A Pd complex of a tridentate pincer CNC bis-carbene ligand as a robust homogenous Heck catalyst†

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Received (in Irvine, CA, USA) 2nd October 2000, Accepted 6th December 2000
First published as an Advance Article on the web

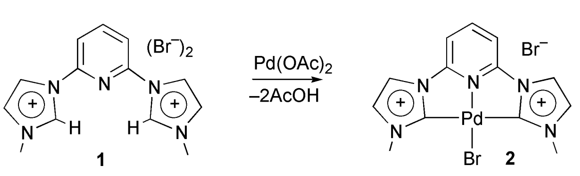
The bis-carbene precursor, 1, gives a thermally very robust Pd(II) catalyst for Heck coupling that maintains activity even in boiling diethylacetamide (bp 184 °C) in air.

One common and significant limitation of some homogeneous catalysts is their relatively rapid deactivation, particularly when high temperatures or harsh conditions are needed; this is often the case for cross-coupling reactions and alkane functionalization.[1] The facility of P–C bond cleavage reactions has been implicated in catalyst deactivation of phosphine complexes.[2] For example, the deactivation of the $[\mathrm{IrH_2(tfa)(P\{C_6H_4F\}_3)_2}]$ catalyst in alkane dehydrogenation was shown to correlate with the appearance of C_6H_5F, the product of P–aryl hydrogenolysis.[3]

The recent discovery of imidazole-based carbenes[4] and of their effectiveness as ligands[5] offers an opportunity to develop phosphine-free homogeneous catalysis. These carbenes are not only excellent ligands for late transition metals but are also able to promote a variety of catalytic reactions, including C–C[6] and C–N[7] coupling and olefin metathesis.[8] The thermal stability of carbene complexes is often high and they lack sensitive bonds that might be cleaved in any deactivation process. Since thermal stability of phosphine complexes can be improved by incorporation into a chelating ligand, as in the well known 'pincer' phosphines,[9] the same strategy might be useful in enhancing stability in the carbene case. Several authors have recently reported thermally stable palladium complexes active for the Heck reaction either with carbene or with pincer phosphines of both mono- and multi-dentate types as ligands.[6b,d,e,i,j,10]

We now report that the known carbene precursor,[11] **1**, readily formed by an improved synthesis (95% yield), reacts with Pd(OAc)$_2$ to give a carbene complex, **2**, as shown in Scheme 1 (ESI†). The thermal stability of the product is emphasized by the fact that the final stage of the synthesis of **2** takes place at 160 °C.

Fig. 1 shows the structure and metric parameters of the resulting complex from an X-ray structure determination.‡ The molecule is flat with a ligand bite angle of 79°. Otherwise, the metric parameters are similar to those previously found for related complexes.[6b,d] The Pd–C distance (2.038(6) Å) indicates that the bond is essentially single with very little back donation, as expected for this strongly Fischer-type carbene. This Pd–C distance is somewhat longer than in most prior cases,[6b,d] probably because the two high *trans*-effect carbene ligands are mutually *trans*.



Scheme 1

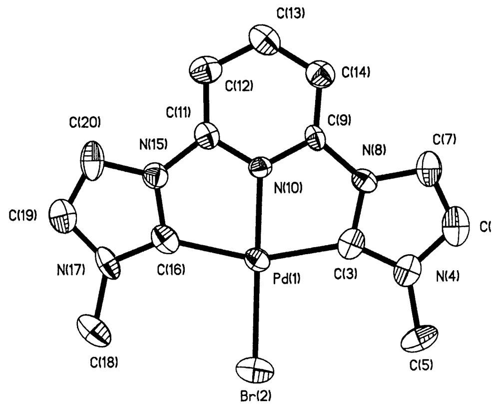
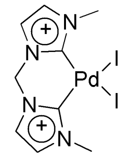


Fig. 1 ORTEP diagram of complex **2** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(10) 1.979(4), Pd(1)–C(3) 2.033(6), Pd(1)–C(16) 2.044(6), Pd(1)–Br(2) 2.4099(7); N(10)–Pd(1)–C(3) 78.9(2), N(10)–Pd(1)–C(16) 79.6(2), C(3)–Pd(1)–C(16) 158.5(2), N(10)–Pd(1)–Br(2) 179.03(13), C(3)–Pd(1)–Br(2) 100.29(16), C(16)–Pd(1)–Br(2) 101.18(16). Thermal ellipsoids are drawn at 50% probability.

The stability that ligand **1** imparts to complex **2** is apparent from comparison with other Heck catalysts containing chelating ligands. Catalysts **3**[6d,e] and **4**[12] are very active for the Heck reaction when used under nitrogen at 140 °C. Complex **3**, however, is reported[6e] to decompose in dimethylacetamide (DMA, bp 165 °C) above 70 °C. Our own work shows that in refluxing DMA in air, complex **3** begins to deposit Pd black after 8 h and complex **4** deposits Pd black after 17 h, while our complex, **2**, is unchanged (> 24 h). Other Pd pincer complexes, of PCP and SCS types, are also known as Heck catalysts.[10]



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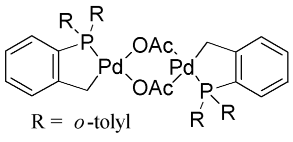

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The new complex **2** shows catalytic activity under argon for a standard Heck reaction between PhI and styrene (Table 1, entry 1) in refluxing diethylacetamide (DEA, bp 184 °C) in the presence of NaOAc as base.§ We find that with 0.2 mol% catalyst, good yields and turnover frequencies are found. Complex **2** shows comparable activity to the Heck catalysts, **3** and **4**, at least for PhI (Table 1, entries 1–3). Bromobenzene and styrene can also be converted to *trans*-stilbene in essentially quantitative yield in the presence of 5 mol% catalyst, NaOAc, and refluxing DMA, within 1 h (Table 2, entry 1). Surprisingly, but not uniquely,[10b,c,e] the catalyst retains activity even under air (Table 2, entry 2). Iodobenzene and styrene can also be converted to *trans*-stilbene in near quantitative yield in the presence of 5 mol% **2**, NaOAc, and refluxing DMA in a reflux

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† Electronic supplementary information (ESI) available: synthesis details and NMR data. See http://www.rsc.org/suppdata/cc/b0/b008038l/

DOI: 10.1039/b008038l

Table 1 Comparison of yields for catalysts **2**–**4** for the reaction of PhI with styrene in refluxing DEA to form *trans*-stilbene (under Ar with 0.2 mol% catalyst and NaOAc)[a]

Entry	Catalyst	0.5 h	1 h	1.5 h	2 h	4 h
1[b]	**2**	48, 494	58, 298	67, 230	73, 188	85, 109
2	**3**	36, 370	48, 247	62, 213	72, 185	84, 108
3	**4**	50, 514	61, 314	67, 230	75, 193	90, 116

[a] Reported as: yield (%), TOF [mol product/(mol Pd × h)]. Yield determined by ^{1}H NMR based on amount of product *vs*. amount of starting material remaining. [b] Average of two runs.

Table 2 Heck reaction between aryl halides and styrene to form *trans*-stilbene. All reactions carried out in refluxing DMA with NaOAc as base

Entry (air/Ar)	Aryl halide	**2** (mol %)	Reaction time/h	Stilbene yield (%)[a]	TOF [mol prod./(mol Pd)(h)]
1 (Ar)	PhBr	5	1	> 99	20
2 (air)	PhBr	5	1	> 99	20
3 (air)	PhI	5	1	> 99	20
4 (air)	PhI	1	1	89	89
5 (air)	PhI	0.0001	20	33	16.500
6 (Ar)[b]	*p*-(CHO)C_6H_4Cl	5	20	75	15

[a] Yield determined by ^{1}H NMR based on amount of product *vs*. amount of starting material remaining. [b] In the presence of *n*-Bu_4NBr (20 mol% *vs*. Pd).

apparatus open to the air (Table 2, entry 3). A yield of 89% can still be obtained in only 1 h if 1 mol% of **2** is used (Table 2, entry 4). To see if the TOF could be improved at low loading, we find that as little as 10^{-4} mol% of **2** still gives a TOF of 16.500 after 20 h under air (Table 2, entry 5). Aryl chlorides react more slowly (Table 2, entry 6). Other alkenes react satisfactorily—for example, *n*-butyl acrylate and PhI give the Heck product in 99% yield after 1 h in refluxing DMA with 1 mol% catalyst.

In view of recent studies that find evidence that the active species can be metallic palladium,[13] we checked **2**–**4** for heterogeneity by the Hg drop test.[14] Heck catalysis with **2**–**4** was unaffected by the presence of Hg, and no induction period is observed for **2**, so a homogeneous active species is likely.

On the standard model of the Heck reaction, with $[Pd(0)\{PR_3\}_2]$ as the key intermediate, a pincer carbene might seem to be a poor choice, even if the carbene is an acceptable replacement for the tertiary phosphine of the standard system. On the Amatore–Jutand model,[15] however, $[Pd(0)(OAc)\{PR_3\}_2]^-$ is the key intermediate. Our work supports this model if the pyridine part of the pincer ligand is considered as replacing the OAc group. It is true that $[Pd(0)XL_2]^-$ would normally be expected to adopt a trigonal geometry, but the presumed intermediate Pd(0) form of the metal being d^{10}, there should be no strong penalty to adopt the pincer geometry. Eisenstein and Clot[16] are currently looking at such mechanistic issues in detail.

The results are of interest not so much as an advance in Heck catalysis—other catalysts can be better[6,10]—but as an indication that chelating carbenes can provide ligand systems that give high catalytic activity with excellent stability, even in air. This approach should be widely applicable to the development of non-phosphine late metal homogeneous catalysis.

We thank US DOE (J. A. L.) and NSF (R. H. C.) for funding and Matthew Torres for some preliminary observations.

Notes and references

‡ *Crystal data for* **2**: $C_{11}H_7Br_2N_5Pd{\cdot}H_2O$, monoclinic, space group $P2(1)/n$, a = 8.7782(4), b = 14.3181(6), c = 13.5684(6) Å, α = 90, β = 107.1600(10), γ = 90°, Z = 4, D = 2.011 g cm^{-3}, μ = 6.044 mm^{-1}, 5300 measured reflections, 1467 [R(int) = 0.0310] independent reflections, R = 0.0225 [$F > 2\sigma(F)$]. Crystals were grown by diffusion of CH_2Cl_2 into a DMSO solution. Data collection: Siemens Smart CCD diffractometer (λ = 0.71073 Å). The structure was solved by direct methods and was refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. CCDC 182/1880. See http://www.rsc.org/suppdata/cc/b0/b008038l for crystallographic files in .cif format. The diffraction frames were integrated using the SAINT[17] package and corrected for absorption with SADABS.[18]

§ *General Heck procedure*: NaOAc (360 mg, 4.4 mmol) and the catalyst were placed in a 3-necked flask fitted with a reflux condenser and degassed. Aryl halide (4 mmol), styrene (640 μL, 5.6 mmol), and solvent (DMA or DEA, 5 mL), were added under Ar or air. The reaction vessel was placed into an oil bath preheated to the desired temperature. Aliquots (200 μL) were removed after fixed times and added to 10 mL CH_2Cl_2. The organic layer was extracted five times with 10 mL portions of water and dried with $MgSO_4$. The mixture was then filtered and the CH_2Cl_2 removed *in vacuo*. The residue was dissolved in $CDCl_3$ or CD_2Cl_2 and analyzed by ^{1}H NMR (400 MHz).

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