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Synthesis of the First *r*NHC (Remote N-Heterocyclic Carbene) Complexes with No Heteroatom in the Carbene Carbon-Containing Ring

Oliver Schuster and Helgard G. Raubenheimer*

Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Stellenbosch, South Africa

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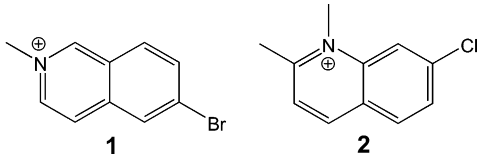
Two cationic carbene complexes with no heteroatom in the ring containing the carbene carbon, *trans*-bromo(2-methyl-2,6-dihydroisoquinolin-6-ylidene)bis(triphenylphosphine)palladium(II) triflate (**3**) and *trans*-chloro(1,2-dimethyl-1,7-dihydroquinolin-7-ylidene)bis(triphenylphosphine)palladium(II) triflate (**4**), were synthesized by oxidative substitution of Pd(PPh_3)$_4$ with N-methylated 6-bromoisoquinolinium and 7-chloro-2-methylquinolinium cations, respectively. Compound **3** was also prepared by methylation of neutral *trans*-bromo(2-methylisoquinolin-6-yl)bis(triphenylphosphine)palladium(II) (**5**). All complexes were unambiguously characterized by NMR and X-ray crystallographic studies.

In recent investigations, we have observed that complexes bearing N-heterocyclic carbene ligands with remote heteroatoms (*r*NHC) are superior in their performance compared to their "classic" NHC analogues in C,C-coupling catalysis.[1,2] Computational studies have shown that these new ligands are even stronger σ donors than their well-known counterparts.[2,3]

In a further development of this concept, we herein present the first *r*NHC complexes with no heteroatom in the carbene carbon-containing ring; i.e., the nitrogen is located in an adjacent annealed aromatic ring. Existing literature procedures were followed or slightly modified to prepare the target ligand precursors 6-bromo-2-methylisoquinolinium triflate (**1**) and 7-chloro-1,2-dimethylquinolinium triflate (**2**) (Figure 1).[4] A slight excess of methyl triflate was used to alkylate the corresponding substrates in dichloromethane. The crude product was washed with cold tetrahydrofuran to give compounds **1** and **2** in excellent yields.



1 **2**

Figure 1. Ligand precursors **1** and **2** with the triflate counterions omitted.

Following Stone's method,[5] the cationic complexes *trans*-bromo(2-methyl-2,6-dihydroisoquinolin-6-ylidene)bis(triphenylphosphine)palladium(II) triflate (**3**) and *trans*-chloro(1,2-dimethyl-1,7-dihydroquinolin-7-ylidene)bis(triphenylphosphine)palladium(II) triflate (**4**) were obtained by oxidative addition according to Schemes 1 and 2, when the ligand precursors **1** and **2** were reacted with Pd(PPh_3)$_4$ at 70 °C in toluene overnight. Filtration and washing with toluene afforded the complexes as off-white powders. Recrystallization from dichloromethane/pentane gave colorless crystals in excellent (91%) and satisfying (66%) yields, respectively.

While compound **3** could also be prepared easily and in good yield by changing the sequence of the synthetic steps (i.e., first oxidative addition and second alkylation, Scheme 2), the attempted synthesis of **4** following this route, by reacting 7-chloro-2-methylquinoline with Pd(PPh_3)$_4$, surprisingly yielded exclusively palladium black and free PPh_3 at a variety of temperatures.

The complexes **3**−**5** are soluble in polar solvents such as dichloromethane or chloroform and insoluble in pentane or toluene. Even under moist atmospheric conditions, decomposition in solution is slow. Solids need to be heated to over 170 °C for **4** and even 190 °C for **3** and **5** before a purple color indicates the formation of elemental palladium.

The single resonances observed for the complexes **3**−**5** in the ^{31}P NMR spectrum, lying in a narrow range between 24.6 and 25.4 ppm, show the equivalence of the two phosphorus ligands in each compound, indicating a rigid trans configuration in solution because no evidence of a fast ligand exchange could be observed.

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* To whom correspondence should be addressed. E-mail: hgr@sun.ac.za. Fax: +27 21 808 3849. Tel: +27 21 808 3850.

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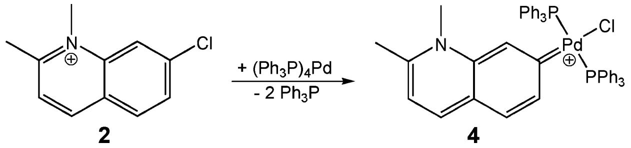
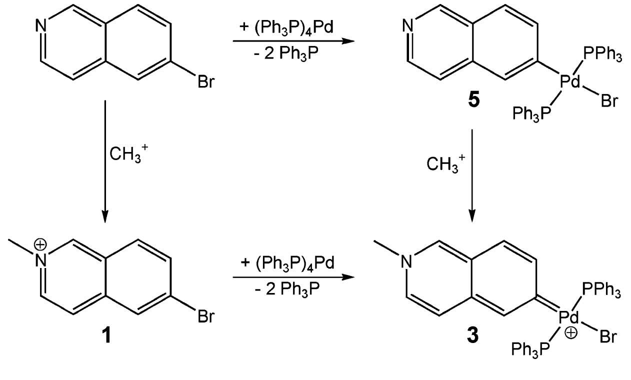
10.1021/ic060963k CCC: $33.50

Scheme 1. Sythesis of **4** (Triflate Counterions Omitted for Clarity)



Scheme 2. Sythesis of **3** via Two Different Routes (Triflate Counterions Omitted for Clarity)



The carbene carbon atoms of **3** (6-C) and **4** (7-C) resonate at 187.0 and 180.7 ppm, respectively, in their ^{13}C NMR spectra. Downfield shifts of 52.5 and 37.4 ppm, with reference to the analogous carbon resonances for the alkylated ligand precursors, occur upon oxidative addition. Both signals appear as triplets with coupling constants of 4.8 Hz, again emphasizing the trans arrangement of the phosphines in solution. Carbene formation can be assumed because the alkylation of **5** gives rise to a severe 20.5 ppm downfield shift of the 6-C resonance (166.5 ppm), while the other carbon resonances are much less affected [average 3(2) ppm], although they are nearer to the region of change. Moreover, only a singlet is observed in compound **5** opposed to the triplet in **3** (vide supra), indicating a change in the mode of binding.

The molecular structures of **3**−**5** were determined by X-ray diffraction analysis.[6−8] As can be seen in Figures 2−4, the palladium ions in the cationic complexes occur in a distorted square-planar environment with the two phosphines trans to each other and bending away from the halides a little. This distortion is, for obvious reasons, more prominent in the bromide-containing examples. The steric demand of the *r*NHC ligands is minimal because the angles between the planes, defined through the cyclic carbene ligands, on the

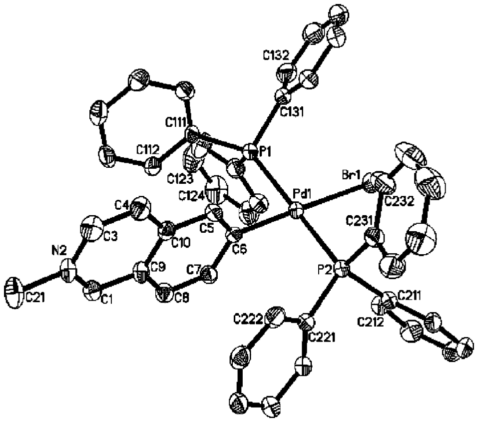


Figure 2. Molecular structure of compound **3** (ORTEP drawing with 50% probability ellipsoids; H atoms, counterions, and solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [deg]: Pd1−Br1 2.5193(5), Pd1−P1 2.3301(11), Pd1−P2 2.3249(10), Pd1−C6 2.005(4); Br1−Pd1−P1 92.15(3), Br1−Pd1−P2 91.63(3), Br1−Pd1−C6 178.73(11), P1−Pd1−P2 173.32(4), P1−Pd1−C6 88.55(11), P2−Pd1−C6 87.78(11).

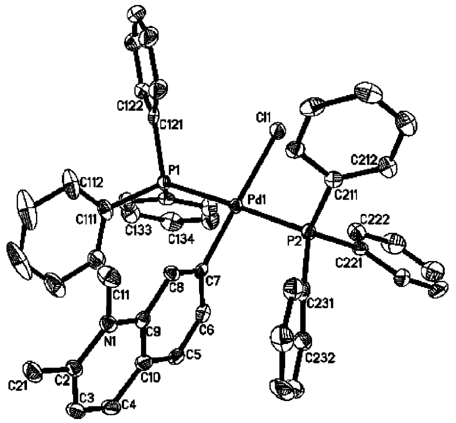


Figure 3. Molecular structure of compound **4** (ORTEP drawing with 50% probability ellipsoids; H atoms, counterions, and solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [deg]: Pd1−Cl1 2.4005(12), Pd1−P1 2.3380(11), Pd1−P2 2.3175(11), Pd1−C7 1.998(4); Cl1−Pd1−P1 92.35(4), Cl1−Pd1−P2 90.27(4), Cl1−Pd1−C7 179.16(10), P1−Pd1−P2 176.57(4), P1−Pd1−C7 88.39(10), P2−Pd1−C7 89.01(10).

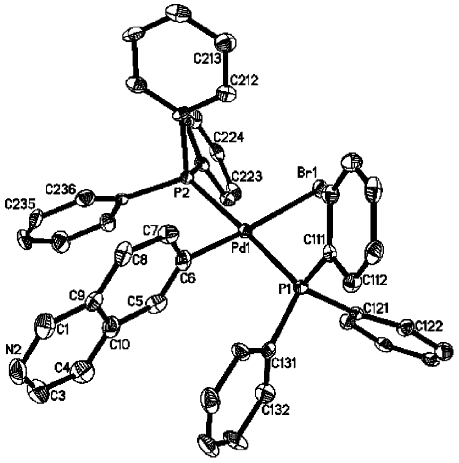


Figure 4. Molecular structure of compound **5** (ORTEP drawing with 50% probability ellipsoids; H atoms, counterions, and solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [deg]: Pd1−Br1 2.5198(5), Pd1−P1 2.3259(15), Pd1−P2 2.3315(15), Pd1−C6 2.014(4); Br1−Pd1−P1 92.25(4), Br1−Pd1−P2 92.61(4), Br1−Pd1−C6 172.66(11), P1−Pd1−P2 173.93(3), P1−Pd1−C6 88.2(2), P2−Pd1−C6 86.5(2).

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(6) Crystal data for **3**: $C_{47}H_{39}BrF_3NO_3P_2PdS$, $M = 1003.10$, monoclinic, space group $P2(1)/n$, $a = 13.0765(14)$ Å, $b = 27.951(3)$ Å, $c = 16.4035(17)$ Å, $\alpha = 90°$, $\beta = 100.537(2)°$, $\gamma = 90°$, $V = 5894.1(11)$ Å^3, $Z = 4$, $D_c = 1.130$ g cm^{-3}, $F(000) = 2014$, $\mu = 11.23$ cm^{-1}, $T = 100(2)$ K, 533 parameters refined with 11 083 [$R_{int} = 0.0357$] unique reflections to R1 [$I > 2\sigma(I)$] = 0.0509.

(7) Crystal data for **4**: $C_{50}H_{45}Cl_5F_3NO_3P_2PdS$, $M = 1142.52$, triclinic, space group $P\bar{1}$, $a = 11.033(3)$ Å, $b = 13.351(4)$ Å, $c = 18.598(5)$ Å, $\alpha = 80.788(5)°$, $\beta = 75.116(5)°$, $\gamma = 72.122(5)°$, $V = 2510.0(13)$ Å^3, $Z = 2$, $D_c = 1.512$ g cm^{-3}, $F(000) = 1160$, $\mu = 7.95$ cm^{-1}, $T = 100(2)$ K, 597 parameters refined with 9277 [$R_{int} = 0.0235$] unique reflections to R1 [$I > 2\sigma(I)$] = 0.0432.

(8) Crystal data for **5**: $C_{48}H_{42}BrCl_6NP_2Pd$, $M = 1093.78$, monoclinic, space group $P2(1)$, $a = 10.1637(9)$ Å, $b = 22.087(2)$ Å, $c = 10.9083(17)$ Å, $\alpha = 90°$, $\beta = 110.8640(10)°$, $\gamma = 90°$, $V = 2288.2(4)$ Å^3, $Z = 2$, $D_c = 1.588$ g cm^{-3}, $F(000) = 1100$, $\mu = 17.35$ cm^{-1}, Flack = 0.412(10), $T = 100(2)$ K, 533 parameters refined with 8303 [$R_{int} = 0.0249$] unique reflections to R1 [$I > 2\sigma(I)$] = 0.0509.

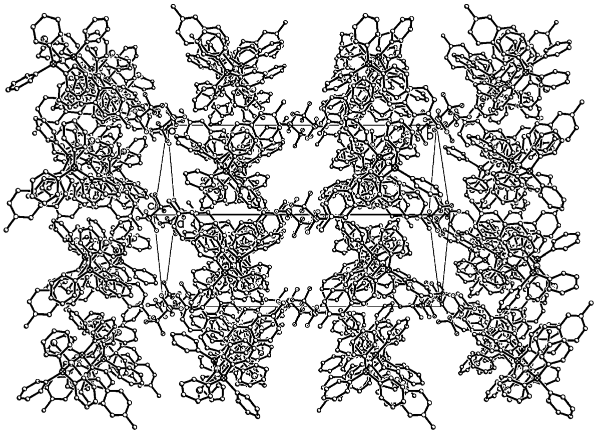

Figure 5. Projection of the crystal structure of compound **3** along the *ac* vector (arbitrary radii; solvent molecules omitted).

one hand, and the coordination sphere, on the other hand, very closely approach 90°. The Pd−C distances of all complexes fall within a very narrow range between 1.998 and 2.014 Å. Hence, with respect to their metal−carbon bonds, there is no difference between carbene **3** and pro carbene complex **5**. This is in harmony with CCSD data,[9] where complexes of the type *trans*-(aryl)$(PPh_3)_2$PdX and *trans*-(NHC)$(PPh_3)_2$PdX (X = Br, Cl) cannot be discriminated by their Pd−C or Pd−X bond lengths. The variations in the C−C/C=C bond lengths within the corresponding rings are also negligible. Therefore, molecular structural data are not useful probes to confirm or dismiss carbene formation.

All compounds crystallize with at least two solvent molecules per formula unit. This is mostly due to the cavities provided between the carbene ligand and the phenyl rings of the phosphines. In the case of complex **3**, no less than five severely distorted dichloromethane molecules have been identified in the asymmetric unit. These are mainly located in channels along the *ac* vector made available by the ionic network (Figure 5). Anions and cations pack in layers along the *ac* plane, with the former sharing the plane with the solvent providing said columnar space. In agreement with this microscopic observation, single-crystalline blocks of **3** immediately break apart to give thin weathered plates when removed from the mother liquor at room temperature.

In summary, **3** and **4** represent the first reported *r*NHC complexes with no heteroatom in the ring that contains the carbene carbon. They are accessible in good yields following straightforward, established routes and can be handled for a reasonable amount of time under atmospheric conditions, even in solution. While the heteroatom in **4** is not more remote than that in known 1,4-dihydropyridin-4-ylidene or 1,4-dihydroisoquinolin-4-ylidene complexes (three bonds),[1−4] **3** pushes the boundaries of this new class of ligands a little further (five bonds). At what stage of heteroatom remoteness such complexes become immonium salts rather than carbene complexes and especially how precisely discrimination can be established require further attention. At the moment, NMR measurement seems to be the only method to identify carbene complex formation because bond distances do not discriminate effectively. In future studies, we will determine whether these compounds are suitable as catalysts for C,C-coupling. To better understand the nature of these ligands and their relationship to standard NHCs, quantum mechanical calculations will accompany these investigations. We believe that this new class of ligands provides many possibilities for application, especially if they could be attached to a range of metal centers.

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Note Added after ASAP Publication. There was an error in Figure 1 in the version published ASAP September 1, 2006; the corrected version was published ASAP September 5, 2006.

Supporting Information Available: Synthetic procedures for **3**−**5** and their precursors as well as crystallographic data for **3**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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