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Synthesis of the First C-2 Cyclopalladated Derivatives of 1,3-Bis(2-pyridyl)benzene. Crystal Structures of [Hg(N-C-N)Cl], [Pd(N-C-N)Cl], and [Pd$_2$(N-C-N)$_2$(μ-OAc)]$_2$[Hg$_2$Cl$_6$]. Catalytic Activity in the Heck Reaction

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The synthesis of C-2 cyclopalladated derivatives of 1,3-bis(2-pyridyl)benzene (N-CH-N) has been achieved for the first time through a transmetalation reaction. C-2 mono- and dinuclear complexes have been obtained by reaction of Pd(OAc)$_2$ and the organomercury(II) compound [Hg(N-C-N)Cl] (**1**) as precursors. The new species **2**−**11** were characterized in solution and, in the case of [Pd(N-C-N)Cl] (**2**) and [Pd$_2$(N-C-N)$_2$(OAc)]$_2$[Hg$_2$Cl$_6$] (**11**) as well as of [Hg(N-C-N)Cl] (**1**), in the solid state. The X-ray crystal structures unambiguously show the pincer behavior of the N-C-N ligand in the palladium species and the linear coordination C−Hg−Cl in the mercury precursor. Displacement of the coordinated halide gives cationic species such as [Pd(N-C-N)(H$_2$O)][BF$_4$] (**5**) or, in the absence of donor solvents or anions, the dinuclear halide-bridged species [Pd$_2$(N-C-N)$_2$(μ-X)][BAr′$_4$] (X = Cl (**6**), Br (**7**), I (**8**); Ar′ = 3,5-(CF$_3$)$_2$-C$_6$H$_3$). For comparison purposes [Pd(N-C-N)(OAc)] (**9**) and [Pd$_2$(N-C-N)$_2$(μ-OAc)]-[BAr′$_4$] (**10**) were also prepared. The mononuclear complexes **2**, **4**, **5**, and **9** are high-performance catalysts in the Heck reaction of iodobenzene and methyl acrylate, even at moderate temperatures. Under microwave heating a turnover frequency as high as 280 000 h^{-1} is observed with complex **2** at the nominal temperature of 135 °C.

Introduction

Palladium(II) and platinum(II) organometallic derivatives with terdentate mono- or dianionic ligands with pyridine nitrogen donors are well-known. Five- and six-membered cyclometalated species with N-C-N,[1] C-N-C,[2] and N-N-C[3] sequences of donor atoms have been reported and sometimes compared[4] with the N-N-N coordination complexes of the isostructural 2,2′:6′,2″-terpyridine. The N-N-C derivatives have been widely investigated, and many examples have been reported, with both metal−C(sp^2) and metal−C(sp^3) bonds. At variance, species with the dianionic ligands C-N-C, which imply a trans C−metal−C arrangement, are still rare.[2] The so-called pincer ligands, N-C-N, where C is an anionic aryl carbon atom, have attracted great attention:[5] their derivatives are currently of paramount interest, owing to the array of their potential applications.[6] In the case of late transition metals the synthesis of mononuclear pincer N-C-N species is not that straightforward, as in this case direct C$_{\text{aryl}}$−H activation is the exception instead of the rule. Alternative strategies, which have been recently reviewed,[6] comprise oxidative addition of carbon−halogen bonds, transmetalation, and, more recently, even transcyclometalation. A perusal of the literature shows that the behavior of these types of ligands is often hardly predictable and that the choice of the best-suited synthetic methodology is not that trivial. This fact is well exemplified by the reactiv-

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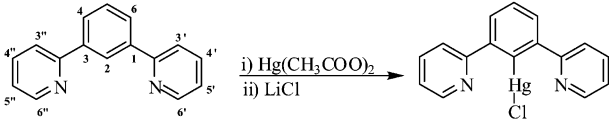
ity of bis(pyridine) N-C-N arylpincer ligands. Although these derivatives have been less investigated by far than the analogous diamino species, their peculiar behavior is readily apparent, even from the very few reports published thus far. With 1,3-bis(2-pyridyl)benzene direct C−H activation has been successfully achieved in the case of platinum(II):[1b] regioselective monometalation takes place at C-2 of the benzene ring, as previously observed for ruthenium and osmium,[7] giving [Pt(N-C-N)Cl] in fairly good yields. Despite numerous attempts under different conditions with several precursors, this was not the case for palladium: no C-2 metalation was achieved and either adducts, [Pd(N−CH−N)Cl_2]$_2$, or dimeric 4,6-bis-palladated derivatives were isolated.[1b,8] In sharp contrast, introduction of a spacer, e.g. −C(O)− or −CH(Me)−, between the central aryl ring and the pyridine substituents promotes ready palladation at C-2 to give [Pd(N-C-N)X] (X = OAc, Cl) derivatives involving two six-membered palladacyclic rings, as reported by Canty et al. several years ago.[1a,9]

Here we report the synthesis of the first C-2 cyclopalladated derivatives of 1,3-bis(2-pyridyl)benzene obtained by transmetalation of the corresponding arylmercury derivative. Also described are the X-ray crystal structures of the mercury derivative [Hg(N-C-N)Cl] (**1**), that of [Pd(N-C-N)Cl] (**2**), and that of a more complex species, [Pd_2(N-C-N)$_2$(OAc)]$_2$[Hg_2Cl_6] (**11**), isolated in the course of the transmetalation reaction. Preliminary results on the catalytic activity of a range of these new complexes in the Heck reaction, between iodobenzene and methyl acrylate, are reported as well.

Results and Discussion

The ligand 1,3-bis(2-pyridyl)benzene, N−CH−N, was prepared from 1,3-dicyanobenzene and acetylene, in the presence of a cobalt catalyst according to a literature procedure.[11]

Cardenas et al. have previously shown that carbon palladation does not take place when 1,3-bis(2-pyridyl)benzene is reacted with $Li_2[PdCl_4]$ or with other Pd(II) chloride species but that C−H activation readily occurs in the reaction with [Pd(OAc)$_2$]. Rather surprisingly, this does not result in the formation of a C-2 metal bond, but instead it leads to the isolation of dimeric species with bridging acetato ions between two doubly 4,6-metalated units.[1b] In view of the potential interest of a C-2 palladated derivative of this N−CH−N ligand, e.g. as a catalytic precursor,[12] we deemed it worthwhile to pay some more effort to its preparation through transmetalation. Transmetalation of aryllithium species has been widely applied, but lithiation of N-C(H)-N ligands is not straightforward, as it is frequently not regioselective. Hence, since mercury(II) salts, particularly the acetate, are known to easily attack aromatic compounds,[13] we decided to synthesize the mercury derivative and try a metal-exchange reaction. Indeed, reaction of the ligand with [Hg(OAc)$_2$] in methanol, after treatment with LiCl, affords [Hg(N-C-N)Cl] (**1**), albeit in moderate yield (ca. 60%).



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The ^1H NMR spectrum of **1** confirms the occurrence of C-metalation: of the six resonances observed, two, at δ 7.98 (d, 2H) and 7.52 (t, 1H), are easily assigned to $H_4 + H_6$ and H_5, respectively, of the aryl ring. The former resonance is flanked by satellites due to coupling to ^{199}Hg, ^4J(Hg−H) = 69 Hz,[14] proving a covalent C(2)−Hg bond. The four resonances of the pyridyl rings are almost unchanged with respect to the free ligand: in particular, the most deshielded resonance, ca. δ 8.7, assigned to the proton close to the nitrogen atom, is almost coincident in the two spectra, suggesting uncoordinated pyridine rings. On the whole, however, the NMR spectrum does not allow us to assign the exact structure of complex **1**.

The X-ray diffraction study of a single crystal, obtained by slow diffusion of isopropyl ether into a dichloromethane solution of **1**, confirms that the ligand does not behave as a pincer and that coordination around the mercury ion is linear, as often is the case for R−Hg−Cl species.[15] A view of **1** is given in Figure 1, and principal metric parameters are reported in the figure caption. Hg−Cl and Hg−C(2) bonds and the Cl−Hg−C(2) angle are normal.[16] The Hg−N(1) and Hg−N(2) distances of 2.747(3) and 2.722(3) Å, respectively, are in our opinion nonbonding, because the nitrogen lone pairs do not point at the metal atom,[17] but it is

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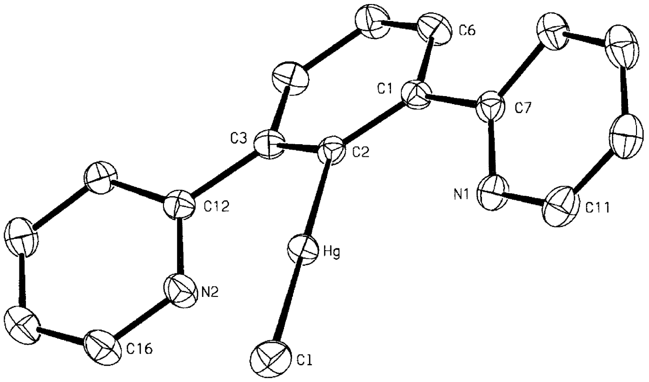
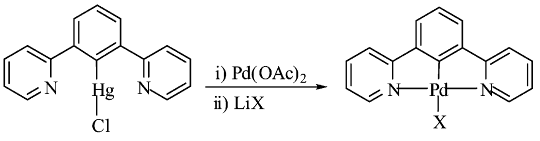


Figure 1. ORTEP view of **1**. Ellipsoids are drawn at the 30% probability level. Principal bond parameters: Hg−Cl = 2.324(1) Å, Hg−C(2) = 2.073(3) Å, Cl−Hg−C(2) = 179.3(1)°.

worth mentioning that in other cases similar values have been considered weakly bonding (compare for instance Hg−N = 2.70(2) Å in ref 18).[18,19] The three aromatic rings are strictly planar. The dihedral angles between their best planes are C(1)/C(6)−N(1)/C(11) = 26.7(2)°, C(1)/C(6)−N(2)/C(16) = 24.7(2)°, and N(1)/C(11)−N(2)/C(16) = 16.7(3)°.

Reaction of the mercury derivative **1** with palladium(II) acetate (molar ratio 1:1) affords an orange-red species (see below) which after exchange with the appropriate lithium halide, LiCl, LiBr, or LiI, cleanly gives the cyclometalated complexes [Pd(N-C-N)X] (X = Cl (**2**), Br (**3**), I (**4**)). All of them display a high thermal stability.



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X= Cl, **2**; Br, **3**; I, **4**

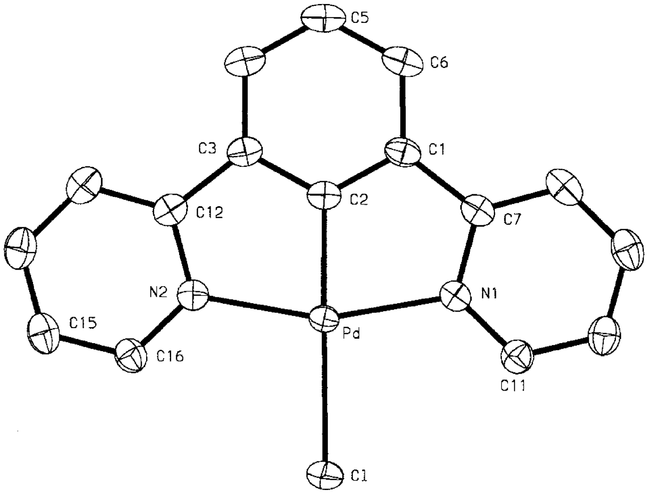


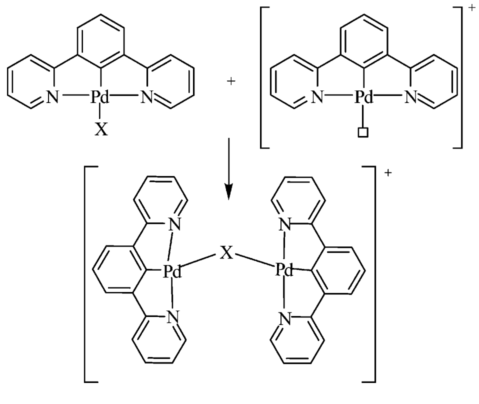
Figure 2. ORTEP view of **2**. Ellipsoids are as in Figure 1.

Table 1. Selected Distances (Å) and Angles (deg) in 2 with Estimated Standard Deviations (Esd's) on the Last Figure in Parentheses

Pd−Cl	2.427(1)	Pd−N(1)	2.065(1)
Pd−N(2)	2.063(1)	Pd−C(2)	1.910(2)
Cl−Pd−N(1)	99.6(1)	Cl−Pd−N(2)	100.4(1)
Cl−Pd−C(2)	179.2(1)	N(1)−Pd−N(2)	160.1(1)
N(1)−Pd−C(2)	80.0(1)	N(2)−Pd−C(2)	80.1(1)

The ^{1}H NMR spectra of complexes **2**−**4** are unexceptional: the pattern observed, six sharp resonances in the aromatic region, is consistent with an anionic N-C-N ligand. The resonances at δ 8.95 (ddd, 2H; **2**), δ 9.24 (d br, 2H; **3**), δ 9.50 (broad, 2H; **4**), assigned to $H_{6'}$ and $H_{6''}$, are deshielded with respect to the free ligand and shifted more and more downfield on going from **2** to **3** and to **4**. This trend, previously reported for analogous systems,[20] supports the N-C-N pincer-like coordination of the ligand. The X-ray structure determination of **2** (crystals suitable for the X-ray analysis were obtained by slow diffusion of isopropyl ether into a dichloromethane solution of **2**) proves the mononuclear nature of these complexes and the terdentate behavior of the ligand. The structure closely reminds that of the related platinum derivative:[1b] an ORTEP diagram of **2** is shown in Figure 2. Principal bond lengths and angles are reported in Table 1. The Pd atom displays a square-planar coordination with a very slight tetrahedral distortion, maximum distances from the best plane being +0.007(1) and −0.011(1) Å for N(1) and C(2), respectively. All bond lengths and angles are as expected. The whole molecule can be considered essentially planar, maximum distances from the least-squares plane being +0.053(2) and −0.034(2) Å for C(15) and C(5), respectively.

From the neutral species **2**−**4**, cationic derivatives can be obtained by abstraction of the halide ion. Reaction of compound **2** with Ag[BF$_4$] in dichloromethane/acetone affords the solvento cationic complex [Pd(N-C-N)(H$_2$O)][BF$_4$] (**5**). Reaction of **2**−**4** with Na[BAr′$_4$] (Ar′ = 3,5-(CF$_3$)$_2$-C$_6$H$_3$), in dichloromethane under strictly anhydrous conditions, leads to the dinuclear halide-bridged species [Pd$_2$(N-C-N)$_2$(μ-X)][BAr′$_4$] (X = Cl (**6**), Br (**7**), I (**8**)). The reaction, likely driven to completeness by the insolubility of NaX in dichloromethane, gives compounds **6**−**8** even with an excess of Na[BAr′$_4$]. The formation of the nontrivial monobridged complexes **6**−**8** indicates the high reactivity of the coordinative unsaturated fragment [Pd(N-C-N)]$^+$: in the absence of other



X= Cl, **6**; Br, **7**; I, **8**; OAc, **10**

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donors, it hooks the neutral reagent [Pd(N-C-N)Cl], to attain saturation.[21]

We investigated also the first product of the reaction of [Pd(OAc)$_2$] with the mercury precursor [Hg(N-C-N)-Cl] (**1**) in a 1:1 molar ratio. The reaction was carried out in ethanol/dichloromethane solution at reflux temperature. After removal of the solvents, the crude product was taken up with dichloromethane to give, after filtration, a yellow solution. From the solution an orange-red solid was obtained by evaporation of the solvent. Recrystallization from dichloromethane/diethyl ether gave samples which were repeatedly submitted to elemental analyses: the C, H, and N values were found to be poorly reproducible, suggesting that more species are formed. On the other hand, the ^{1}H NMR spectra show in the aromatic region only one set of signals indicative of a [Pd(N-C-N)] unit. Accordingly, the samples were thought to be mixtures of [Pd(N-C-N)-(OAc)], the expected product, and of other species, possibly an ionic isomer, [Pd$_2$(N-C-N)$_2$(μ-OAc)][OAc], or other salts (e.g. chloride, chloromercurates, ...) of the same cation. Indeed, the IR spectra show a rather complex pattern in the region of the acetate absorptions[22] and in the ^{1}H NMR spectrum the integral ratio between the aromatic protons of the ligand and the methyl protons of the acetate is somewhat erratic. To get a better insight into the nature of the reaction products, the mononuclear acetate [Pd(N-C-N)(OAc)] (**9**) was prepared through an exchange reaction:

$$[\mathrm{Pd(N{-}C{-}N)Cl}] + \mathrm{Ag(OAc)} \rightarrow [\mathrm{Pd(N{-}C{-}N)(OAc)}] + \mathrm{AgCl}\downarrow$$

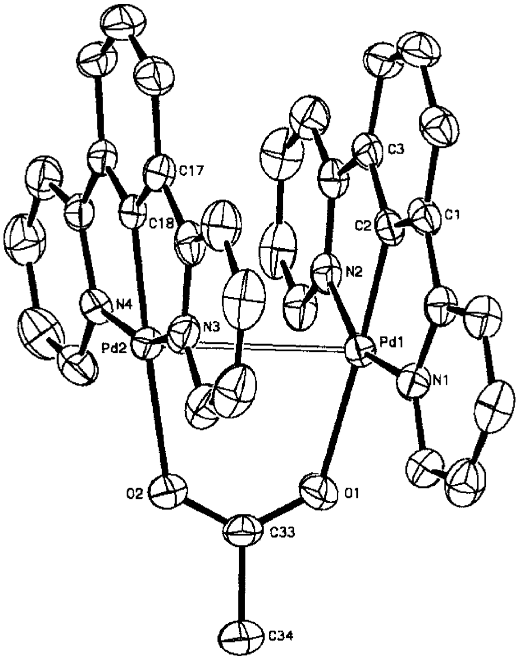

Figure 3. ORTEP view of a monomeric cation in **11**·EtOH. Ellipsoids are as in Figure 1.

Table 2. Selected Distances (Å) and Angles (deg) in 11·EtOH with Estimated Standard Deviations (Esd's) on the Last Figure in Parentheses

Hg−Cl(1)	2.637(2)	Hg−Cl(1)′	2.591(2)
Hg−Cl(2)	2.430(3)	Hg−Cl(3)	2.429(3)
Pd(1)−Pd(1)′	3.253(1)	Pd(1)−Pd(2)	3.069(1)
Pd(1)−O(1)	2.163(4)	Pd(1)−N(1)	2.065(4)
Pd(1)−N(2)	2.063(4)	Pd(1)−C(2)	1.905(5)
Pd(2)−O(2)	2.149(3)	Pd(2)−N(3)	2.052(4)
Pd(2)−N(4)	2.060(4)	Pd(2)−C(18)	1.908(5)
Cl(1)−Hg−Cl(1)′	88.8(1)	Cl(1)−Hg−Cl(2)	113.9(1)
Cl(1)−Hg−Cl(3)	108.8(1)	Cl(1)′−Hg−Cl(2)	109.0(1)
Cl(1)′−Hg−Cl(3)	111.5(1)	Cl(2)−Hg−Cl(3)	120.4(1)
Hg−Cl(1)−Hg′	91.2(1)		
O(1)−Pd(1)−N(1)	96.2(1)	O(1)−Pd(1)−N(2)	103.9(1)
O(1)−Pd(1)−C(2)	173.8(2)	N(1)−Pd(1)−N(2)	159.7(2)
N(1)−Pd(1)−C(2)	80.0(2)	N(2)−Pd(1)−C(2)	80.1(2)
O(2)−Pd(2)−N(3)	100.4(2)	O(2)−Pd(2)−N(4)	99.3(2)
O(2)−Pd(2)−C(18)	177.8(1)	N(3)−Pd(2)−N(4)	160.1(2)
N(3)−Pd(2)−C(18)	80.1(2)	N(4)−Pd(2)−C(18)	80.3(2)
Pd(2)−Pd(1)−Pd(1)′	164.7(1)		

The yellow complex **9** reacts with Na[BAr′$_4$] in dichloromethane to afford the dinuclear compound [Pd$_2$(N-C-N)$_2$(μ-OAc)][BAr′$_4$] (**10**), analogous to the halide-bridged species **6**−**8**. Comparison of the ^{1}H NMR spectra of compounds **9** and **10** with that of the orange-red material, particularly with regard to the most deshielded resonances, rules out the presence of the mononuclear species **9** (in the orange-red material) and points to a mixture of different salts of the unique dinuclear cation [Pd$_2$(N-C-N)$_2$(μ-OAc)]$^+$. Final evidence for the dinuclear cation [Pd$_2$(N-C-N)$_2$(μ-OAc)]$^+$ was attained when a crystal, serendipitously grown from an ethanolic solution, was found suitable for X-ray analysis, **11**. The structure consists of the packing of [Pd$_2$(N-C-N)$_2$(μ-OAc)]$^+$ cations, [Hg$_2$Cl$_6$]$^{2-}$ anions, and EtOH molecules in the molar ratio 2:1:1. An ORTEP view of the cation is shown in Figure 3. Principal distances and angles are reported in Table 2. To the best of our knowledge, the structure of the present cation is the first example of a palladium derivative where two equal complex moieties are bridged by a single acetato ligand. In the [Hg$_2$Cl$_6$]$^{2-}$ dianion the metal atoms are in a distorted-tetrahedral coordination, each of them being bonded to two terminal and two double-bridging chloride ligands.[23] The dianion lies around a crystallographic 2-fold axis and displays normal bond lengths and angles. In the cation the Pd(1)−Pd(2) distance is 3.069(1) Å. If this interaction is not considered (but see below), both Pd atoms are in a square-planar coordination with a slight tetrahedral distortion. Maximum distances from the best plane of Pd(1) are +0.084(4) and −0.064(4) Å for C(2) and N(1), respectively. For Pd(2), maximum distances from the best plane are +0.049(5) Å for N(4) and −0.056(4) Å for C(18). The dihedral angle for these two least-squares planes is 18.5(2)°: i.e., the two planes are clearly nonparallel. The [Pd$_2$(N-C-N)$_2$(μ-OAc)]$^+$ cations are packed in stacked dimers, as shown in Figure 4. The Pd(1)−Pd(1′) distance is 3.253(1) Å, not much longer than the Pd(1)−Pd(2) distance mentioned above. The Pd(2)−Pd(1)−Pd(1′) angle is 164.7(1)°, and the metal

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[21] The influence of the anion on the stabilization of similar mono- vs dinuclear cations has been recently thoroughly discussed: van de Broeke, J.; Heeringa, J. J. H.; Chuchuryukin, A. V.; Kooijman, H.; Mills, A. M.; Spek, A. L.; van Lenthe, J. H.; Ruttink, P. J. A.; Deelman, B. J.; van Koten, G. *Organometallics* **2004**, *23*, 2287 and references therein.

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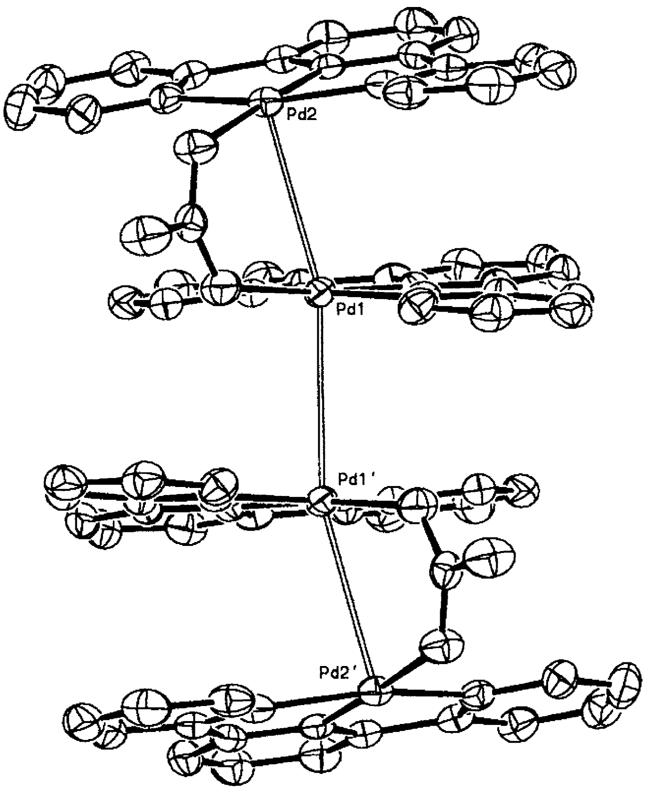


Figure 4. ORTEP view of a cationic dimeric couple in **11**. Ellipsoids are as in Figure 1. Intermetallic distances and angles: Pd(1)−Pd(2) = 3.069(1) Å, Pd(1)−Pd(1′) = 3.253(1) Å, Pd(2)−Pd(1)−Pd(1)′ = 164.7(1)°.

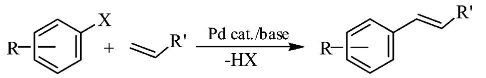
Table 3[a]

pincer com	t (h)	T (°C)	yield (%)[b]	TON[c]	TOF (h^{-1})[d]
[Pd(N-C-N)Cl] (**2**)	14	110	75	75 000	5 357
[Pd(N-C-N)Cl] (**2**)[e]	0.33	135	93	93 000	281 818
[Pd(N-C-N)Cl] (**2**)	14	135	98	98 000	7 036
[Pd(N-C-N)I] (**4**)	14	110	66	65 500	4 679
[Pd(N-C-N)(OH$_2$)][BF$_4$]·H$_2$O (**5**)	14	110	84	83 500	5 964
[Pd$_2$(N-C-N)$_2$(μ-Cl)][BAr′$_4$] (**6**)	14	110			
[Pd(N-C-N)(OAc)] (**9**)	14	110	99	100 000	7 143
[Pd(N-C-N)(OAc)] (**9**)	5	110	97	97 000	19 400
[Pd(N-C-N)(OAc)] (**9**)	2	110	93	93 000	46 500
[Pd$_2$(N-C-N)$_2$(μ-OAc)][BAr′$_4$] (**10**)	14	100			

[a] Reaction conditions: PhI, 2 mmol; methyl acrylate, 3 mmol; NEt$_3$, 3 mmol; amount of catalyst (mol %), 0.001; DMF, 10 mL. [b] Isolated yield. [c] TON = turnover number, in units of mol of product/mol of catalyst. [d] TOF = turnover frequency, in units of mol of product/((mol of catalyst) h). [e] Reaction carried out in a microwave oven.

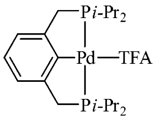
coordination planes of the two dinuclear units are rotated ca. 90° with respect to each other, as can be seen in Figure 4. In light of this packing, the aforementioned Pd−Pd distance can be considered weakly bonding.[3g] Pd−C and Pd−N bond lengths are very similar to those found in **2** (see Tables 2 and 3). The Pd(1)−O(1) and Pd(2)−O(2) bond lengths, 2.163(4) and 2.149(3) Å, respectively, are both elongated by the trans influence of the aryl carbon atoms. The acetato ligand is strictly planar, and the dihedral angles between its plane and the best planes of Pd(1) and Pd(2) are 97.3(1) and 92.3(1)°, respectively. At variance with **2**, the two whole Pd(N$_2$C$_{16}$)O moieties in **11** show large deviations from planarity, in the range +0.263(5) and −0.308(5) Å for Pd(1) and +0.232(5) and −0.159(6) Å for Pd(2). This is probably due to the π stacking between the four neighboring planes.

Catalytic Activity. The Heck reaction provides for the coupling of a suitable aryl halide to an olefin through the formation of a new C−C bond between two sp^2 carbons.[24]

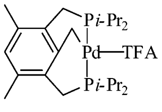


Due its wide scope and its enormous synthetic potential, this reaction is one of the most frequently applied among the synthetic methodologies reliant on transition-metal catalysis. Palladium is the metal of choice for this process, and a large variety of Pd(II) complexes have been tested and found catalytically active in this coupling.

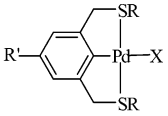
Aryl pincer palladium complexes have been poorly utilized until recently.[25] Both phenyl-PCP phosphino[26] and phenyl-SCS pincer sulfide[27] complexes **12a** and **13** are active catalysts in promoting the coupling of phenyl iodide with acrylic acid esters at 110−140 °C. The



12a



12b



13

catalytic activity of these complexes is not tremendously impressive, as it ranges between 150 and 1500 h^{-1} (TOF) with the SCS and the PCP ligands, respectively. This notwithstanding, given the exceptional thermal stability of the tridentate system, extremely high turnover numbers (TON) can be attained if long reaction times are applied (over 500 000 in 350 h with the PCP phosphino species).[26]

Both the introduction of electron-releasing substituents in the para position of the phenyl-SCS derivative and the interposition of an sp^3 carbon between the phenyl ring and the metal of the PCP complex lead to catalysts of improved performances, probably because of the increased electron density at the metal. For instance, the palladium benzyl PCP-pincer ligand **12b** is 1 order of magnitude more active (13 000 h^{-1} at 140 °C) than the related phenyl derivative and is also capable of activating phenyl bromide toward the coupling with acrylate.[26]

The catalytic activity of the aryl pincer SCS Pd(II) complex is substantially preserved, even when the ligand is attached to a soluble polymer,[27a] and is strongly reduced but not suppressed when sterically demanding groups such as *tert*-butyl are positioned on the sulfur donors.[27b] Quite recently the fluorous SCS pincer palladium complex **13** (R = C$_6$H$_4$-p-C$_6$F$_{13}$) has been synthesized and shown to be catalytically active under both microwave and thermal heating. This complex has the advantage that at the end of the reaction

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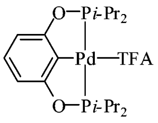
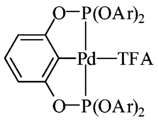
it can be recovered by solid fluorous phase extraction and reused in the same or in different Heck couplings.[28]

The catalytic activity of pincer PCP complexes increases significantly on increasing the π-acceptor character of the P-donor. While PCP phosphino catalysts are totally inactive toward aryl chloride, the corresponding PCP phosphinito derivatives such as **14** have been found to be highly active in promoting the Heck coupling of aryl chloride.[29] An even more active catalyst is obtained when the pincer Pd complex is supported by a phosphite donor, as in the case of **15** (Ar = *p*-anisyl). In the presence of hydroquinone as an additive, an incredibly high TON (8 900 000!) has been achieved with this catalyst in the coupling of iodobenzene with butyl acrylate at 180 °C.[30]

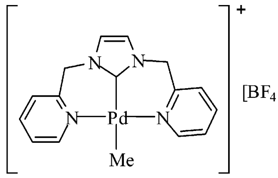


14

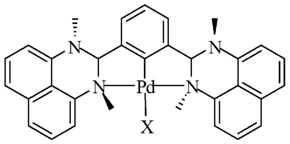


15

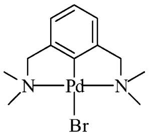
As to the utilization of NCN pincer palladium catalysts in the Heck reaction, to the best of our knowledge there are no more than two precedents in the recent literature which are pertinent to our case. In the first one the cationic Pd(II) complex **16**, featuring a tridentate carbene ligand flanked by two 2-picolyl fragments capable of trans coordination to the metal, has shown a good catalytic activity in the coupling of 4-bromoacetophenone with *n*-butyl acrylate, where a TOF slightly higher than 5000 h^{-1} has been recorded at 120 °C.[31]



16



17a



17b

The second report describes an unusual NCN pincer ligand featuring additional N donors, whose presence is assumed to provide a less rigid tridentate coordination to the metal.[10] The relevant Pd complex **17a** performs well in the coupling of para-substituted aryl halides to methyl acrylate, where exceptionally high peaks of catalytic activity have been sometimes reached. For instance, in the reaction of 4-tolyl iodide at 110 °C an impressive TON value of 4.3×10^6 corresponding to an average TOF of 350 000 h^{-1} has been attained in 12 h with a homeopathic amount of Pd complex (100 ppb of Pd/mmol of iodide). These values are over 1 order of magnitude higher than those recorded with the more simple NCN pincer complex **17b** without any additional N donor. It is claimed that the observed increase in activity and stability is related to the dynamic behavior of the complex **17a**, which follows from the presence of additional coordination sites.[10]

We have tested our complexes in the benchmark Heck reaction of iodobenzene with methyl acrylate (Table 3). The experiments have been run for 14 h at 100−135 °C at a substrate to Pd ratio of 10^4, using DMF as solvent and triethylamine as base. In all cases the reaction is completely diastereoselective and methyl *trans*-cinnamate is obtained as the exclusive reaction product. No apparent precipitation of palladium was noticed during the reaction, and the solutions at the end of the experiments were always clear and transparent.

As a general trend, the mononuclear complexes **2**, **4**, and **5** are quite close in activity, while at variance the dinuclear species **6** and **10** are completely inactive under the same conditions. At 110 °C the TOF's improve slightly on moving from the iodo derivative **4** (4700 h^{-1}) to the cationic aquo fluoborate **5** (6.000 h^{-1}) with the chloro complex **2** lying between (5400 h^{-1}). Application of microwave heating to the nominal temperature of 135 °C causes an exceptional increase of the catalytic activity of the chloro complex **2**, with a TOF of over 280 000 h^{-1} being reached. Notably, this figure overrides by far the value attained at the same temperature but with thermal heating (7000 h^{-1}).

The best catalyst in the range of complexes screened is the acetato derivative **9**, which is able to provide nearly quantitative conversions in 2−3 h even at 110 °C with very high TOF's in the early times of the reaction (46 500 h^{-1} after 2 h). This is one of the highest activities ever reported for this reaction at this temperature.

Conclusions

The results obtained in this study point out that aryl NCN pincer pyridine Pd(II) complexes are catalysts of high activity in the Heck reaction. This allows us to obtain high reaction rates (TOF > 45 000 h^{-1}) even at fairly low temperatures (110 °C) and to run the reaction at high substrate loading. Although apparently the scope of the reaction is limited to aryl iodides, the catalytic activities observed are comparably much higher than those recorded with the corresponding pincer PCP and SCS complexes and indicate a great potential for complexes of similar design in the asymmetric version of this reaction.

Experimental Section

General Considerations. All reactions for the preparation of novel compounds were carried out under nitrogen using standard Schlenk-type flasks. Test reactions for the catalytic activity of catalysts in the Heck reaction were carried out in air. Workup procedures were done in air. Reagents were purchased from Aldrich Chemical Co. and used as received. [Pd(OAc)$_2$] was obtained from Engelhard. The salt Na[BAr′$_4$]

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(sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) was synthesized by the literature method.[32]

Solvents were distilled and purified prior to use according to standard methods. ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR300 and a Varian Mercury VX spectrometer (400 MHz). Chemical shifts are given in ppm relative to internal TMS (^{1}H and ^{13}C). Flash chromatography was performed using Merck silica gel 60 (230−400 mesh). Elemental analyses (C, H, N) were performed with a Perkin-Elmer 240B elemental analyzer by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Infrared spectra were recorded with a Jasco FT-IR 480P using Nujol mulls.

Synthesis of the Ligand 1,3-Bis(2-pyridyl)benzene (N-CH-N). A solution of 1,3-dicyanobenzene (10.00 g, 0.078 mol) and (η^5-cyclopentadienyl)cobalt 1,5-cyclooctadiene (500.0 mg) in degassed anhydrous toluene (100 mL) was introduced, by suction, into a 0.2 L autoclave, evacuated from the air (0.1 Torr). The reaction vessel was pressurized to 13 bar with acetylene and then rocked and heated to 120 °C for 20 h. After cooling and release of the residual gas, the solvent was evaporated and the brown residue treated with HCl (5%) and NaOH (5%), then extracted with Et_2O, and dried on Na_2SO_4 to give the crude 1,3-bis(pyridyl)benzene, as a pale brown oil. Column chromatography on silica gel 60, using benzene/acetone (10:1) as eluent, gave 16.48 g (0.071 mol, yield 91%) of N-CH-N as a light yellow oil.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.30 (ddd, J(H−H) = 7.5, 4.8, 1.5 Hz, 2H (H5′, H5″)); 7.62 (t, J(H−H) = 7.8 Hz, 1H (H5)); 7.82 (tm, J(H−H) = 7.5 Hz, 2H (H4′, H4″)); 7.90 (dm, ^{3}J(H−H) = 7.5 Hz, 2H (H3′, H3″)); 8.11 (dd ^{3}J(H−H) = 7.8 Hz, ^{4}J(H−H) = 2.1 Hz, 2H (H4, H6)); 8.74 (m, overlapping 1H + 2H (H2 + H6′, H6″)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (ddd, J(H−H) = 7.5, 4.8, 1.5 Hz, 2H (H5′, H5")); 7.58 (t, ^{3}J(H−H) = 7.8 Hz, 1H (H5)); 7.76 (td, J(H−H) = 7.5, 1.8 Hz, 2H (H4′, H4")); 7.84 (dm, ^{3}J(H−H) = 7.8 Hz, 2H (H3′, H3″)); 8.05 (dd, ^{3}J(H−H) = 7.8 Hz, ^{4}J(H−H) = 2.1 Hz, 2H (H4, H6)); 8.62 (t, ^{4}J(H−H) = 2.1 Hz, 1H (H2)); 8.71 (m, 2H (H6′, H6″)). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, APT): δ 156.93 (C); 149.43 (CH); 139.66 (C); 136.56 (CH); 129.01 (CH); 127.25 (CH); 125.33 (CH); 122.06 (CH); 120.48 (CH).

Synthesis of [Hg(N-C-N)Cl] (1). A mixture of N-CH-N (239.7 mg, 1.03 mmol) and mercury(II) acetate (320.4 mg, 1.00 mmol) in absolute ethanol (20 mL) was heated under reflux for 24 h. Afterward a solution of lithium chloride (94 mg) in methanol (15 mL) was added and the mixture was heated for 15 min. The solution was poured into distilled water (100 mL): the white precipitate that formed was filtered off, washed with water and ice-cold methanol, and dried to give [Hg(N-C-N)Cl] (**1**).

Yield: 270 mg, 57%. Mp: 203−204 °C. Anal. Calcd for $C_{16}H_{11}ClHgN_2$: C, 41.08; H, 2.35; N, 5.99. Found: C, 41.04; H, 2.29; N, 5.92. ^{1}H NMR (300 MHz, $CDCl_3$,): δ 7.35 (ddd, J(H−H) = 7.5, 5.1, 1.2 Hz, 2H (H5′, H5")); 7.52 (t, ^{3}J(H−H) = 7.5 Hz, 1H (H5)); 7.81 (ddd, J(H−H) = 7.8, 7.5, 2.1 Hz, 2H (H4′, H4″)); 7.87 (dm, ^{3}J(H−H) = 7.8 Hz, 2H (H3′, H3″)); 7.98 (d, ^{3}J(H−H) = 7.5 Hz, ^{4}J(Hg−H) 69 Hz, 2H (H4, H6)); 8.73 (ddd, J(H−H) = 5.1 Hz, 2.1 Hz; 1.0 Hz, 2H (H6′, H6″)).

Transmetalation Reactions. Synthesis of [Pd(N-C-N)X] (X = Cl (2), Br (3), I (4)). A suspension of compound **1** (120.0 mg, 0.26 mmol) in ethanol (20 mL) was added to a solution of palladium(II) acetate (57.7 mg, 0.26 mmol) in dichloromethane (8 mL), and the mixture was heated under reflux for 4 h. The deep yellow solution was filtered through Celite, and the resulting solution was evaporated to dryness. The solid residue was washed with diethyl ether, filtered off, and dried in vacuo to yield a bright orange-red solid. Yield: 160.3 mg. IR (Nujol; ν_{max}/cm^{-1}): 1578 w, 1541 m, 1410 w, 1317 m.

Typically, to a suspension of the orange-red solid in methanol (50 mL) was added, with stirring, an excess of lithium halide (Cl, Br, or I). The mixture was stirred for 1 h at room temperature. The pale yellow solid that formed was filtered off, washed with methanol and diethyl ether, and finally dried in vacuo. Analytical samples of compounds **2**−**4** were obtained by recrystallization from dichloromethane-diethyl ether.

[Pd(N-C-N)Cl] (2). Yield: 56.3 mg, 58% (on Pd). Mp: stable up to 290 °C. Anal. Calcd for $C_{16}H_{11}ClN_2Pd$: C, 51.46; H, 2.95; N, 7.50. Found: C, 50.82; H, 2.86; N, 7.22. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.13, (dd, ^{3}J(H−H) = 8.0, 7.6 Hz, 1H (H5)); 7.21 (ddd,, J(H−H) = 7.8, 5.8, 1.6 Hz, 2H (H5′, H5″)); 7.36 (d, ^{3}J(H−H) = 7.8 Hz, 2H (H4, H6)); 7.62 (ddd, J(H−H) = 7.8, 1.6, 0.8 Hz, 2H (H3′, H3″)); 7.84 (td, ^{3}J(H−H) = 7.8, 1.6, 2H (H4′, H4″)); 8.95 (ddd, J(H−H) = 5.8, 1.6, 0.8 Hz, 2H (H6′, H6″)).

[Pd(N-C-N)Br] (3). Yield: 62.9 mg, 58%. Mp: stable up to 290 °C. Anal. Calcd for $C_{16}H_{11}BrN_2Pd$: C, 46.02; H, 2.66; N, 6.71 Found: C, 45.43; H, 2.79; N, 6.46. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.26, (dd, ^{3}J(H−H) = 8.1, 7.2, 1H (H5)); 7.31 (ddd, J(H−H) = 8.1, 5.7, 1.5, 2H (H5′, H5″)); 7.48 (d, ^{3}J(H−H) = 7.5 Hz, 2H (H4, H6)); 7.73 (ddd, J(H−H) = 8.1, 1.5 Hz, 2H (H3′, H3″)); 7.94 (td, J(H−H) = 8.1, 1.8 Hz, 2H (H4′, H4″)); 9.24 (d br, ^{3}J(H−H) = 5.7 Hz, 2H (H6′, H6″)).

[Pd(N-C-N)I] (4). Yield: 66.4 mg, 55%. Mp: stable up to 290 °C. Anal. Calcd for $C_{16}H_{11}IN_2Pd$: C, 41.36; H, 2.39; N, 6.03. Found: C, 41.58; H, 2.42; N, 6.22. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.25−7.30 (m, 3H (H5′, H5″ + H5)); 7.47 (d, ^{3}J(H−H) = 7.8 Hz, 2H (H4, H6)); 7.73 (dd, ^{3}J(H−H) = 8.1 Hz, 2H (H3′, H3″)); 7.92 (td, J(H−H) = 8.1, 1.8 Hz, 2H (H4′, H4″)); 9.50 (broad, 2H (H6′, H6″)).

Synthesis of [Pd(N-C-N)(H_2O)][BF_4]·H_2O (5). To a solution of **2** (49.7 mg, 0.13 mmol) in 10 mL of dichloromethane was added with stirring at room temperature 0.13 mmol of Ag[BF_4] (25.9 mg) dissolved in 15 mL of acetone. The yellow color of the solution immediately faded, and AgCl was formed. After it was stirred for 1 h, the mixture was filtered and the resulting solution was evaporated to dryness. The crude product was recrystallized from acetone/diethyl ether to give the analytical sample of compound **5**.

Yield: 56.4 mg, 94%. Mp: stable up to 290 °C. Anal. Calcd for $C_{16}H_{13}BF_4N_2OPd_2$·H_2O: C, 41.69; H, 3.25; N, 6.08. Found: C, 41.99; H, 2.97; N, 5.90. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.25 (t broad, ^{3}J(H−H) = 7.4 Hz, 1H (H5)); 7.44 (m, broad, 2H (H5′, H5″)); 7.57 (d, broad, ^{3}J(H−H) = 6.6 Hz, 2H (H4, H6)); 8.01 (m, broad, 2H (H3′, H3″)); 8.15 (m, broad, 4H (H4′, H4″) + (H6′, H6″)). ^{1}H NMR (300 MHz, $(CD_3)_2CO$; after D_2O exchange): δ 7.21, (t, ^{3}J(H−H) = 7.7 Hz, 1H (H5)); 7.45 (ddd, J(H−H) = 7.8, 5.5, 1.3 Hz, 2H (H5′, H5″)); 7.52 (d, ^{3}J(H−H) = 7.7 Hz, 2H (H4, H6)); 7.94 (d, broad, ^{3}J(H−H) = 7.8 Hz, 2H (H3′, H3″)); 8.11 (td, J(H−H) = 7.8, 1.5 Hz, 2H (H4′, H4″)); 8.41 (d broad, ^{3}J(H−H) = 5.5 Hz, 2H (H6′, H6″)).

Synthesis of [Pd_2(N-C-N)$_2$(μ-X)][BAr′$_4$] (X = Cl (6), Br (7), I (8)). To a solution of Na[BAr′$_4$] (36.3 mg, 0.041 mmol) in 10 mL of dichloromethane was added with stirring at room temperature 0.082 mmol of [Pd(N-C-N)X] (30.6, 34.4, 38.1 mg for X = Cl, Br, I, respectively) dissolved in 20 mL of the same solvent. The yellow color of the solution immediately faded, and a NaX precipitate was formed. After it was stirred for 1 h, the mixture was filtered and the resulting solution evaporated to dryness. Analytical samples of compounds **6**−**8** were obtained by recrystallization from dichloromethane/diethyl ether.

[Pd_2(N-C-N)$_2$(μ-Cl)][BAr′$_4$] (6). Yield: 62.6 mg, 97%. Mp: stable up to 290 °C. Anal. Calcd for $C_{64}H_{34}BClF_{24}N_4Pd_2$: C, 48.83; H, 2.18; N 3.56. Found: C, 48.72; H, 1.88; N, 3.53. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.24 (ddd, J(H−H) = 7.8, 5.4, 1.2 Hz, 4H (H5′, H5″)); 7.33 (dd, ^{3}J(H−H) = 7.2, 8.4 Hz, 2H (H5)); 7.51 (d, ^{3}J(H−H) = 7.8 Hz, 4H (H4, H6)); 7.57 (s br, 4H (H_p)); 7.73 (s broad, 8H (H_o)); 7.77 (dm, ^{3}J(H−H) = 7.8 Hz, 4H (H3′, H3″)); 7.96 (td, J(H−H) = 7.8, 1.5 Hz, 4H (H4′, H4″)); 9.08 (d br, ^{3}J(H−H) = 5.4 Hz, 4H (H6′, H6″)).

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Table 4. Crystallographic Data

	1	**2**	**11**·C_2H_5OH
formula	$C_{16}H_{11}ClHgN_2$	$C_{16}H_{11}ClN_2Pd$	$C_{70}H_{56}Cl_6Hg_2N_8O_5Pd_4$
M	467.32	373.13	2128.78
color	colorless	pale yellow	yellow
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$C2/c$
a (Å)	7.207(1)	8.856(1)	24.846(2)
b (Å)	12.816(1)	16.798(1)	15.030(1)
c (Å)	15.167(1)	9.079(1)	19.479(2)
α (deg)	90	90	90
β (deg)	90	93.49(1)	105.39(1)
γ (deg)	90	90	90
V (Å^3)	1400.9(2)	1348.1(2)	7013.3(11)
Z	4	4	4
F(000)	872	736	4072
D_c (g cm^{-3})	2.216	1.838	2.016
T (K)	296	296	296
cryst dimens (mm)	0.169 × 0.225 × 0.394	0.225 × 0.253 × 0.366	0.096 × 0.152 × 0.366
μ(Mo Kα) (cm^{-1})	111.7	15.47	56.39
min−max transmissn factors	0.459−1.00	0.875−1.00	0.663−1.00
scan mode	ω	ω	ω
frame width (deg)	0.30	0.30	0.30
time per frame (s)	15	20	20
no. of frames	3050	2475	2450
detector−sample dist (cm)	4.00	4.00	4.00
θ range (deg)	3.00−26.00	3.00−26.00	3.00−26.00
reciprocal space explored	full sphere	full sphere	full sphere
no. of rflns (total, indep)	28 480, 4259	22 718, 4105	45 737, 7686
R_{int}	0.0424	0.0231	0.0451
final R_2 and R_{2w} indices[a] (F^2, all rflns)	0.037, 0.048	0.031, 0.062	0.057, 0.083
conventional R1 index ($I > 2\sigma(I)$)	0.020	0.020	0.033
no. of rflns with $I > 2\sigma(I)$	3709	3612	4561
no. of variables	181	181	442
goodness of fit[b]	0.943	1.101	1.052

[a] $R_2 = [\sum(|F_o^2 - kF_c^2|)/\sum F_o^2]$, $R_{2w} = [\sum w(F_o^2 - kF_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $[\sum w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (PF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v is the number of variables, and P, the ignorance factor, is 0.02 for **1**, 0.04 for **2**, and 0.03 for **11**·C_2H_5OH.

[Pd$_2$(N-C-N)$_2$(μ-Br)][BAr′$_4$] (7). Yield: 63.7 mg, 96%. Mp: 240−242 °C. Anal. Calcd for $C_{64}H_{34}BBrF_{24}N_4Pd_2$: C, 47.49; H, 2.12; N, 3.46. Found: C, 46.94; H, 2.06; N, 3.46. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.20 (ddd, J(H−H) = 7.5, 5.4, 1.5 Hz, 4H (H5′, H5″)); 7.30 (dd, ^3J(H−H) = 8.4, 7.2 Hz, 2H (H5)); 7.46 (d, ^3J(H−H) = 7.8 Hz, 4H (H4, H6)); 7.57 (s, 4H (H$_p$)); 7.72−7.74 (m, 4H + 8H (H3′, H3′ + H$_o$)); 7.93 (td, J(H−H) = 7.5, 1.5 Hz, 4H (H4′, H4″)); 9.17 (d br, ^3J(H−H) = 5.4 Hz, 4H (H6′, H6″)).

[Pd$_2$(N-C-N)$_2$(μ-I)][BAr′$_4$] (8). Yield: 66.2 mg, 97%. Mp: 226−228 °C. Anal. Calcd for $C_{64}H_{34}BF_{24}IN_4Pd_2$: C, 46.15; H, 2.06; N, 3.36. Found: C, 46.05; H, 2.01; N, 3.36. ^{1}H NMR (CD_2Cl_2): δ 7.17 (m br, 4H (H5′, H5″)); 7.30 (t, ^3J(H−H) = 7.5 Hz, 2H (H5)); 7.44 (d, ^3J(H−H) = 7.5 Hz, 4H (H4, H6)); 7.58 (s br, 4H (H$_p$)); 7.70−7.75 (m, 4H + 8H (H3′, H3″ + H$_o$)); 7.91 (td, J(H−H) = 7.8, 1.5 Hz, 4H (H4′, H4″)); 9.37 (d br, ^3J(H−H) = 5.4 Hz, 4H (H6′, H6″)).

Synthesis of [Pd(N-C-N)(OAc)] (9). To a solution of [Pd(N-C-N)Cl] (54.3 mg, 0.146 mmol) in 10 mL of a mixture of tetrahydrofuran and dichloromethane (5:1 v/v) was added, with stirring at room temperature, 24.4 mg (0.146 mmol) of Ag(OAc). The mixture was left to react for 3 h in the dark. The AgCl precipitate was filtered off and the yellow solution evaporated to dryness. The crude product was recrystallized from dichloromethane to give the analytical sample, compound **9**.

Yield: 52.2 mg, 93%. Mp: 218−220 °C. Anal. Calcd for $C_{18}H_{14}N_2O_2Pd{\cdot}H_2O$: C, 52.13; H, 3.89; N, 6.75. Found: C, 51.94; H, 3.69; N, 6.64. IR (Nujol; ν_{max}/cm^{-1}): 1578 m, 1338 m. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.11 (s, 3H, (CH_3)), 7.22 (dd, ^3J(H−H) = 8.0, 7.3 Hz, 1H (H5)); 7.31 (ddd, J(H−H) = 7.8, 5.6, 1.5 Hz, 2H (H5′, H5″)); 7.44 (d, ^3J(H−H) = 7.8 Hz, 2H (H4, H6)); 7.72 (d br, ^3J(H−H) = 7.8 Hz, 2H (H3′, H3″)); 7.93 (td, J(H−H) = 7.8, 1.7 Hz, 2H (H4′, H4″)); 8.63 (d, broad, ^3J(H−H) = 5.6 Hz, 2H (H6′, H6″)).

Synthesis of [Pd$_2$(N-C-N)$_2$(μ-OAc)][BAr′$_4$] (10). Method A. To a solution of Na[BAr′$_4$] (57.4 mg, 0.065 mmol) in 10 mL of dichloromethane was added with stirring at room temperature 0.13 mmol of [Pd(N-C-N)(OAc)] (**9**; 51.4 mg) dissolved in 10 mL of the same solvent. The yellow solution immediately became orange, and a precipitate was formed. After 2 h of stirring at room temperature the orange solution was filtered and evaporated to dryness. The crude product was recrystallized from dichloromethane/diethyl ether to give the analytical sample, compound **10**.

Yield: 189.0 mg, 91%. Mp: 258−260 °C. Anal. Calcd for $C_{66}H_{37}BF_{24}N_4O_2Pd_2$: C, 49.62; H, 2.33; N, 3.51. Found: C, 48.97; H, 2.93; N, 3.30. IR (Nujol; ν_{max}/cm^{-1}): 1545 m, 1355 m. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.46 (s, 3H (CH_3)), 6.91 (ddd, J(H−H) = 7.8, 5.6, 1.5 Hz, 4H (H5′, H5″)); 6.99 (m, 6H (H4, H6 + H5)); 7.28 (d, ^3J(H−H) = 7.8 Hz, 4H (H3′, H3″)); 7.58 (s, 4H (Hp)); 7.68 (td, ^3J(H−H) = 7.8, 1.7 Hz, 4H (H4′, H4″)); 7.75 (s broad, 8H (Ho)); 7.99 (d, broad, ^3J(H−H) = 5.6 Hz, 4H (H6′, H6″)).

Method B. To a solution of the orange-red solid (see Transmetalation Reactions) from which complex **11** was obtained (270.5 mg in 20 mL of ethanol) was added, with stirring at room temperature, 230.3 mg (0.26 mmol) of Na[BAr′$_4$] dissolved in 10 mL of dichloromethane. The solution was stirred for 2 h and then filtered and evaporated to dryness. The crude product was recrystallized from dichloromethane/diethyl ether to give compound **10** Yield: 184.7 mg (0.116 mmol).

Synthesis of [Pd$_2$(N-C-N)$_2$(μ-OAc)]$_2$[Hg$_2$Cl$_6$]·EtOH (11·EtOH). Crystals of **11**·EtOH suitable for X-ray analysis were obtained as follows: the orange-red solid (see Transmetalation Reactions) was dissolved by refluxing a suspension in EtOH. When the solution was cooled to room temperature, two forms of crystals (yellow and red) were obtained. The X-ray analysis was successful unfortunately only in the case of the yellow form, **11**·EtOH.

Catalytic Reactions. To a 25 mL Schlenk flask were added catalyst (0.001%), triethylamine (0.42 mL, 3.0 mmol), iodobenzene (2.0 mmol), methyl acrylate (0.27 mL, 3 mmol), and DMF (10 mL). The mixture was refluxed at 110 °C into an oil bath. After 14 h (except where otherwise reported), the reaction mixture was extracted with dichloromethane (5 mL) and water (10 mL). The organic layer was washed four times with 10 mL portions of water and dried with $MgSO_4$. The mixture was then filtered and the dichloromethane removed in vacuo. A pure product was obtained by flash column chromatography on silica gel with a mixture of hexane and diethyl ether as eluent (12/1 v/v). The purity of the product was confirmed by comparison with ^1H NMR of the authentic sample.

Microwave reactions were conducted using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC). The machine consists of a continuous focused microwave power delivery system with operator-selectable power output from 0 to 300 W. Reactions were performed in glass vessels (capacity 10 mL) sealed with a septum. The pressure is controlled by a load cell connected to the vessel via a 14 gauge needle, which penetrates just below the septum surface. The temperature of the contents of the vessel was monitored using a calibrated infrared temperature control mounted under the reaction vessel. All experiments were performed using a stirring option whereby the contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel.

X-ray Data Collection and Structure Determinations of 1, 2, and 11·EtOH. Crystal data are summarized in Table 4; other experimental details are listed in the Supporting Information. The diffraction experiments were carried out on a Bruker SMART CCD area-detector diffractometer at 296 K. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[33] and an empirical absorption correction was applied (SADABS)[34] to the collected reflections. The calculations were performed using the Personal Structure Determination Package[35] and the physical constants tabulated therein.[36] The structures were solved by direct methods (SHELXS)[37] and refined by full-matrix least squares using all reflections and minimizing the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on F^2). In **11**·EtOH the ethanol molecule is disordered on a 2-fold axis. All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms of the acetato ligand in **11**·EtOH were detected in the final Fourier maps and not refined. The hydrogen atoms of the disordered EtOH molecule were neglected. The remaining hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å), with the thermal parameter B 1.10 times that of the carbon atom to which they are attached, and not refined. For noncentrosymmetric **1** full refinement of the correct structure enantiomorph led to $R_2 = 0.037$ and $R_{2w} = 0.048$, full refinement of the wrong one led to $R_2 = 0.069$ and $R_{2w} = 0.131$. In the final Fourier maps the maximum residuals were 1.76(29) e Å^{-3} at 0.85 Å from Hg, 0.26(66) e Å^{-3} at 1.02 Å from C(5), and 1.19(35) e Å^{-3} at 1.61 Å from Cl(3) for **1**, **2**, and **11**·EtOH, respectively.

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Supporting Information Available: Tables giving atomic coordinates for non-hydrogen atoms, positional and thermal parameters for hydrogen atoms, anisotropic thermal parameters (U's) for non-hydrogen atoms, and all distances and angles for compounds **1**, **2** and **11**·EtOH; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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