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Preparation of Metal−Imidazolidin-2-ylidene Complexes by Oxidative Addition

Alois Fürstner,* Günter Seidel, Doris Kremzow, and Christian W. Lehmann

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

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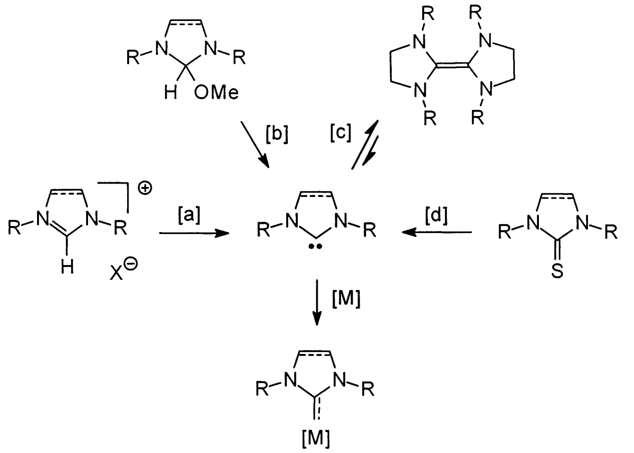
Summary: An entry into (chiral) palladium complexes bearing N-heterocyclic carbene (NHC) ligands is outlined on the basis of the oxidative addition of Pd(PPh$_3$)$_4$ to easily accessible (enantiopure) 2-chloro-1,3-disubstituted imidazolinium salts. This procedure is complementary to existing methodology that relies on metathetic ligand exchange reactions without changing the oxidation state of the involved metal center.

Transition-metal complexes with N-heterocyclic carbene (NHC) ligands show considerable potential as catalysts for organic synthesis and fine chemical production.[1] They are usually prepared by ligand exchange or salt metathesis on treatment of a suitable metal precursor [M] with the appropriate carbene, formed as a discrete or a transient species by one of the methods depicted in Scheme 1.[1−5] In none of these established procedures does the metal template change its oxidation state.

Although these methods are widely applicable, the conditions used for the generation of the required N,N′-disubstituted imidazol(idin)-2-ylidenes are somewhat limiting, because they require either strongly basic or highly reducing media and/or involve thermal stress. Therefore, it seems appropriate to develop alternative methods which might help to improve the accessibility of these useful catalysts even further.

Scheme 1. Common Routes to Metal−Imidazol(idin)-2-ylidene Complexes



[a] Legend: [a] base (e. g. KOtBu, KH, BuLi) in THF or liquid NH$_3$;[2] [b] thermolysis (α-elimination);[3] [c] cf. ref 4; [d] K in THF.[5]

As part of our program aiming at the design of novel metal−NHC catalysts and their applications to advanced organic synthesis,[6] we considered that oxidative addition of a low-valent metal to a 2-chloro-1,3-disubstituted imidazolinium salt may open an as yet largely unexplored entry. This concept seemed particularly promising, because Stone et al. have demonstrated early on in a series of elegant studies that related oxidative addition reactions of metals to 2-chlorothiazolium or 2-chloro-1-methylpyridinium salts afford the corresponding carbene complexes in good to excellent yields.[7] Surprisingly, though, it seems that this potentially general and versatile method has not been applied to the synthesis of metal−imidazol(idin)-2-ylidene complexes, except for one special case.[8,9] Importantly, however, this novel method promises a broad substrate scope and might allow for substantial structural variations, since the required 2-chloro-1,3-disubstituted imidazolinium salts can be easily prepared from cyclic ureas or thioureas on treatment with, for example, oxalyl chloride. Moreover, the *N*,*N*′-dimethyl derivatives **1a**−**c** (X = PF$_6$, BF$_4$, Cl) used as the model compounds in this exploratory study are even commercially available, serving as excellent dehydrating agents for a host

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* To whom correspondence should be addressed. E-mail: fuerstner@mpi-muelheim.mpg.de. Fax: +49 208 306 2994. Tel: +49 208 306 2342.

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[3] (a) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

[4] Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185.

[5] (a) Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem. Eur. J.* **1999**, *5*, 1931. (b) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

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[7] (a) Fraser, P. J.; Roper, W. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 102. (b) Fraser, P. J.; Roper, W. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 760. (c) See also: Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139.

[8] A DFT-based study of oxidative insertion reactions with formation of carbene complexes has recently been published; cf.: McGuinness, D. S.; Cavell, K. J.; Yates, B. F.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 8317. This paper also reports a preparative experiment involving the oxidative insertion of Pt(PPh$_3$)$_4$ into 2-*iodo*-1,3,4,5-tetramethylimidazolium tetrafluoroborate prepared by treatment of the *free* carbene with iodine.

[9] For related reports on oxidative additions to the C−H bond of imidazolium salts see ref 8 and the following for leading references: (a) McGuinness, D. S.; Cavell, K. J.; Yates, B. F. *Chem. Commun.* **2001**, 355. (b) Gründemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2163.

10.1021/om021022s CCC: $25.00
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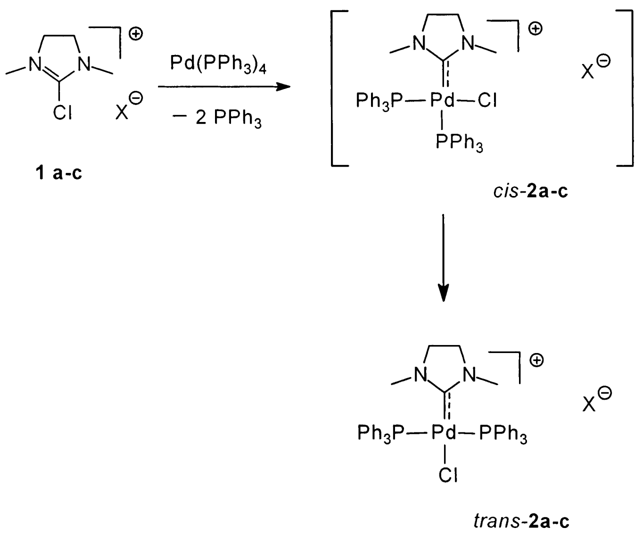
Scheme 2[a]



[a] Reagents and conditions: $Pd(PPh_3)_4$ (1 equiv), CH_2Cl_2, reflux; see text.

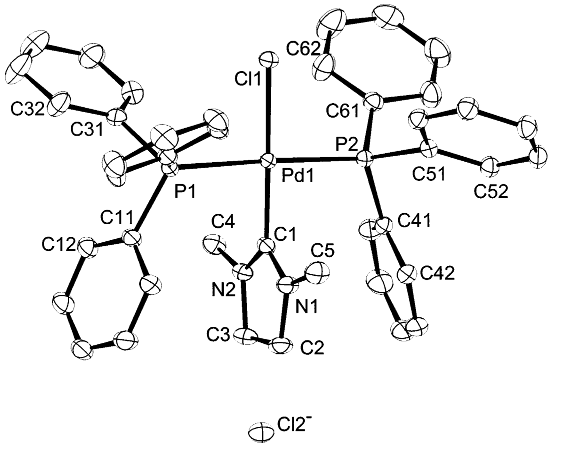


Figure 1. Molecular structure of *trans*-**2c**. Hydrogen atoms and all CH_2Cl_2 solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd1−C1 = 1.975(3), Pd1−P1 = 2.3390(8), Pd1−P2 = 2.3474(8), Pd1−Cl1 = 2.3559(7), C1−N1 = 1.323(4), N1−C2 = 1.475(4), C1−N2 = 1.329(4), N2−C3 = 1.468(4), C2−C3 = 1.532(5); C1−Pd1−P1 = 88.49(9), C1−Pd1−P2 = 88.26(9), P1−Pd1−P2 = 176.01(3), C1−Pd1−Cl1 = 177.27(9), P1−Pd1−Cl1 = 89.61(3), P2−Pd1−Cl1 = 93.73(3), C1−N1−C2 = 112.4(3), C1−N2−C3 = 112.1(3), N1−C1−N2 = 110.2(3), N1−C2−C3 = 102.2(3), N2−C3−C2 = 102.9(3).

of esterification, chlorination, oxidation, and rearrangement reactions as well as for heterocycle synthesis.[10,11]

Treatment of the imidazolinium salt **1a** (X = PF_6) with an equimolar amount of $Pd(PPh_3)_4$ in refluxing CH_2Cl_2 leads to a clean reaction which can be nicely monitored by ^{31}P NMR spectroscopy. Initially, two sets of signals at δ_P 31.8 (d, J = 24 Hz) and δ_P 21.2 (d, J = 24 Hz) are detected, which converge over a period of ca. 6 h to a singlet at δ_P 22.5 ppm; 2 equiv of PPh_3 is released concomitantly. This course reflects the formation of *cis*-**2a** as the primary product, which isomerizes with time to the more stable *trans*-**2a**. After extraction of the free PPh_3, *trans*-**2a** was isolated as a white solid in analytically pure form (72%) by recrystallization from $CHCl_3$.[12] The imidazolinium salt **1b** (X = BF_4) reacts analogously, affording the compound *trans*-**2b** (δ_P 22.8 ppm) in similar yield (Scheme 2).[13]

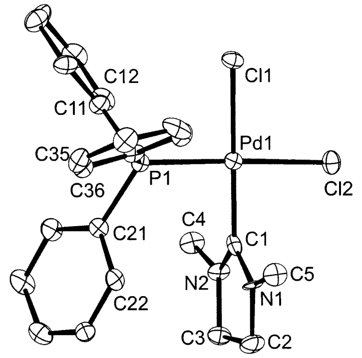


Figure 2. Molecular structure of **3**. Hydrogen atoms and THF solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Pd1−C1 = 1.968(8), Pd1−P1 = 2.251(2), Pd1−Cl2 = 2.355(2), Pd1−Cl1 = 2.3676(19), C1−N2 = 1.334(9), N2−C3 = 1.471(10), C1−N1 = 1.339(10), N1−C2 = 1.467(10), C2−C3 = 1.529(11); C1−Pd1−P1 = 92.2(2), C1−Pd1−Cl2 = 85.9(2), P1−Pd1−Cl2 = 178.04(8), C1−Pd1−Cl1 = 178.0(2), P1−Pd1−Cl1 = 87.46(7), Cl2−Pd1−Cl1 = 94.50(7), C1−N2−C3 = 112.4(6), C1−N1−C2 = 111.4(6), N2−C1−N1 = 109.5(6), N2−C3−C2 = 101.5(6), N1−C2−C3 = 103.3(6).

The reactivity of chloride **1c** (X = Cl) follows the same trend, giving rise to the expected cationic complex *trans*-**2c** (δ_P 22.8 ppm) in 87% yield after recrystallization from $CHCl_3$/pentane. Its structure in the solid state is depicted in Figure 1.[14] The solution structure must be similar, as the carbene center in *trans*-**2c** resonates as a triplet at δ_C 194.9 ppm (J = 6.9 Hz), thus indicating the presence of two phosphorus atoms at degenerate positions. However, the crude mixture formed from **1c** and $Pd(PPh_3)_4$ invariably contains small amounts of other complexes in addition to **2c**; one of them (δ_P 27.7 ppm) cleanly regenerates when recrystallized **2c** is dissolved in CD_2Cl_2 or THF. Although we were unable so far to isolate this new compound on a preparative scale, crystals were picked out from a coprecipitate and were analyzed by X-ray crystallography, which showed that this product is the *neutral* palladium *di*chloride complex *cis*-**3** (Figure 2).[14,15] Therefore, the particular behavior of **2c** in solution is deemed to reflect the higher

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(10) (a) Fujisawa, T.; Mori, T.; Fukumoto, K.; Sato, T. *Chem. Lett.* **1982**, 1891. (b) Isobe, T.; Ishikawa, T. *J. Org. Chem.* **1999**, *64*, 5832. (c) Isobe, T.; Ishikawa, T. *J. Org. Chem.* **1999**, *64*, 6984. (d) Isobe, T.; Ishikawa, T. *J. Org. Chem.* **1999**, *64*, 6989. (e) Isobe, T.; Fukuda, K.; Ishikawa, T. *J. Org. Chem.* **2000**, *65*, 7770.

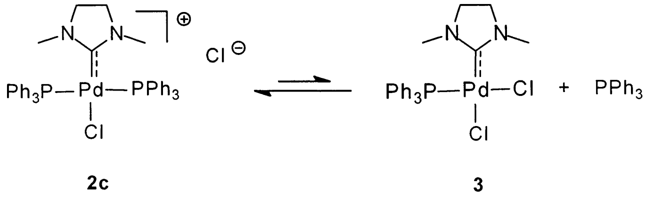
(11) For applications from our laboratory see: (a) Fürstner, A.; Albert, M.; Mlynarski, J.; Matheu, M. *J. Am. Chem. Soc.* **2002**, *124*, 1168. (b) Fürstner, A.; Mlynarski, J.; Albert, M. *J. Am. Chem. Soc.* **2002**, *124*, 10274.

(12) For experimental details and analytical data see the Supporting Information.

(13) For related complexes prepared by an entirely different multistep route see: Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93.

(14) Crystal data for **2c**: $\{[C_{41}H_{40}ClN_2P_2Pd]^+Cl^-\}\cdot 7CHCl_3$, M_r = 1635.57, colorless, crystal dimensions 0.15 × 0.12 × 0.06 mm, triclinic, $P\bar{1}$ (No. 2), T = 100 K, a = 14.4426(3) Å, b = 14.6316(3) Å, c = 16.3023(4) Å, α = 90.7160(10)°, β = 98.3380(10)°, γ = 94.8700(10)°, V = 3395.18(13) Å^3, Z = 2, ρ = 1.600 Mg m^{-3}, μ(Mo Kα) = 1.260 mm^{-1}, 40 763 reflections measured, 25 295 unique (R_{int} = 0.043). Final $R_w(F^2)$ = 0.175 (all data) and R1 = 0.067 ($I > 2\sigma(I)$) with goodness of fit on F^2 S = 1.02 (CCDC 191645). Crystal data for **3**: $C_{23}H_{25}Cl_2N_2PPd\cdot 1.5C_4H_8O$, M_r = 645.88, colorless, crystal dimensions 0.08 × 0.04 × 0.02 mm, orthorhombic, *Pbcn* (No. 60), T = 100 K, a = 28.9418(10) Å,

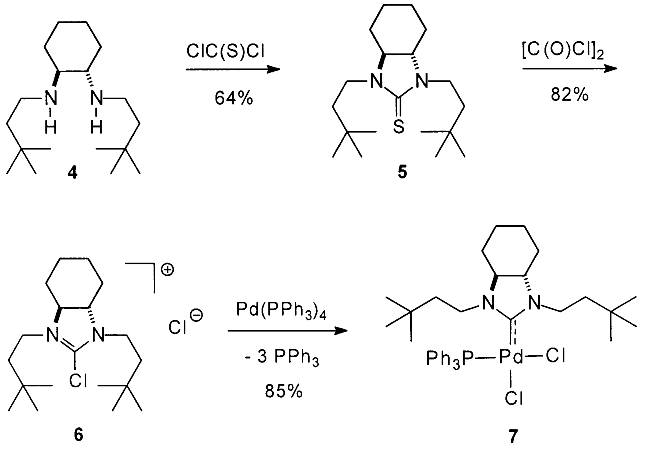
Scheme 3. Equilibrium between the Cationic and the Neutral Pd−NHC Complexes 2c and 3



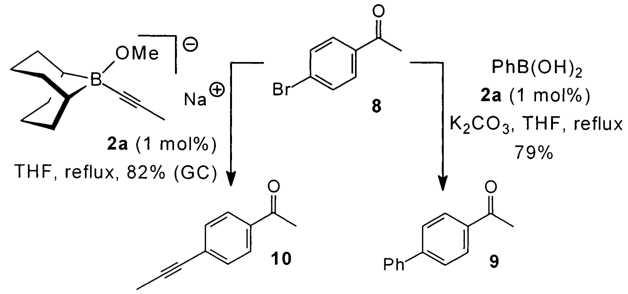
nucleophilicity of the chloride ion as compared to the PF_6^- and BF_4^- ions that accompany compounds **2a**,**b**, respectively. Obviously, the chloride is able to enter into the coordination sphere of the Pd(2+) center in **2c** and replace one of the PPh_3 ligands, thus leading to the formation of **3** and release of an equivalent amount of PPh_3, as detected by ^{31}P NMR (Scheme 3).[16] This propensity is more pronounced in case of the enantiomerically pure NHC complex **7**, which is obtained as the only product on treatment of the chiral imidazolinium salt **6** with $Pd(PPh_3)_4$ under similar conditions (Scheme 4). Compound **6** is readily obtained from the commercial diamine **4** on treatment with thiophosgene, followed by reaction of the resulting thiourea **5** with oxalyl chloride. In view of the host of 1,2-diamines that are available in optically pure form by various well-established methods and their excellent track record as ligand scaffolds for a variety of enantioselective transformations,[17] this new method bears considerable promise for further investigations.

Preliminary experiments show that these novel Pd−NHC complexes are active catalysts for Suzuki reactions (Scheme 5).[18] Specifically, cross coupling of 4-bromoacetophenone **8** with $PhB(OH)_2$ in the presence of 1 mol % of **2a** affords the expected product **9** in 79% yield. The

Scheme 4. Preparation of an Enantiopure Palladium−NHC Complex by Oxidative Addition



Scheme 5. Suzuki Cross-Coupling Reactions Catalyzed by *trans*-2a



alkynyl unit from the borate formed in situ from 9-MeO-9-BBN and NaC≡CMe[19] is transferred with similar ease to give alkyne **10**. More systematic investigations on the scope of the new method as well as on the catalytic performance of the resulting metal−imidazolidin-2-ylidene complexes, including enantiomerically pure ones, are presently underway.

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Supporting Information Available: Text giving details on the preparation of the chiral imidazolinium salt **6** and the palladium complexes together with the analytical and spectroscopic data of all new compounds and tables giving single-crystal X-ray information on complexes **2c** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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$b = 17.7340(6)$ Å, $c = 11.2349(3)$ Å, $V = 5766.4(3)$ Å^3, $Z = 8$, $\rho = 1.488$ Mg m^{-3}, μ(Mo Kα) = 0.912 mm^{-1}, 39 321 reflections measured, 6580 unique ($R_{int} = 0.21$). Final $R_w(F^2) = 0.198$ (all data) and R1 = 0.094 ($I > 2\sigma(I)$) with goodness of fit on F^2 $S = 1.10$ (CCDC 191644).

[15] For related NHC- and phosphine-containing complexes prepared by entirely different routes see: (a) Casellato, U.; Corain, B.; Zecca, M.; Michelin, R. A.; Mozzon, M.; Graziani, R. *Inorg. Chim. Acta* **1989**, *156*, 165. (b) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *585*, 348. (c) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145.

[16] In addition, small amounts of $(PPh_3)_2PdCl_2$ are invariably detected.

[17] Reviews: (a) Lucet, D.; Le Gall, T.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2580. (b) Bennani, Y. L.; Hanessian, S. *Chem. Rev.* **1997**, *97*, 3161.

[18] Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

[19] (a) Fürstner, A.; Seidel, G. *Tetrahedron* **1995**, *51*, 11165. (b) Fürstner, A.; Leitner, A. *Synlett* **2001**, 290.