_2$H$_3$]$_2^+$[PdCl$_4$]$^{2-}$: Ortwerth, M. F.; Wyzlic, M. J.; Baughman, R. G. *Acta Crystallogr.* **1998**, *C54*, 1594.

Table 4. Characteristic ^{1}H NMR Resonances for the Species Present during the Reaction of 1−1′-Di-*tert*-butyl-3,3′-methylenediimidazolium Diiodide 2b with $Pd(OAc)_2$ in d_6-DMSO (25 °C)[a]

compd	4,4′,5,5′-H	2,2′-H	*t*-Bu	OAc	N−CH_2−N
2b	8.07, 8.18	9.53	1.63		6.55
2b + PdI_2	8.05 (d, $^3J_{HH}$ = 1.8 Hz) 8.17(d, $^3J_{HH}$ = 1.8 Hz)	9.49	1.63		6.54
2b + $Pd(OAc)_2$	8.16(×2)	9.80	1.57	1.70	6.80
3b	7.73, 7.98 (×2), 8.05	11.16	1.63, 1.88	1.67	7.01
4b	7.97 (×2, m), 8.01 (m), 8.13 (m)	9.64 (m)	1.63, 1.87		6.79
5b[b]	7.56 (br), 7.68 (br)		1.83		6.30, 6.60 (AB, $^2J_{HH}$ = 12.8 Hz)

[a] For comparative purposes, data for compound **2b** and the palladate species [1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium][PdI_4] are also included. Hydrogen atom numbering of the imidazolium/imidazolin-2-diylidene rings is according to the systematic heterocycle numbering scheme. When the heterocycle ring proton resonances could be distinguished, the primed position refers to the imidazolium pendant arm of complexes **3b** and **4b**. Multiplicities are shown in parentheses after the chemical shift when not observed as a sharp singlet resonance. [b] ^{1}H NMR resonances at 100 °C due to fluxional exchange processes broadening the resonances at room temperature.

ppm). We account for this as being due to H-bond formation between that hydrogen and the noncoordinated oxygen center of the terminally bound *trans*-acetato moiety of the palladium center, which has been authenticated in the solid state by X-ray crystal structure determination (see section 3.3). This results in the formation of a 10-membered $C_4HN_2O_2Pd$ ring[15] which appears to be nonexchanging due to the magnitude of the chemical shift change observed for the proton in the 2′-position in this species relative to the related species listed in Table 4. We note that the initially formed palladate species described above, [1,1′-di-*tert*-butyl-3,3′-methylenediimidazolium]$^{2+}$[$PdI_2(OAc)_2$]$^{2-}$, exhibits a smaller downfield chemical shift change relative to the [PdI_4]$^{2-}$ analogue of 0.27 ppm, indicating that similar but exchanging H-bonds are likely to be present in that case also. Further evidence for the existence of the nonfluxional H-bond in complex **3b** can be seen in the direct comparison with its triiodo analogue **4b**, prepared intentionally by the addition of excess NaI (or MeI with heating) to **3b**. Complex **4b** has been shown to have a solid-state structure analogous to that of **3b** (except for the *trans*-acetato moiety; see section 3.3), and in that case an upfield chemical shift change of 1.52 ppm is observed for the proton in the 2′-position relative to complex **3b**. Only weak inter- and intramolecular contacts between the hydrogen atoms in the 2′-, 4′-, and 5′-positions of the pendant imidazolium arm and the palladium-bound iodides in complex **4b** are observed in the solid state, and these are not expected to be retained in solution, resulting in significant chemical shift changes for the protons of the imidazolium functionality.

3.2. Adapted Synthetic Procedure for the Synthesis of Analogous Complexes and Its Limitations. We have successfully utilized the improved synthetic procedure optimized for the *tert*-butyl-substituted complexes **5** to prepare a large range of analogous complexes.[16] Included are examples based on the imidazolin-2-ylidene heterocyclic ring system featuring primary, secondary, and tertiary alkyl substituents (including chiral derivatives): CH_3,[2] $(CH_2)_3OH$,[17] $CH_2(C_6H_5)$,[17] $CH_2C(H)=CH_2$,[18] $CH_2C(H)=CMe_2$,[18] Cy, (*R*)- and (*S*)-C(H)(aryl)Me,[18] and *t*-Bu, as well as Ph and Mes,[5] aryl substituents with various steric demands. A limited range of analogues based on both the benzimidazolin-2-ylidene and triazolin-2-ylidene heterocyclic ring systems have been prepared in addition.[19] We note that intermediate mono(carbene) complexes analogous to complexes **3** and **4** (isolated and observed by NMR studies for the *tert*-butyl-substituted case) are not always observed in less bulky systems, but we postulate that the reactions are nevertheless expected to proceed in an analogous manner. Presumably the reduced steric bulk in these cases renders the complexes of type **3** reactive enough at the reaction temperature of 50 °C to be not isolable or even observable and yield complexes of type **5** spontaneously. Deliberate attempts to prepare such analogues of complexes **4** by the reaction of the diimidazolium diiodide salt with a 0.5:0.5 stoichiometric amount of PdI_2 and $Pd(OAc)_2$ results in the formation of the desired analogues along with complexes of type **5b**, PdI_2, and the diimidazolium diiodide salt (only in the case of *tert*-butyl-substituted complexes does it represent an alternative way to prepare complex **4b** in good yield).

We have been unable to prepare analogues to complexes **5** featuring N,N′ linkages between the imidazolin-2-ylidenes other than methylene, such as complexes of type **6** (linkages attempted: ethylene, propylene,

(15) Although the 10-membered ring formed due to H-bonding is believed to be stable in solution, fluxionality in the ring is apparently due to the singlet resonance observed for the methylene hydrogens in the complex at room temperature.

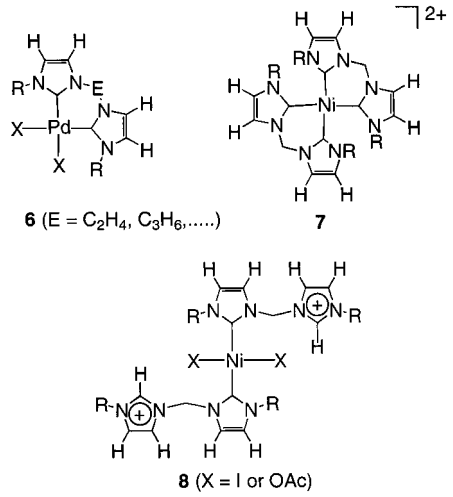
(16) ^{1}H NMR details of the other analogues prepared (400 MHz, 100 °C, d_6-DMSO): (1,1′-dicyclohexyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) dibromide, δ 1.2−2.1 (20 H, br m, Cy(CH_2)), 5.09 (2 H, br m, Cy(CH)), 6.26 (2 H, br, CH_2), 7.52, 7.62 (4 H, s, CH(imid)); (1,1′-diphenyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) dibromide, δ 6.58 (2 H, br, CH_2), 7.50−8.00 (14 H, br, CH(imid), CH(Ph)); (1,1′-diphenyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) diiodide, δ 6.51 (2 H, br, CH_2), 7.50−7.90 (14 H, br, CH(imid), CH(Ph)).

(17) Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. Submitted for publication.

(18) Gardiner, M. G.; Herrmann, W. A.; Schwarz, J. Unpublished results.

(19) (1,1′-dibenzyl-3,3′-methylenedibenzimidazoline-2,2′-diylidene)-palladium(II) dibromide: mp >300 °C; ^{1}H NMR (400 MHz, d_6-DMSO, 25 °C, ppm) δ 6.23 (4H, AB, $^2J_{HH}$ = 15.4 Hz, NCH_2Ph), 6.92 (2H, AB, $^2J_{HH}$ = 13.9 Hz, NCH_2N), 7.24−7.96 (m, 18H, CH(Ph)); ^{13}C NMR (100.53 MHz; d_6-DMSO, 25 °C, ppm): δ 172.54 ($C_{carbene}$), 136.42, 133.72, 133.46, 128.96, 128.16, 127.88, 124.79, 124.59, 112.95, 111.88 ($C_{aromatic}$), 58.79 (NCH_2N), 52.66 (NCH_2Ph); MS (FAB, *m*/*z* (%)) 1308 (25) [2M − Br]$^+$, 615 (100) [M − Br]$^+$, 535 (37) [M − 2Br]$^+$. Anal. Found: C, 50.23, H, 3.64, N, 8.14. Calcd for $C_{29}H_{24}N_4PdBr_2$ (694.76): C, 50.13, H, 3.48, N, 8.06. (1,1′-dibenzyl-3,3′-methyleneditriazolin-2,2′-diylidene)palladium(II) dibromide: mp >300 °C; ^{1}H NMR (400 MHz, d_6-DMSO, 25 °C, ppm) δ 5.56 (4 H, AB, $^2J_{HH}$ = 15.0 Hz, NCH_2Ph), 6.63 (2 H, AB, $^2J_{HH}$ = 13.6 Hz, NCH_2N), 7.05−7.21 (10 H, br, CH(Ph), 8.67 (2 H, s, NCH); ^{13}C NMR (100.53 MHz; d_6-DMSO, 25 °C, ppm): δ 164.30 ($C_{carbene}$), 146.46 (NCH), 136.89, 130.84, 129.87, 129.65 (CH (Ph)), 68.59 (NCH_2N), 53.10 (NCH_2Ph). Anal. Found: C, 37.98, H, 3.15; N, 14.18. Calcd for $C_{19}H_{18}N_6PdBr_2$ (596.62): C, 38.25, H, 3.04; N, 14.09.

butylene, and *o*-xylylene). In situ ^{1}H NMR experiments



have shown that the starting materials transform directly to unknown decomposition products (with and without Pd black formation) at temperatures of over ca. 50 °C. We account for this reactivity by proposing that the reactions proceed in an manner analogous to that shown in Scheme 1. Mono(carbene) complexes analogous to complexes **3** are formed at these temperatures, but due to the lengthened N,N′ linkage between the imidazolin-2-ylidene and the pendant imidazolium arm, the stable H-bonding interaction between the proton in the 2′-position of the imidazolium functionality and the noncoordinated oxygen center of the terminally bound *trans*-acetato moiety of the palladium center is disfavored. This could then favor deprotonation at another position of the pendant arm at this reaction temperature, leading to the observed decomposition products. In fact, the reactivity even of 1,1′-di-*tert*-butyl-3,3′-alkylenediimidazolium dibromides (alkylene linkage: ethylene, propylene, butylene), which are otherwise identical with the diimidazolium dibromide salts used in Scheme 1, results in this occurring. Attempts to prepare these types of complexes via the now well-established alternative free carbene methodology[1,20] results in no detectable amounts of palladium carbene complexes (this approach can be used to prepare the chelating bis(carbene) complexes featuring a methylene linkage between the imidazolin-2-ylidenes; however, the yields are much lower relative to those via the in situ carbene generation methodology shown in Scheme 1). Ab initio MO calculations on the N−H imidazolium cation, $[C_3N_2H_5]^+$, yield charge population densities with little variation on the carbon-based hydrogen centers in the 2- and 4(5)-positions in the range +0.297 to +0.307.[14c] This is consistent with our postulation of H-bonding of the acetato moiety to other sites of the imidazolium pendant arms (other than the 2′-position leading to complexes **5**) in mono(carbene) palladium intermediates analogous to complex **3b** when the spacer linkage between the heterocyclic rings is increased. While these calculated population densities do not

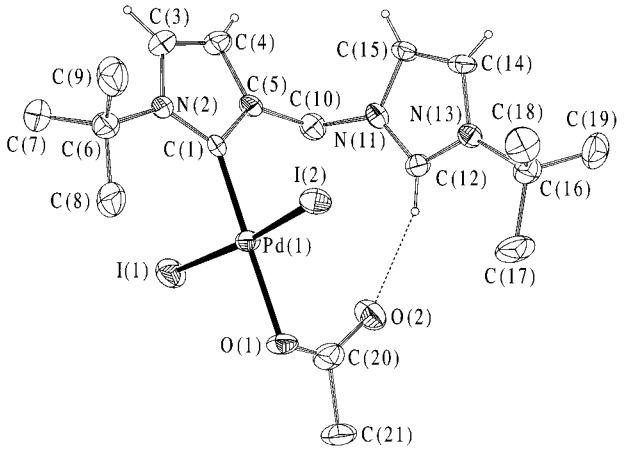


Figure 1. Molecular structure of [1,1′-di-*tert*-butyl-3,3′-methylene(imidazolium)imidazolin-2-ylidene]palladium(II)-acetate *trans*-diiodide (**3b**), showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. For clarity the methyl and methylene hydrogen atoms are omitted.

reflect the thermodynamic acidities of the protons concerned, such alternative H-bond interactions not found for **3b** could facilitate proton removal at other relatively acidic sites, leading to the observed decomposition (be it either deprotonation at the 4′- or 5′-position of the imidazolium ring or at the spacer linkage itself). Alternatively, the observed decomposition could arise through the thermal decomposition of $Pd(OAc)_2$.

Further, we feel that intermediate species featuring pendant imidazolium arms are important intermediates which have prevented us from preparing the bis-(carbene)nickel dihalide complexes analogous to complexes **5**. In that case, the reactions conducted in a manner analogous to that shown in Scheme 1 proceed to yield the dicationic tetrakis(carbene)nickel complexes **7**.[6] We have accounted for this reactivity as being due to the initial formation of bis(carbene)nickel diacetate/diiodide complexes, **8**, which then undergo preferred intramolecular deprotonations in the 2′-positions of their pendant imidazolium arms to yield the observed dicationic complexes **7** in the presence of further equivalents of acetate anions. In situ ^{1}H NMR detection and deliberate attempts to prepare such species have, however, been unsuccessful.

3.3. X-ray Crystal Structures of Complexes 3b, 4b, and 5b. Crystals of complexes **3b**, **4b**, and **5b** suitable for X-ray crystal structure determination were grown by slow evaporation of acetonitrile solutions. The crystal structure determination of complex **3b** has shown the compound to be monomeric with the imidazolium-functionalized carbene ligand binding to the palladium(II) center through the imidazolin-2-ylidene carbene center. The acetate anion binds in an η^1 terminal fashion in a *trans* position relative to the carbene ligand. The remaining two coordination sites of the distorted square planar coordinated palladium center are occupied by iodide anions. In addition, a H-bond is observed between the acidic proton in the 2′-position of the imidazolium pendant arm of the carbene ligand and the noncoordinated oxygen center of the acetate anion, forming a 10-membered ring (Figure 1). A partial occupancy disorder of the acetate anion was apparent during the least-squares refinement of the

(20) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *J. Eur. Chem.* **1996**, *2*, 772. (c) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. Ger. Offen. DE-447066, Hoechst AG, 1994.

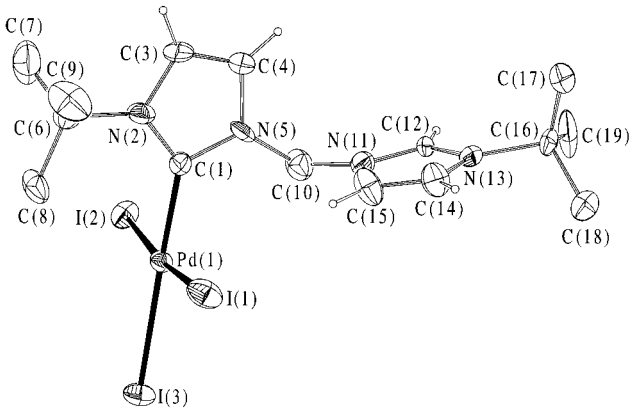


Figure 2. Molecular structure of [1,1′-di-*tert*-butyl-3,3′-methylene(imidazolium)imidazolin-2-ylidene]palladium(II) triiodide (**4b**), showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. For clarity the methyl and methylene hydrogen atoms are omitted.

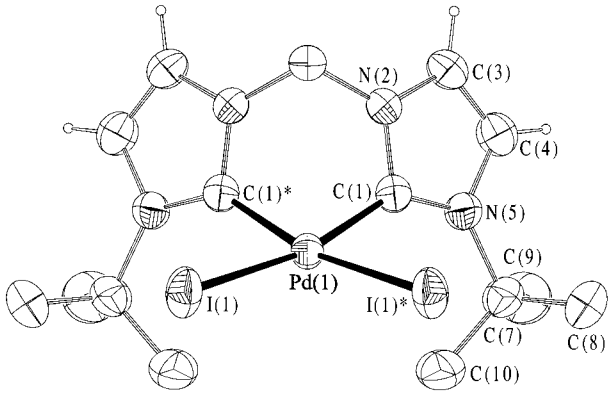


Figure 3. Molecular structure of (1,1′-di-*tert*-butyl-3,3′-methylenediimidazoline-2,2′-diylidene)palladium(II) diiodide−acetonitrile (**5b**), showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. For clarity the methyl and methylene hydrogen atoms and the noncoordinated acetonitrile molecule are omitted.

structure. Difference Fourier maps lead us to conclude that this was due to a partial occupancy of iodide, equating to a minor cocrystallization impurity of **4b** (albeit with a molecular conformation at the methylene carbon center different from that observed in its pure state). This was modeled as a 3.2(2)% (refined) occupancy of the iodide at the position of the carbonyl carbon center (C(20)/I(3)) of the acetate anion (Pd−I(3) distance of 2.783 Å; *cf.*, 2.688(1) Å for the *trans*-Pd−I distance in **4b**) and restrained to have the same positional and anisotropic thermal parameters as that of the carbonyl carbon atom. This disorder model lead to final residuals of R1 = 0.0356 and wR2 = 0.0660 (for observed data, $F_o > 4\sigma(F_o)$). The molecular structure of complex **4b** is very closely related to that of complex **3b** with the exception of the *trans*-acetato ligand having been replaced by an iodide anion. This manifests a conformational change at the methylene carbon linking the imidazolin-2-ylidene and imidazolium rings in the absence of the H-bond formed with the acetate ligand in the case of **3b** (Figure 2). There is also a noncoordinating molecule of acetonitrile in the crystal lattice. Molecules of **3b** and **4b** possess no crystallographic or noncrystallographic molecular symmetry (**4b** has approximate C_{2v} molecular symmetry, excluding the imidazolium pendant arm). The crystal structure determination of complex **5b** has shown the compound to be monomeric with the dicarbene ligand chelating the palladium(II) center in a *cis* fashion with a boat conformation being observed for the six-membered C_3N_2-Pd ring. The remaining two coordination sites of the distorted square planar coordinated palladium center are occupied by iodide anions. The molecule possesses crystallographic C_s symmetry, with the symmetry axis passing through the palladium and methylene carbon centers (Figure 3). There is also a noncoordinating molecule of acetonitrile (also located on a mirror plane) in the crystal lattice. Summaries of important bond distances and angles for complexes **3b**, **4b**, and **5b** appear in Tables 1−3.

The Pd−C distances of complexes **3b**, **4b**, and **5b**, 1.953(5), 1.990(9), and 2.004(3) Å, respectively, compare with those found in the dicationic[5] and neutral chelating[3] dicarbene palladium complexes [*cis*-$CH_2\{\overline{NC{=}CN(Me)C}\}_2Pd(NCMe)_2]^{2+}[PF_6]^-_2$ and [*cis*-$CH_2\{\overline{NC{=}CN(Me)C}\}_2PdI_2$] at 1.966(2) and 1.972(3) Å and at 1.988(7) and 1.989(8) Å, respectively, and the related nonchelating complex [*cis*-$\{MeN\overline{C{=}CN(Me)C}\}_2PdI_2$] at 1.990(3) and 1.997(3) Å.[2] The Pd−C distance in **3b** is somewhat contracted relative to the iodide anion in complex **4b** due to the differing *trans* influence of the acetate and iodide anions. The observation of comparable Pd−C distances for complexes **4b** and **5b**, both being *trans* to iodide, indicate that the palladium to carbene bonding interaction is seemingly little affected by the change in angle between the imidazolin-2-ylidene-based ring systems and the coordination plane of the palladium center, measuring 84.9(2), 87.0(3), and 62.6(2)° for complexes **3b**, **4b**, and **5b**, respectively. This last point has already been noted by us as not greatly influencing the bonding between palladium(II) centers and imidazolin-2-ylidene-based carbene ligands,[5,21] and this comparison perhaps provides the most direct evidence of this to date.

The Pd−I distances in complexes **3b**, **4b**, and **5b** fall into two distinct classes. Those *trans* to the carbene ligand in complexes **4b** and **5b** measure 2.688(1) and 2.669(1) Å, respectively, while the *trans*-diiodide anions in complexes **3b** and **4b** are distances of 2.619(2) and 2.628(2) Å and of 2.623(1) and 2.626(1) Å, respectively, from the metal center. The distances in the former pair are slightly lengthened relative to the related chelating and nonchelating complexes [*cis*-$CH_2\{\overline{NC{=}CN(Me)C}\}_2PdI_2$] and [*cis*-$\{MeN\overline{C{=}CN(Me)C}\}_2PdI_2$], 2.6450(9) and 2.6573(8) Å and 2.6479(3) and 2.6572(3) Å, respectively,[2,3] perhaps due to the increased steric influences, at least in the case of **5b**. The latter grouping can be more directly compared with the shorter distances observed in the chiral dicarbene complex [*trans*-$\{(syn\text{-}Ph(Me)CH\{\overline{NC{=}CN(Ph)C}\}_2)\}_2PdI_2$], in which the Pd−I distances measure 2.5924(9) and 2.6251(9) Å.[22]

The Pd−O distance to the η^1-terminally bound acetate anion in the complex **3b**, 2.088(4) Å, is typical and

(21) Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *554*, 175.
(22) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483.

compares with that found in [*cis*-{(*o*-Tol)$_2$PC$_6$H$_4$-*o*-CH$_2$}-Pd(OAc)N(H)Et$_2$], 2.143(1) Å, being *trans* to a benzylic carbon center. This complex also exhibits H-bonding between the noncoordinated oxygen center of the acetate ligand and the acidic N−H proton of a palladium-bound Et$_2$NH molecule.[23] The C−O distances for the acetate anion (C(20)−O(1,2) = 1.183(5), 1.285(5) Å, respectively) do not exhibit the expected variations for a η^1-terminally bound acetate anion, presumably due to refinement artifacts arising from the modeling of the partial occupancy of the iodide anion in the region of the carbonyl carbon center, C(20), and will not be interpreted further.

Angular distortions from ideal square-planar geometry for the palladium centers in complexes **3b**, **4b**, and **5b** are minimal, with the exceptions of those introduced by the six-membered chelate ring for the bidentate dicarbene ligand in complex **5b**. The latter effects have been previously documented by us, and no significant increased effects are noted for this sterically demanding analogue relative to the dimethyl-substituted dicationic[5] and neutral[3] dicarbene palladium complexes [*cis*-CH$_2$-{NC=CN(Me)C}$_2$Pd(NCMe)$_2$]$^{2+}$[PF$_6$]$^-{}_2$ and [*cis*-CH$_2$-{NC=CN(Me)C}$_2$PdI$_2$].

The H-bonding interaction, C=O···H−C, observed between the acidic proton in the 2′-position of the imidazolium pendant arm of the carbene ligand and the noncoordinated oxygen center, O(2), of the acetate anion is typical in its relevant geometries (the hydrogen atom concerned, H(12), was positionally refined with a riding isotropic displacement parameter): O(2)···H(12) = 2.17(5) Å, H(12)−C(12) = 0.89(5) Å, C(20)−O(2)···H(12) = 131.9°, O(2)···H(12)−C(12) = 164.9°. This H-bonding geometry relates to that observed in [*cis*-{(*o*-Tol)$_2$PC$_6$H$_4$-*o*-CH$_2$}Pd(OAc)N(H)Et$_2$], in which the H-bond is formed between an acetate and the acidic N−H proton of a secondary amine to form an eight-membered ring.[23] In addition to the H-bond mentioned above for complex **3b**, several intermolecular H···I interactions between the ring protons of both the imidazolin-2-ylidene- and imidazolium-based ring systems in complexes **3b**, **4b**, and **5b** are observed. These are not considered to be strong interactions though and are expected only to be of solid-state packing necessity. These weak interactions compare with those observed in the related diimidazolium tetrachloropalladate complexes.[14] C−C and C−N bond distances within the imidazolin-2-ylidene- and imidazolium-based ring systems in complexes **3b**, **4b**, and **5b** are consistent with our previous observations and bonding descriptions for imidazolin-2-ylidene carbene palladium complexes.[2,3,5,24] Other bond distances and angles within the molecules **3b**, **4b**, and **5b** are unexceptional and do not require comment.

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Supporting Information Available: Full listings of atomic coordinates, U_{ij} values, bond distances and angles, and summaries of the X-ray diffraction data for compounds **3b**, **4b**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Louie, J.; Hartwig, J. F. *Angew. Chem.* **1996**, *108*, 2531; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2359.

(24) Herrmann, W. A.; Goossen, L. J.; Artus, G. R. J.; Köcher, C. *Organometallics* **1997**, *16*, 2472.