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Dinuclear Ortho-Metalated Palladium(II) Compounds with N,N- and N,O-Donor Bridging Ligands. Synthesis of New Palladium(III) Complexes

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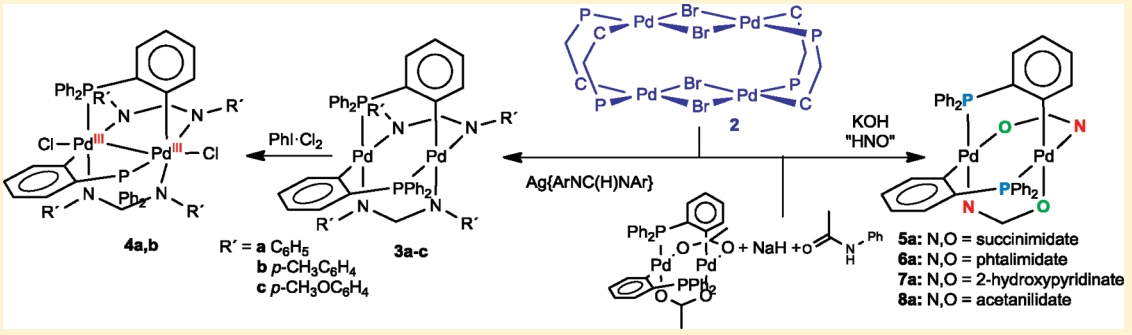
Supporting Information

ABSTRACT:



New dinuclear ortho-metalated palladium(II) compounds with *N,N′*-diarylformamidinates, $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2$ (R′ = C_6H_5, **3a**; R′ = *p*-$CH_3C_6H_4$, **3b**; R′ = *p*-$CH_3OC_6H_4$, **3c**) and N,O-donor ligands, $Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$ (*N,O* = succinimidate (**5**), phtalimidate (**6**), 2-hydroxypyridinate (**7**), acetanilidate (**8**)) have been synthesized and characterized by NMR spectroscopy and X-ray diffraction methods. The oxidation with iodobenzene dichloride gave new and rare Pd_2^{6+} compounds, $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2Cl_2$ (R′ = C_6H_5, **4a**; R′ = *p*-$CH_3C_6H_4$, **4b**). DFT calculations on the $Pd_2^{4+} \rightarrow Pd_2^{6+}$ oxidation reaction show that the substituents on the amidinate N atoms have a greater effect on the reaction energy than the substituents on the C atom. DFT calculations also confirm that for $Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$ compounds the symmetric isomers with N atoms trans to O atoms are the most stable complexes. The palladium dimers were tested as precursors of catalysts in tandem diboration/arylation/oxidation reactions.

INTRODUCTION

Palladium complexes have been shown to be good catalysts in a wide spectrum of catalytic reactions.[1−5] A large family of dinuclear palladium(II) compounds with the metal atoms at a variable distance has been reported.[6] A representative group of compounds shows two bridging ligands, frequently carboxylate ligands, and two cyclometalated ligands in a chelating coordination mode.[7] Compounds with bridging metalated ligands are also known.[8−19] The typical paddle-wheel structure, common for other transition metals, is only observed in a limited number of palladium compounds, these being the two palladium atoms connected by four bridging N,N-donor (amidinates, guanidinates, and triazenates),[20−25] or N,O-donor ligands (6-methyl-2-hydroxypyridinate).[26]

In the last few years we have investigated the synthesis, characterization, and reactivity of di- and tetranuclear palladium compounds with ortho-metalated triphenylphosphines acting as bridging P,C-donor ligands (Scheme 1).[27−29] Some of the compounds of type **B** exhibit, by cyclic voltammetry, two reversible oxidation processes indicative of two consecutive one-electron oxidations to produce species with a Pd_2^{6+} core.[29]

Considerable efforts have been dedicated to prepare paddle-wheel compounds with a Pd_2^{6+} core, without much success.[20−22,30,31] The first compound of this type, $Pd_2(hpp)_4Cl_2$ (hpp = anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), was synthesized in low yields and was structurally characterized in 1998 by Cotton and co-workers.[25] The molecule contains a Pd−Pd single bond as well as an axial chloride ligand on each palladium center. Relatively stable in the solid state, it decomposes rapidly in solution.

We succeeded in preparing compounds of type **C** (Scheme 1) in good yield by reaction of compounds of type **B** with iodobenzene dichloride.[32] This was the first time in which paddle-wheel dinuclear palladium(III) compounds have been

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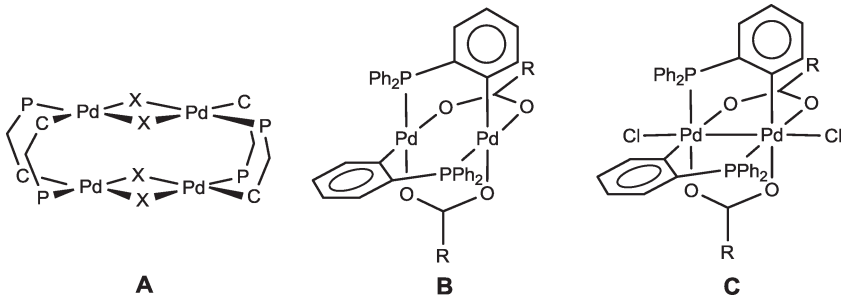
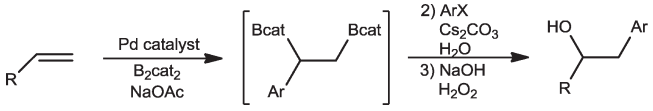
Scheme 1. Tetra- and Dinuclear Ortho-Metalated Palladium(II) and -(III) Compounds



Scheme 2. Tandem Diboration/Suzuki−Miyaura Cross-Coupling Reaction/Oxidation



obtained pure in high yields. Compounds with the general formula $Pd_2[(C_6H_4)PPh_2]_2(O_2CR)_2Cl_2$ were structurally similar to their Pd_2^{4+} precursors, but they contain a Pd−Pd single bond and an axial chloride ligand on each palladium center (just as in the case of $Pd_2(hpp)_4Cl_2$). Some of them were stable in solution of chlorinated solvents for over 48 h. Crystals could be stored at room temperature and in air for weeks without apparent decomposition. The carboxylate substituents are an important factor in the stabilization of the products. Compounds are diamagnetic with shortened Pd−Pd distances. The presence of a Pd−Pd single bond in these complexes was supported by hybrid HF/DFT calculations on a simplified model.[32]

Palladium complexes did catalyze the diboration of alkenes,[33] despite the unfavorable oxidative addition of a diboron reagent to Pd(0).[34,35] Compounds of types **A**−**C** have been shown to be efficient precursors of catalytic diboration of alkenes, this being the first time that the dinuclear palladium(III) compound has been tested in catalysis.[36] Interestingly, $Pd_2[(C_6H_4)PPh_2]_2(O_2CH_3)_2Cl_2$ and $Pd_4[(C_6H_4)PPh_2]_4Br_4$ were highly active for the catalytic tandem diboration/arylation/oxidation of alkenes, highlighting that the same palladium species catalyzed the two catalytic cycles for diboration and arylation sequences with total conversion from the substrate (Scheme 2). This was the first example of multifaceted properties of a palladium complex participating in different cycles with identical success.[36] Recently Powers and Ritter showed that some reactions of C−Cl, C−Br, and C−O bond formation take place through dinuclear palladium(III) compounds.[37]

New, stable dinuclear palladium(II) complexes with diphenyl-(3-methyl-2-indolyl)phosphine ($C_9H_8NPPh_2$) in a P,N-bridging coordinated mode have been also synthesized and characterized.[38] The compound $Pd_2[(C_6H_4)PPh_2]_2[C_9H_7NPh_2][O_2CCH_3]$ induced a highly successful β-boration/arylation reaction of electron-deficient alkenes (99% conversion, 89% isolated yield when dimethylacrylamine was the substrate).[38]

Looking for Pd_2^{4+} precursors of Pd_2^{6+} compounds, we present in this paper two new families of paddle-wheel ortho-metalated palladium(II) compounds with bridging N,N- and N,O-donor ligands. Paddle-wheel Pd_2^{4+} compounds with four bridging *N,N′*-diarylformamidinate ligands have been shown to be promising candidates for chemical oxidation.[24] In the search for new, stable metalated Pd_2^{6+} compounds, the nitrogen donor atoms were expected to increase the electronic charge on the metal atoms. The complexes have been tested in the catalytic reaction: tandem diboration/arylation/oxidation of alkenes.

RESULTS AND DISCUSSION

Dinuclear Palladium Compounds with Bridging Formamidinate Ligands. *Synthesis.* The reactions of $Pd_4[(C_6H_4)PPh_2]_4Br_4$ (**2**) with the different *N,N′*-diarylformamidinates[39] **1a**−**c** produced three new Pd_2^{4+} complexes with the general formula $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2$ (R′ = C_6H_5, **3a**; R′ = *p*-$CH_3C_6H_4$, **3b**; R′ = *p*-$CH_3OC_6H_4$, **3c**) in good yields (78−87%) (Scheme 3).

All three compounds were structurally characterized by single-crystal X-ray diffraction methods (Figure 1). In the case of **3c**, due to the poor quality of the data, some of the atoms had to be refined isotropically. Selected bond distances and angles for the three compounds are given in Table 1.

The three compounds have very similar structures. In comparison to the Pd_2^{4+} carboxylate compounds $Pd_2[(C_6H_4)PPh_2]_2(O_2CR)_2$, the most striking differences are the significantly larger P−Pd−Pd−P torsion angles of **3a**−**c**, very similar to those of the Pd_2^{6+} carboxylate compounds $Pd_2[(C_6H_4)PPh_2]_2(O_2CR)_2Cl_2$.[33] Only the stereoisomers R_P and S_M have been obtained from the four different possible arrangements generated by the configurational chirality and torsion angles P−Pd−Pd−P (Scheme 4).[29]

Electrochemical Studies. The new Pd_2^{4+} complexes **3a**−**c** were investigated by cyclic voltammetry in CH_2Cl_2 as solvent (Figure 2). The initial anodic scan shows two couples A_1/C_1 and A_2/C_2 at potential values between +0.75 and +1.25 V (**3a**), +0.60 and +1.10 V (**3b**), and +0.50 and +0.85 V (**3c**). When the voltammograms were recorded at low scan rates and the potential was switched at 0.15−0.20 V past the peak A_1, the anodic-to-cathodic peak separation for the first couple (A_1/C_1) was close to 0.059 V, suggesting a reversible one-electron transfer.

The formal electrode potentials vs AgCl/Ag for the A_1/C_1 couples of **3a**−**c**, calculated as the half-sum of the anodic and cathodic peak potentials, are +0.792, +0.664 and +0.524 V, respectively, decreasing with the electron-donating ability of the aryl substituents at the formamidinate ligands. The same result is found for the formal

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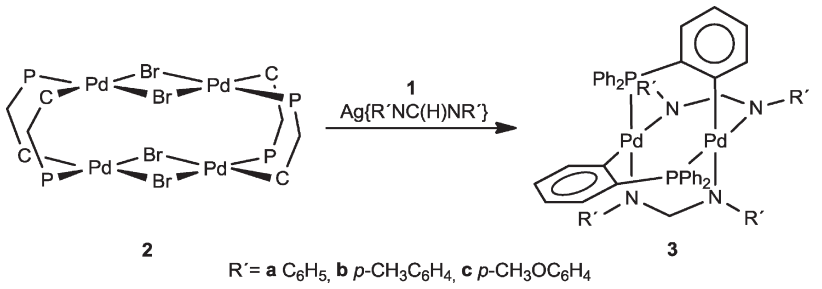
Scheme 3. Synthesis of $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2$ Compounds 3a−c



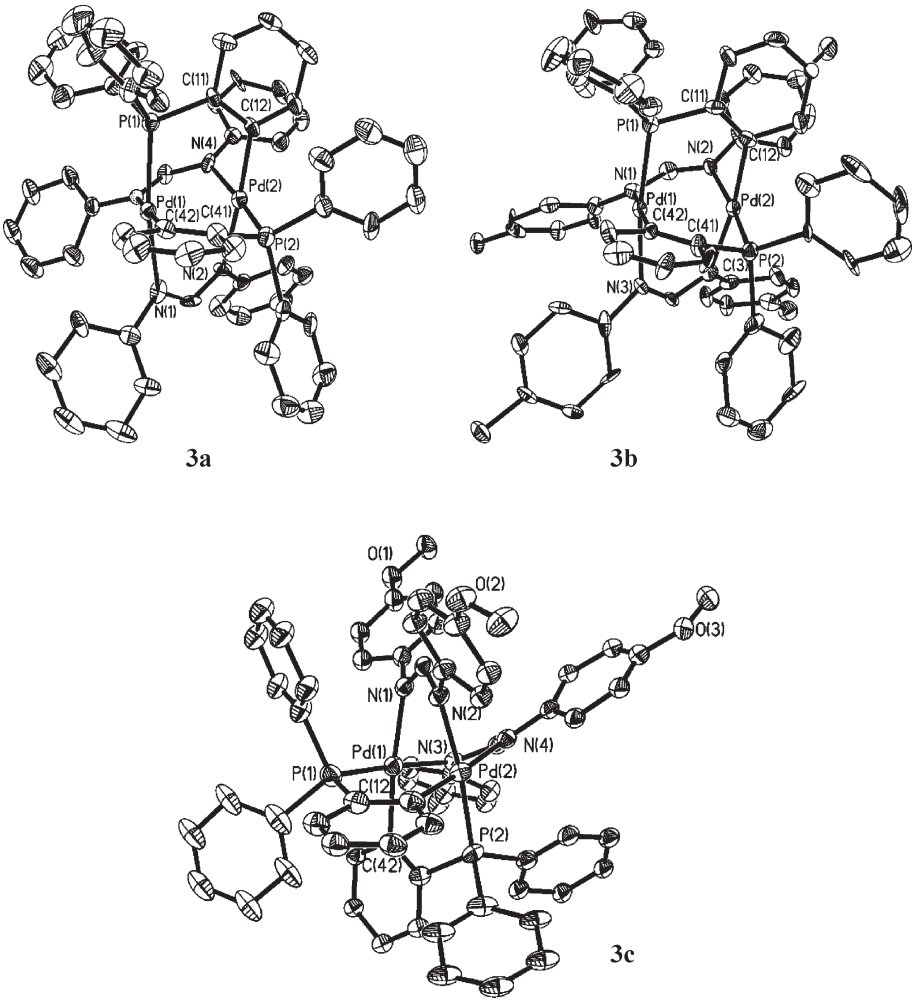


Figure 1. ORTEP views of **3a**−**c** with ellipsoids representing 30% probability and H atoms omitted for clarity.

electrode potentials for the A_2/C_2 couples, which are +1.179, +1.043, and +0.803 V, respectively.

In the case of **3a**, the peak A_2 at 1.179 V might correspond to the oxidation of Pd_2^{5+} in the core or to the oxidation of the *N*,*N*′-diphenylformamidinate ligand. The cyclic voltammetry of *N*,*N*′-diphenylformamidine and silver *N*,*N*′-diphenylformamidinate showed in each case an irreversible peak at a value close to 1.2 V, supporting the idea that a ligand oxidation takes place. When the scan was initiated in the negative direction, no reduction processes of the parent Pd complexes were detected in the available potential region (down to −1.8 V).

The observed electrochemical behavior can be described as two consecutive one-electron-transfer processes, starting from the Pd_2^{4+} complexes to successively yield $[Pd_2^{5+}]^+$ and $[Pd_2^{6+}]^{2+}$ cationic species. The relatively large separation between the two associated A_1/C_1 and A_2/C_2 couples indicates a certain Pd−Pd interaction. In spite of the observed behavior for **3a**, its oxidation with Cl_2 afforded the corresponding Pd_2^{6+}

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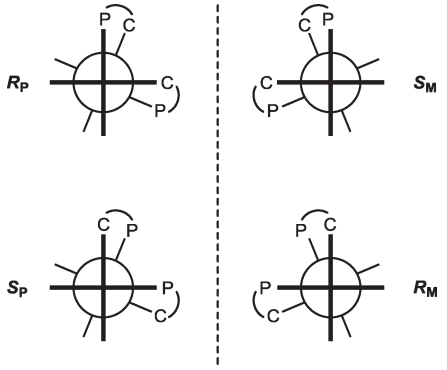
Table 1. Selected Distances (Å) and Angles (deg) for Compounds 3a−c

	3a	3b	3c
Pd(1)−Pd(2)	2.715(3)	2.717(2)	2.711(3)
Pd(1)−P(1)	2.284(7)	2.263(5)	2.282(10)
Pd(1)−$N_{trans\text{-}P}$	2.11(2)	2.102(13)	2.07(3)
Pd(1)−$N_{trans\text{-}C}$	2.138(18)	2.155(12)	2.15(2)
Pd(1)−C(42)	2.02(2)	2.010(15)	2.03(3)
P(1)−Pd(1)−Pd(2)	86.49(17)	86.20(13)	86.8(3)
P(1)−Pd(1)−Pd(2)−P(2)	100.0(3)	101.46(17)	103.3(3)

Scheme 4. Four Possible Stereoisomers of the $\{Pd_2[(C_6X_4)PPh_2]_2\}^{2+}$ Building Block



compound that was well-characterized by NMR spectroscopy. All the results coincide with those observed for the carboxylate complexes $Pd_2[(C_6H_4)PPh_2]_2[O_2CR]_2$, although these show generally higher electrode potentials for the A_1/C_1 and A_2/C_2 couples (between +0.840 and +1.490 V).[29]

Computational analysis of the frontier molecular orbitals shows that the HOMO orbitals consist of a mixture of the palladium d orbitals and the formamidinate ligands for all compounds **3a**−**c** (Figure S1 in the Supporting Information). In all cases, similar σ^* orbitals are formed with only slightly differing composition. With the aryl substitution of the nitrogen ligands, the HOMO orbitals were destabilized (E_{HOMO} = −4.70, −4.59, and −4.42 eV for **3a**−**c**, respectively), which can explain the observed shift in the formal electrode potentials. Furthermore, the energy of the HOMO-1, which consists mainly of the formamidinate ligands, was very close to the energy of the HOMO with slightly decreasing differences of 0.20, 0.16, and 0.13 eV for **3a**−**c**, respectively. Destabilization of the HOMO-1 energy similar to that of the HOMO energy was also predicted by the calculations, indicating that the one-electron-oxidation process originates from both the metal-based and the formamidinate-based orbitals.

Chemical Oxidation of Formamidinate Compounds, Pd_2^{4+} → Pd_2^{6+}. The oxidation of compounds **3a**−**c** with iodobenzene dichloride showed different results for **3a**,**b** on one hand and **3c** on the other. In the case of the phenyl- and *p*-tolyl-substituted formamidinate compounds **3a**,**b**, the typical color change from yellow to red was observed after addition of the oxidizing agent and clean products could be isolated as red solids. They were characterized by NMR spectroscopy as the Pd_2^{6+} complexes with general formula $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2$

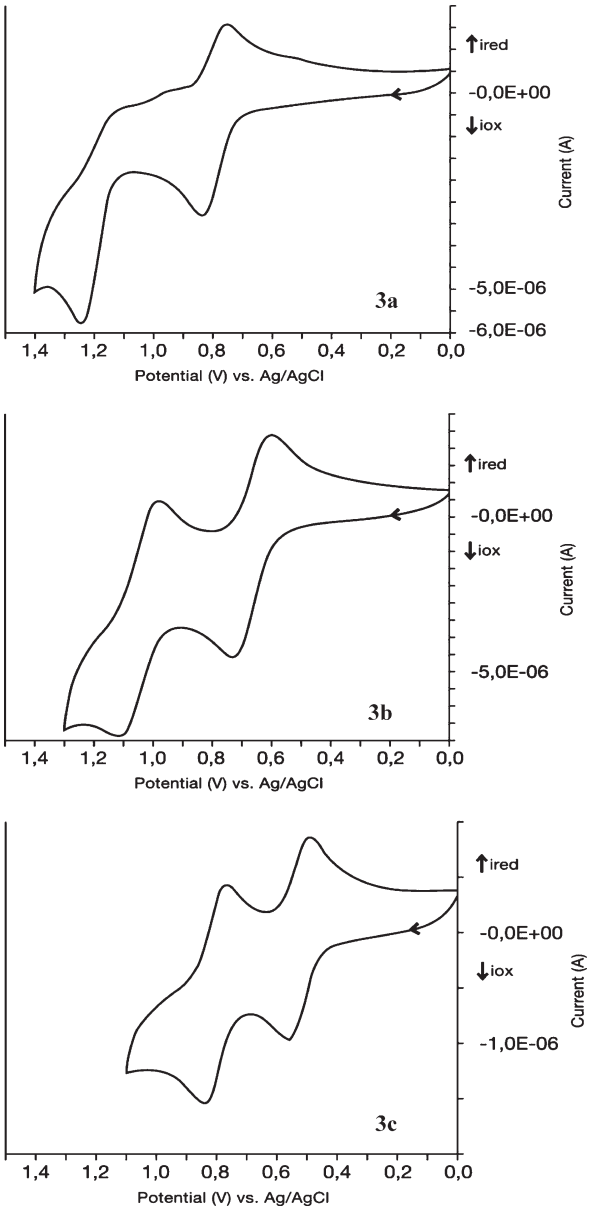


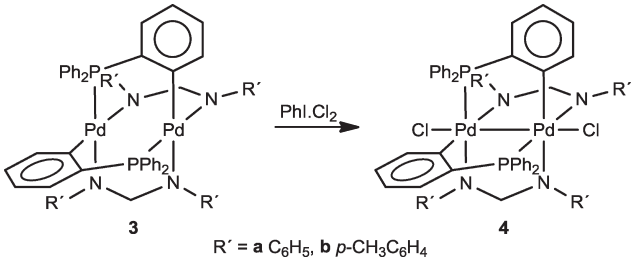
Figure 2. Cyclic voltammograms of **3a**−**c**.

(R′ = C_6H_5, **3a**; R′ = *p*-$CH_3C_6H_4$, **3b**; R′ = *p*-$CH_3OC_6H_4$, **3c**) (Scheme 5).

However, in the case of the *p*-anisyl-substituted formamidinate compound **3c** the appearance of a brown precipitate indicated a decomposition of the starting compound. **3c** is easily and reversibly oxidized in cyclic voltammetry but does not give a stable Pd_2^{6+} complex by oxidation with iodobenzene dichloride. The oxidation with bromine led to decomposition in the case of all three compounds **3a**−**c**.

The Pd_2^{6+} compounds **4a**,**b**, however, were also not as stable as was hoped for. They decompose in solution even more quickly than the Pd_2^{6+} trifluoroacetate complex $Pd_2[(C_6H_4)PPh_2]_2(O_2CCF_3)_2Cl_2$. The ^{13}C NMR spectra had to be recorded at −20 °C in order to slow down the decomposition and obtain clean results. Single crystals of X-ray diffraction quality could not be grown. The main decomposition product proved to be the tetranuclear Pd(II) compound $Pd_4[(C_6H_4)PPh_2]_4Cl_4$, which was identified by NMR spectroscopy and single-crystal X-ray diffraction.

Scheme 5. Synthesis of Pd_2^{6+} Compounds 4a,b



Scheme 6. Amidinate Ligands in Pd_2^{4+} Complexes

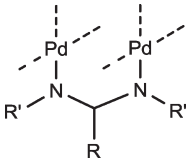


Table 2. Effect of Different Amidinate Ligands on the Reaction Energy and Gibbs Free Energy (kJ/mol) of the Oxidation Reaction:

$$Pd_2[(C_6H_4)PPh_2]_2[R'NC(R)NR']_2 + Cl_2 \rightarrow Pd_2[(C_6H_4)PPh_2]_2[R'NC(R)NR']_2Cl_2$$

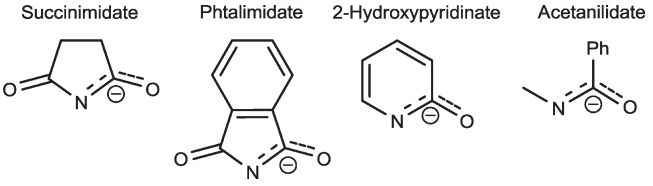
	R′ = H		R′ = Ph	
R	Δ*E*	Δ*G*	Δ*E*	Δ*G*
Ph	−206	−146	−78	−17
CH_3	−211	−149	−81	−19
H	−200	−138	−84	−19
CF_3	−189	−129	−106	−42

Computational Studies on the $Pd_2^{4+} \rightarrow Pd_2^{6+}$ Oxidation Reaction. Density functional theory (DFT) calculations on the $Pd_2^{4+} \rightarrow Pd_2^{6+}$ oxidation reaction were performed to gain insights into the influence of the different ligands and their substituents on the oxidation reaction and to find different amidinate ligands that would give more stable Pd_2^{6+} compounds. As this type of ligand can have different substituents at the N as well as at the C atom (Scheme 6), different combinations of substituents were calculated. The results are shown in Table 2.

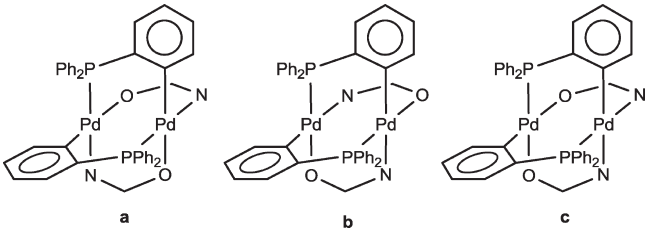
The computational results show that the substituents on the amidinate N atoms have a greater effect on the reaction energy than do the substituents on the central C atom. Pd_2^{6+} complexes with R′ = H are more stabilized. This great difference seems to be caused by steric rather than electronic effects. For the substituents on the C atom, an electron-donating group has a stabilizing effect for R′ = H and a destabilizing effect for R′ = Ph.

We tried to synthesize the benzamidinate complex $Pd_2[(C_6H_4)PPh_2]_2[HNC(Ph)NH]_2$ in order to prove the computational results. Benzamidine was readily obtained from its hydrochloride salt.[40] The complex could not be obtained either by reaction of benzamidine with **2** or $Pd_2[(C_6H_4)PPh_2]_2[O_2CCH_3)]_2$ in the presence of a base or by reaction of **2** with silver benzamidinate.

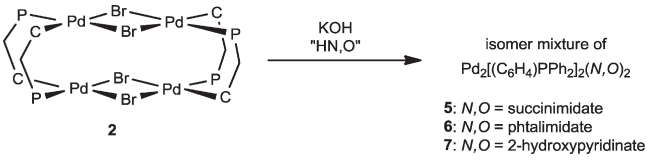
Scheme 7. N,O-Donor Ligands Employed in the Synthesis of New Pd_2^{4+} Compounds



Scheme 8. Possible Isomers for Pd_2^{4+} Compounds with N, O-Donor Ligands



Scheme 9. Synthesis of Pd_2^{4+} Compounds with N,O-Donor Ligands



Mixtures of products were always obtained which decomposed rapidly.

Dinuclear Palladium Compounds with Bridging N,O-Donor Ligands. Four different N,O ligands have been used in the synthesis of a new family of Pd_2^{4+} complexes (Scheme 7).

These ligands coordinate to the Pd_2^{4+} core in a nonsymmetric way which can lead to up to three different isomers (Scheme 8):

(a) The N,O-donor ligands are in a head-to-tail (H-T) arrangement, with the N atoms trans to P atoms. The molecule is C_2 symmetric.

(b) The N,O-donor ligands are in a head-to-tail (H-T) arrangement, with the N atoms trans to the metalated C atoms. The molecule is C_2 symmetric.

(c) The N,O-donor ligands are in a head-to-head (H-H) arrangement. The molecule retains no symmetry.

Synthesis. When the N,O-donor ligand was succinimidate, phthalimidate, or 2-hydroxypyridinate, $Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$ complexes (**5**−**7**) were obtained by adding a mixture of the H(N,O) ligand and potassium hydroxide in methanol to a suspension of **2** in dichloromethane (Scheme 9). The reactions were followed by ^{31}P NMR spectroscopy. The products were obtained in good yields (77−88%), the reactions always giving mixtures of two different isomers: one symmetric (**a** or **b** in Scheme 8) and one asymmetric (**c**).

A typical ^{31}P NMR spectrum is depicted in Figure 3. The singlet peak at 17.4 ppm corresponds to two equal P atoms in a symmetric Pd_2 compound (**a** or **b**), whereas the two doublets at

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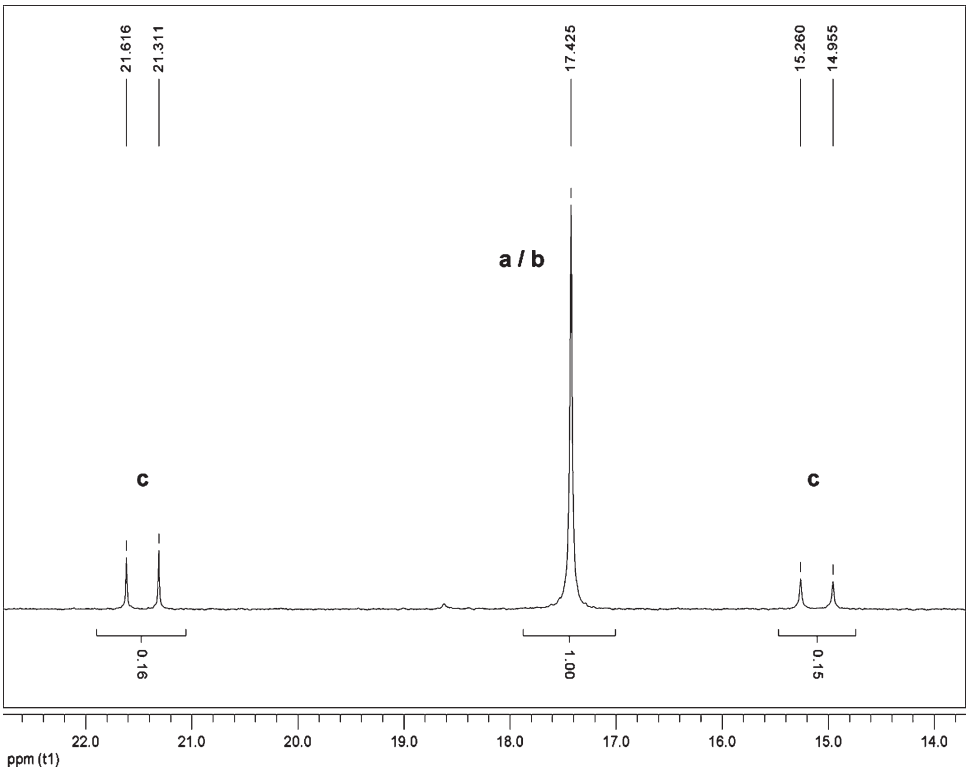

Figure 3. ^{31}P NMR spectrum of the product mixture of the reaction of **2** and succinimidate.

Table 3. a,b:c Ratio for $Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$ Compounds

$Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$	**a,b:c** ratio
5	3:1
6	10:1
7	5:1

21.5 and 15.1 ppm are assigned to the two different P atoms in the asymmetric compound (**c**). The **a,b:c** ratio for the different compounds are displayed in Table 3.

All attempts to separate the isomers by column chromatography were unsuccessful.

Products **5**−7 crystallized well, and single crystals suitable for X-ray diffraction could be obtained. They were shown to be crystals of pure symmetric compounds of type **a** (N atoms trans to P atoms). The molecular structures are depicted in Figure 4, and selected bond lengths and angles can be found in Table 4. Crystals containing pure isomers of the isomers **b** and **c** could not be found.

In the three structures the palladium units are in very similar coordination cores. **7a**, with 2-hydroxypyridinate ligands, has a shorter Pd−Pd distance than the imidate compounds **5a** and **6a**, while the P−Pd−Pd−P torsion angle is smaller for **5a** than for **6a** and **7a**. Bond lengths and angles around the metal core are very similar to those found for the ortho-metalated Pd_2^{4+} compounds with carboxylate ligands,[29] and again only molecules with R_P and S_M conformations were observed.

A single isomer as reaction product was obtained by reacting $Pd_2[(C_6H_4)PPh_2]_2[O_2CCH_3]_2$ and the acetanilidate ligand, using sodium hydride as a base (Scheme 10).

Thus, the product **8** was obtained in good yield (72%) and could be identified by NMR spectroscopy as a cleanly symmetric isomer (**a** or **b** in Scheme 8). There was no trace of the asymmetric isomer in this case. The absolute configuration of the product could not be resolved by X-ray diffraction, as no suitable single crystals could be grown.

5−**8** were reacted with iodobenzene dichloride, but no clean Pd_2^{6+} products could be obtained.

Isomerization of Pd_2 Compounds. When ^{31}P NMR spectra were recorded directly of single crystals that had been shown to contain only symmetric compounds of type **a**, different results were observed. For the 2-hydroxypyridinate compound **7a**, the spectrum showed only the expected singlet, whereas in the case of the imidate products **5a** and **6a**, the spectra confirmed the presence in solution of different isomers, proved to be identical with those of the isomer mixtures of the synthesis reaction, a singlet and two doublets. This indicated that these products in solution exist in a dynamic equilibrium between the two isomers **a** and **c**.

As equilibria of this type usually depend on the nature of the solvent, a series of ^{31}P NMR spectra of the originally obtained mixtures of **5**−7 was recorded in different deuterated solvents. Table 5 gives the symmetric/asymmetric isomer ratios found, depending on the solvent.

In the case of compound **7a**, the solvent has no effect on the symmetric/asymmetric isomer ratio, and no dynamic exchange between the two isomers was observed in solution. However, the solvent has an important effect on the symmetric/asymmetric isomer ratio for compounds **5a** and **6a**, displacing the equilibrium in favor of one isomer or the other. Toluene-d_8, as the least polar solvent of those employed, favors the symmetric and less polar configuration **a**, whereas the more polar solvents

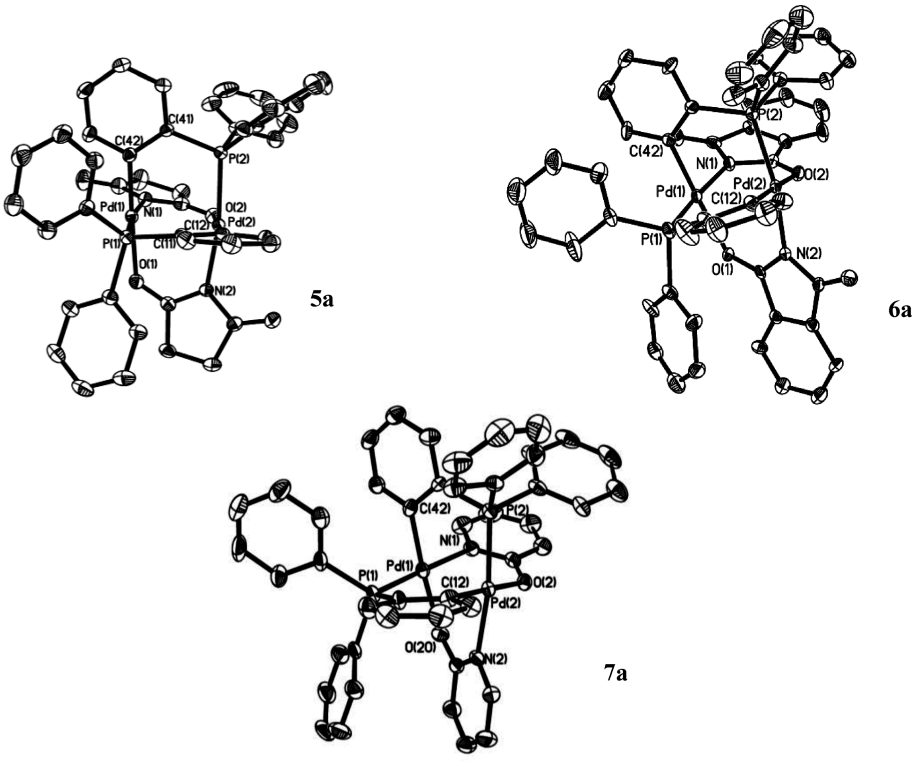

Figure 4. ORTEP views of **5a**−**7a** with ellipsoids representing 30% probability and H atoms omitted for clarity.

Table 4. Selected Distances (Å) and Angles (deg) for Compounds 5a−7a

	5a	6a	7a
Pd(1)−Pd(2)	2.7487(4)	2.7480(9)	2.6860(9)
Pd(1)−P(1)	2.2636(11)	2.268(2)	2.258(2)
Pd(1)−C(42)	1.984(4)	1.993(8)	1.992(9)
Pd(1)−N(1)	2.090(3)	2.090(7)	2.103(8)
Pd(1)−O(1)	2.176(3)	2.170(5)	2.130(7)
P(1)−Pd(1)−Pd(2)	85.98(3)	85.29(6)	84.88(7)
P(1)−Pd(1)−Pd(2)−P(2)	96.26(4)	98.49(8)	100.49(8)

chloroform and dichloromethane favor the more polar asymmetric configuration **c**.

The fact that isomerization is observed for compounds **5** and **6** but not for compounds **7** and **8** can be explained by the latter's lack of a second oxygen atom. For **5** and **6** the isomerization can take place by a simple "sliding" movement of one of the imidate ligands (Scheme 11). A reaction like this has been described for an Rh_2 analogue of **5**, $Rh_2[(C_6H_4)PPh_2]_2(OC_4NH_4O)_2$.[41] Isomerization of **7** or **8** would have to include an additional "rotation" step of the moving ligand, the energy barrier for which seems to be too high at room temperature.

*Density Functional Theory (DFT) Calculations on the Isomers of Compounds **5**, **7**, and **8**.* Density functional theory (DFT) calculations on the different isomers of compounds **5**, **7**, and **8** were performed, and the results of these calculations coincide with the experimental findings (Table 6).

For all three compounds the symmetric isomer **a** was found to be the most stable one by difference. The second symmetric isomer **b** showed to have even higher relative energy than the asymmetric isomer **c**. The difference in relative energies is significantly higher for compound **8** than for the other two compounds. All these results agree with the experimental findings, where **8** was obtained as a pure isomer (due to the calculations it can be concluded to be isomer **a**) and **5** and **7** were obtained as isomer mixtures with more isomer **a** than **c**, while isomer **b** was never observed.

Scheme 10. Synthesis of Pd_2^{4+} Compound 8

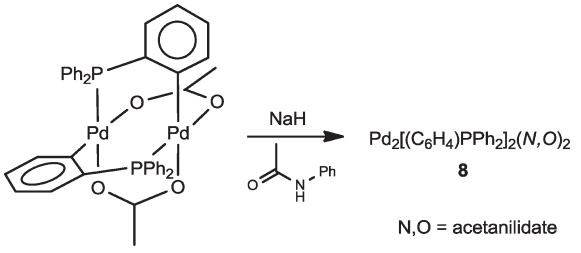

Table 5. Solvent Effect on the Symmetric/Asymmetric Ratio of $Pd_2[(C_6H_4)PPh_2]_2(N,O)_2$ Compounds

	$CDCl_3$	CD_2Cl_2	toluene-d_8
5	3:1	1.5:1	8:1
6	10:1	9:1	26:1
7	5:1	5:1	5:1

Ortho-Metalated Palladium Compounds with Bridging N, N- and N,O-Donor Ligands as Precursors in Catalysis. The catalytic properties of compounds **3a**, **4a**, and **5**, as examples of

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Scheme 11. Possible Isomerization Mechanism for Compound 5

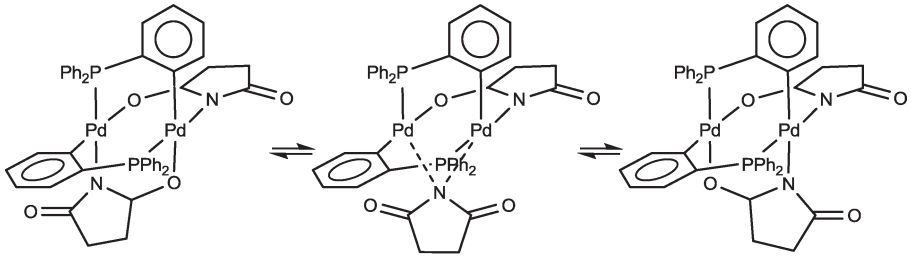


Table 6. Relative Energies and Relative Gibbs Free Energies (kJ/mol) for the Different Isomers of 5, 7, and 8 (Referenced to Respective Isomers a):

	5		7		8	
isomer	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
a	0	0	0	0	0	0
b	14.2	19.9	15.7	21.5	37.4	45.9
c	11.1	18.1	10.0	14.4	28.2	33.8

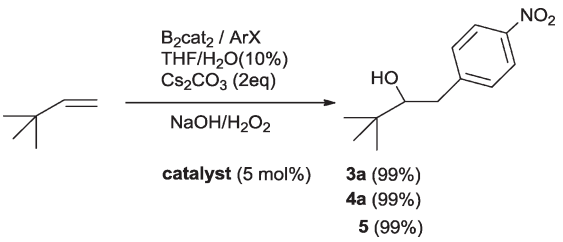
Table 7. Palladium Complexes with N,O- and N,N-Donor Bridging Ligands Mediate the Catalytic Diboration of Alkenes[a]

Entry	Catalytic system	Substrate	$T_{Diboration}$ (°C)	Diboration Conv. (%)[b]
1	**3a**		25	47
2	**4a**		25	69
3	**5**		25	58
4	**3a**		78	95
5	**4a**		78	94
6	**5**		78	97
7	**3a**		25	57
8	**4a**		25	62
9	**5**		25	66

[a] Standard conditions: substrate/Pd = 1/0.05, B_2cat_2 (2 equiv), NaOAc (1 equiv), solvent THF, t = 4 h. [b] Determined by ^{1}H NMR spectroscopy.

palladium dimers with N,N- and N,O-bridging ligands, were explored in the tandem diboration/Suzuki−Miyaura cross-coupling reactions followed by an oxidation pathway, employing the optimized reaction conditions described in the Experimental Section (Scheme 2).

Scheme 12. Palladium Complexes with N,O- and N,N-Donor Bridging Ligands Mediate the Catalytic Diboration/Monoarylation/Oxidation of Alkenes



The diboration reactions with styrene as substrate yielded the diborated product in moderate conversions (47−69% conversion; Table 7, entries 1−3). When the reactions were carried out at 78 °C, almost complete conversion was observed (94−97%, Table 7, entries 4−6). The subsequent Suzuki−Miyaura reactions with 4-nitrobromobenzene as reagent did not yield the desired arylated product. This was not surprising for an aryldiboronate intermediate, despite the recent successful palladium-catalyzed cross-coupling reaction from aryl-substituted secondary boronic esters reported by Crudden et al.[42]

The palladium-catalyzed diboration reaction of 3,3-dimethyl-1-butene yielded moderate conversions at room temperature for the three precursor catalysts (57−66%; Table 7, entries 7−9). No reactions at higher temperatures were carried out, due to the low boiling point of the substrate. However, the subsequent palladium-catalyzed cross-coupling reaction/oxidation allowed the formation of the carbohydroxylated adduct in quantitative conversion (Scheme 12).

Palladium dimers **3a**, **4a**, and **5**, with N,N- and N,O-donor bridging ligands, were shown to be less active than complex **2** and $Pd_2[(C_6H_4)PPh_2]_2(O_2CCH_3)_2Cl_2$, for the catalytic diboration reaction. This difference in catalytic behavior was especially surprising in the case of **4a**, a Pd_2^{6+} complex very similar to $Pd_2[(C_6H_4)PPh_2]_2(O_2CCH_3)_2Cl_2$. It was expected that it would be reduced to $Pd_4[(C_6H_4)PPh_2]_4Cl_4$ when reacted with $B_2(cat)_2$. However, instead of the expected color change from red to yellow, the reaction mixture turned dark brown and the appearance of a very fine precipitate could be observed, very similar to the reactions with Pd_2^{4+} compounds $Pd_2[(C_6H_4)PPh_2]_2(O_2CR)_2$ and also compounds **3a** and **5**. It seems that in all these cases reduction to Pd(0) and the formation of phosphine-stabilized Pd nanoparticles could be involved.[36]

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CONCLUSIONS

New dinuclear ortho-metalated palladium(II) compounds with *N*,*N*′-diarylformamidinates, $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2$ (R′ = C_6H_5, **3a**; R′ = *p*-$CH_3C_6H_4$, **3b**; R′ = *p*-$CH_3OC_6H_4$, **3c**), and N,O-donor ligands, $Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$ (N,O = succinimidate (**5**), phthalimidate (**6**), 2-hydroxypyridinate (**7**), acetanilidate (**8**)) have been synthesized and characterized by NMR spectroscopy and X-ray diffraction methods. The oxidation with iodobenzene dichloride gave Pd_2^{6+} compounds only for the formamidinate complexes $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2Cl_2$ (R′ = C_6H_5, **4a**; R′ = *p*-$CH_3C_6H_4$, **4b**), which were not as stable as the counterpart carboxylate derivatives and evolved to $Pd_4[(C_6H_4)PPh_2]_4Cl_4$ as the main decomposition product. DFT calculations on the $Pd_2^{4+} \rightarrow Pd_2^{6+}$ oxidation reaction show that the substituents on the amidinate N atoms have a greater effect on the reaction energy than the substituents on the C atom. $Pd_2[(C_6H_4)PPh_2]_2[N,O]_2$ (N,O = succinimidate, phthalimidate, 2-hydroxypyridinate) compounds have been obtained as a mixture of isomers with symmetric and asymmetric configurations, but only the symmetric isomer was synthesized when the N,O-donor ligand was acetanilidate. Compounds whose ligands have a second oxygen atom show a dynamic equilibrium between the isomers; this isomerization can take place by a simple "sliding" movement of one of the imidate ligands. DFT calculations confirm that the symmetric isomers with N atoms trans to O atoms are the most stable complexes; only these isomers have been crystallized and characterized by X-ray diffraction methods. The palladium dimers were tested as precursors of catalysts in tandem diboration/arylation/oxidation reactions, providing high activity in the organodiboronate formation, under reflux conditions. The catalytic tandem reaction has been designed to transform the diboronate intermediates into the monoarylated product, which after oxidative workup provides the carbohydroxylated adduct in high yields.

EXPERIMENTAL SECTION

All reactions were carried out under a dry argon (synthesis) or nitrogen (catalysis) atmosphere using Schlenk techniques. Solvents were purified according to standard procedures.[43] Commercially available reagents were used as purchased. Di-*p*-tolylformamidine and di-*p*-anisylformamidine,[44] iodobenzene dichloride ($PhI \cdot Cl_2$),[45] and $Pd(dba)_2$[46] were synthesized according to literature procedures. Solvent mixtures are v/v mixtures. Column chromatography was performed on silica gel (35−70 mesh).

NMR spectra were recorded on Varian Gemini 300 MHz, Varian Mercury 400 MHz, and Bruker Avance 400 MHz spectrometers as solutions in deuterated chloroform at 25 °C, unless specified otherwise. Chemical shifts are reported in ppm, using TMS (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as references. The coupling constants (*J*) are in hertz (Hz).

Elemental analyses were provided by the analytical laboratory of the University of Joensuu, Joensuu, Finland.

X-ray structure determinations were carried out on a Bruker-Nonius Kappa CCD diffractometer (Mo Kα radiation, λ = 0.710 73 Å). The structures were solved by direct methods using the SHELXTL software package.[47] The correct positions for the heavy atoms were deduced from an *E* map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were placed in geometrically generated positions and refined riding on the atom to which they are attached.

All computational calculations were carried out with the Gaussian03 program package.[48] The DFT level of theory with the nonlocal hybrid density functional B3PW91 was selected for the quantum chemical studies.[49,50] The basis set was comprised of a Stuttgart−Dresden effective small core potential augmented with an extra p-polarization function for palladium (SDD(p)) and a standard 6-31G* all-electron basis set for other atoms. This method was found to yield reliable geometries in comparison with the available experimental structures (see Tables S1 and S2 in the Supporting Information). Frequency analysis with no scaling was performed to ensure minima for the optimized structures. Thermodynamic values were calculated at 298 K.

The electrochemical studies were carried out at room temperature with a 273A PAR potentiostat in a three-electrode cell. The working electrode was a Pt electrode with a surface of 3.1 mm^2, the counter electrode a Pt wire, and the reference electrode Ag/AgCl (saturated KCl). The concentration was 0.5 mM for compounds **3a**,**b** but in the case of **3c** was 0.1 mM because of its poor solubility. The solvent was 0.2 M $Bu_4NPF_6-CH_2Cl_2$, and the scan rate was 50 mV/s. Under these conditions E_a for the couple Fc/Fc^+ was 0.550 V.

Preparation of Silver *N*,*N*′-Diarylformamidinates 1a−c. These compounds were prepared by variation of a literature procedure.[39] An aqueous solution of ammonium hydroxide (20%, 0.91 mL, 10 mmol) was added to a solution of the corresponding *N*,*N*′-diarylformamidine (8.89 mmol) in methanol (40 mL). Upon addition of a solution of silver nitrate (1.51 g, 8.89 mmol) in water (5 mL) with vigorous stirring, a white voluminous precipitate formed, which was collected by filtration, briefly washed with methanol, and vacuum-dried in the absence of light. It was used in the following synthesis without further purification. Yield: **1a**, 1.45 g, 54%; **1b**, 2.00 g, 68%; **1c**, 2.26 g, 70%.

Preparation of $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2$ (R′ = C_6H_5, 3a; R′ = *p*-$CH_3C_6H_4$, 3b; R′ = *p*-$CH_3OC_6H_4$, 3c). The corresponding silver diarylformamidinates **1a**−**c** (0.492 mmol) were added to suspensions of **2** (200 mg, 0.112 mmol) in dichloromethane (20 mL), and the mixtures were stirred in the absence of light for 3 h. The resulting yellow solutions were separated from the white precipitates by filtration and then evaporated to dryness. The yellow crude products were dissolved in dichloromethane, filtered over a short plug of silica, and precipitated by addition of hexane to give yellow microcrystalline powders, which were collected by filtration and washed with hexane. Single crystals for X-ray diffraction were grown by slow diffusion of diethyl ether into a dichloromethane solution of the product. Yield: **3a**, 205 mg, 81%; **3b**, 206 mg, 78%; **3c**, 242 mg, 87%.

Characterization data for **3a**: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.52−6.75 (m, 16H, ar), 6.82−6.90 (m, 6H, ar), 6.98−6.99 (m, 2H, −NCHN−), 7.02−7.16 (m, 12H, ar), 7.20−7 0.30 (m, 10H, ar), 7.35−7.49 (m, 4H, ar); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 16.2 (s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 121−151 (ar), 160.9 (s, −NCHN−), 165.5 (m, metalated). Anal. Calcd for $C_{62}H_{50}N_4P_2Pd_2$: C, 66.14; H, 4.48; N, 4.98. Found: C, 66.68; H, 4.86; N, 4.85.

X-ray crystal structure data for **3a**: formula $C_{62}H_{50}N_4P_2Pd_2$, triclinic system, space group $P\bar{1}$, *a* = 13.142(3) Å, *b* = 20.177(4) Å, *c* = 22.774(5) Å, α = 102.44(3)°, β = 97.16(3)°, γ = 91.35(3)°, *V* = 5843(2) $Å^3$, *Z* = 4, crystal dimensions 0.18 × 0.21 × 0.26 mm^3, Mo Kα radiation, 293(2) K, 16 968 reflections, 9121 independent reflection (μ = 0.709 mm^{-1}), refinement (on F^2) with SHELXTL (version 6.1), 1261 parameters, 960 restraints, R1 = 0.0931 ($I > 2\sigma$) and wR2 (all data) = 0.3133, GOF = 1.053, maximum/minimum residual electron density 1.126/−0.730 e $Å^{-3}$.

Characterization data for **3b**: ^1H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 6H, $-CH_3$), 2.22 (s, 6H, $-CH_3$), 6.36−6.38 (m, 4H, ar), 6.54−6.72 (m, 14H, ar), 6.88−6.90 (m, 2H, −NCHN−), 6.91−6.93 (m, 4H, ar), 7.01−7.05 (m, 4H, ar), 7.08−7.15 (m, 8H, ar), 7.18−7.24 (m, 6H, ar), 7.34−7.39 (m, 4H, ar); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 15.8 (s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 20.6 (s, $-CH_3$), 20.7 (s, $-CH_3$), 121−149 (ar), 160.6 (s, −NCHN−), 166.0 (m, metalated). Anal. Calcd for

$C_{66}H_{58}N_4P_2Pd_2$: C, 67.07; H, 4.95; N, 4.74. Found: C, 66.42; H, 5.12; N, 4.94.

X-ray crystal structure data for **3b**: formula $C_{68}H_{62}Cl_4N_4P_2Pd_2$, triclinic system, space group $P\bar{1}$, a = 13.6960(4) Å, b = 14.3380(6) Å, c = 19.0430(7) Å, α = 90.338(3)°, β = 104.917(3)°, γ = 118.008(18)°, V = 3154.9(2) Å^3, Z = 2, crystal dimensions 0.21 × 0.23 × 0.24 mm^3, Mo Kα radiation, 293(2) K, 9661 reflections, 5468 independent reflections (μ = 0.834 mm^{-1}), refinement (on F^2) with SHELXTL (version 6.1), 731 parameters, 0 restraints, R1 = 0.0851 ($I > 2\sigma$) and wR2 (all data) = 0.2654, GOF = 1.063, maximum/minimum residual electron density 1.520/−1.274 e Å^{-3}.

Characterization data for **3c**: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 3.63 (s, 6H, $-CH_3$), 3.70 (s, 6H, $-CH_3$), 6.44−6.48 (m, 8H, ar), 6.58−6.61 (m, 4H, ar), 6.66−6.69 (m, 2H, ar), 6.71−6.76 (m, 10H, −NCHN− + ar), 7.03−7.06 (m, 4H, ar), 7.11−7.14 (m, 4H, ar), 7.17−7.25 (m, 8H, ar), 7.27−7.30 (m, 2H, ar), 7.33−7.37 (m, 4H, ar); ^{31}P NMR (CD_2Cl_2, 162 MHz) δ 17.0 (s); ^{13}C NMR (CD_2Cl_2, 101 MHz) δ 55.48 (s, $-CH_3$), 55.52 (s, $-CH_3$), 112−154 (ar), 160.1 (s, −NCHN−), 166.3 (m, metalated). Anal. Calcd for $C_{66}H_{58}N_4O_4P_2Pd_2$: C, 63.62;, H, 4.69; N, 4.50. Found: C, 64.01; H, 4.97; N, 4.39.

X-ray crystal structure data for **3c**: formula $C_{66}H_{58}N_4O_4P_2Pd_2$, triclinic system, space group $P\bar{1}$, a = 14.564(3) Å, b = 18.997(4) Å, c = 21.815(4) Å, α = 103.35(3)°, β = 96.20(3)°, γ = 93.82(3)°, V = 5812(2) Å^3, Z = 2, crystal dimensions 0.26 × 0.22 × 0.21 mm^3, Mo Kα radiation, 293(2) K, 6173 reflections, 3583 independent reflections (μ = 0.726 mm^{-1}), refinement (on F^2) with SHELXTL (version 6.1), 1406 parameters, 1378 restraints, R1 = 0.0705 ($I > 2\sigma$) and wR2 (all data) = 0.2318, GOF = 1.186, maximum/minimum residual electron density 0.933/−1.025 e Å^{-3}.

Preparation of $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2Cl_2$ (R′ = C_6H_4, 4a). A solution of iodobenzene dichloride (18 mg, 0.066 mmol) in acetonitrile (0.5 mL) was added to a suspension of **3a** (0.044 mmol) in acetonitrile (5 mL) at 0 °C. The suspension immediately changed from yellow to red. After 10 min of stirring the red microcrystalline precipitate was collected by filtration and washed with cold acetonitrile and diethyl ether. Yield: 48 mg, 91%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.06−6.08 (m, 4H, ar), 6.72−6.81 (m, 10H, ar), 6.91−6.94 (m, 2H, ar), 6.98−7.10 (m, 16H, ar), 7.14−7.16 (m, 2H, −NCHN−), 7.30−7.34 (m, 8H, ar), 7.44−7.47 (m, 2H, ar), 7.93−7.96 (m, 2H, ar), 8.26−8.30 (m, 4H, ar). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −16.3 (s). ^{13}C NMR ($CDCl_3$, 75 MHz, 253 K): δ 123−151 (ar), 159.1 (m, metalated), 168.8 (s, −NCHN−).

Preparation of $Pd_2[(C_6H_4)PPh_2]_2[R'NC(H)NR']_2Cl_2$ (R′ = p-$CH_3C_6H_4$, 4b). A solution of iodobenzene dichloride (17 mg, 0.063 mmol) in acetonitrile (0.5 mL) was added to a suspension of **3b** (0.042 mmol) in acetonitrile (5 mL) at 0 °C. Immediately, a red solution was obtained. After 5 min of stirring the solution was evaporated to dryness and the resulting red solid was dissolved in the minimum amount of diethyl ether. Addition of hexane produced a red microcrystalline precipitate, which was collected by filtration and washed with hexane. Yield: 40 mg, 76%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.12 (s, 6H, $-CH_3$), 2.25 (s, 6H, CH_3), 5.93−5.95 (m, 4H, ar), 6.56−6.58 (m, 4H, ar), 6.73−6.77 (m, 4H, ar), 6.85−6.93 (m, 10H, ar), 7.05−7.23 (m, 10H, −NCHN− + ar), 7.29−7.33 (m, 6H, ar), 7.41−7.45 (m, 2H, ar), 7.90−7.93 (m, 2H, ar), 8.25−8.30 (m, 4H, ar). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −16.4 (s). ^{13}C NMR ($CDCl_3$, 75 MHz, 253 K): δ 20.9 (s, $-CH_3$), 21.0 (s, $-CH_3$), 123−149 (ar), 159.4 (m, metalated), 168.6 (s, −NCHN−).

Preparation of $Pd_2[(C_6H_4)PPh_2]_2(N,O)_2$ (5, N,O = Succinimidate; 6, N,O = Phthalimidate; 7, N,O = 2-Hydroxypyridinate). The protonated N,O-donor ligand (0.270 mmol) and potassium hydroxide (0.270 mmol) were dissolved in the minimum amount of methanol. This solution was added at 0 °C to a solution of **2** (100 mg, 0.056 mmol) in dichloromethane (10 mL). After it was stirred for 1 h at the same temperature, the solution was evaporated to dryness. The yellow crude product obtained was extracted with dichloromethane, filtered over a short plug of silica, and precipitated by addition of hexane to give a yellow microcrystalline powder, which was collected by filtration and washed with hexane. In solution the products were mixtures of the symmetric product **a** and the asymmetric product **c**. Single crystals of **5a**, **6a**, and **7a** for X-ray diffraction were grown by slow diffusion of diethyl ether into a dichloromethane (**5a**) or chloroform (**6a**, **7a**) solution of the products. Yield: **5**, 92 mg, 88%; **6**, 96 mg, 83%; **7**, 80 mg, 77%.

Characterization data for **5**: ^{31}P NMR ($CDCl_3$, 162 MHz) **a**, δ 16.8 (s); **c**, δ 20.8 (d, J = 37), 14.5 (d, J = 37); **a**:**c** ratio 3:1. Anal. Calcd for $C_{44}H_{36}N_2O_4P_2Pd_2$: C, 56.73; H, 3.90; N, 3.01. Calcd for $C_{44}H_{36}N_2O_4P_2Pd_2\cdot CH_2Cl_2$: C, 53.17; H, 3.77; N, 2.76. Found: C, 52.72; H, 3.77; N, 2.75.

X-ray drystal structure data for **5a**: formula $C_{45}H_{38}Cl_2N_2O_4P_2Pd_2$, orthorhombic system, space group $Pbca$, a = 19.2370(2) Å, b = 20.3130(2) Å, c = 21.4700(3) Å, V = 8398.64(17)Å^3, Z = 8, crystal dimensions: 0.23 × 0.20 × 0.18 mm^3, Mo Kα radiation, 293(2) K, 54 202 reflections, 9553 independent reflections (μ = 1.107 mm^{-1}), refinement (on F^2) with SHELXTL (version 6.1), 515 parameters, 0 restraints, R1 = 0.0511 ($I > 2\sigma$) and wR2 (all data) = 0.1508, GOF = 1.063, maximum/minimum residual electron density 0.940/−1.392 e Å^{-3}.

Characterization data for **6**: ^{31}P NMR ($CDCl_3$, 162 MHz) **a**, δ 16.2 (s); **c**, δ 20.3 (d, J = 37), 14.4 (d, J = 37); **a**:**c** ratio 10:1. Anal. Calcd for $C_{52}H_{36}N_2O_4P_2Pd_2$: C, 60.78; H, 3.53; N, 2.73. Calcd for $C_{52}H_{36}N_2O_4P_2Pd_2\cdot 2CHCl_3$: C, 51.21; H, 3.02; N, 2.21. Found: C, 51.84; H, 3.09; N, 2.28.

X-ray crystal structure data for **6a**: formula $C_{105}H_{73}Cl_3N_4O_{11}P_4Pd_4$, monoclinic system, space group $P2_1/c$, a = 12.842(3) Å, b = 22.648(5) Å, c = 33.392(7) Å, β = 90.89(3)°, V = 9711(3) Å^3, Z = 2, crystal dimensions 0.26 × 0.23 × 0.19 mm^3, Mo Kα radiation, 293(2) K, 30 394 reflections, 15 111 independent reflections (μ = 0.939 mm^{-1}), refinement (on F^2) with SHELXTL (version 6.1), 1166 parameters, 0 restraints, R1 = 0.0915 ($I > 2\sigma$) and wR2 (all data) = 0.2662, GOF = 1.050, maximum/minimum residual electron density 2.722/−2.119 e Å^{-3}.

Characterization data for **7**: ^{31}P NMR ($CDCl_3$, 162 MHz) **a**, δ 17.9 (s); **c**, δ 20.3 (d, J = 28), 16.9 (d, J = 28); **a**:**c** ratio 5:1. Anal. Calcd for $C_{46}H_{36}N_2O_2P_2Pd_2$: C, 59.82; H, 3.93; N, 3.03. Calcd for $C_{46}H_{36}N_2O_2P_2Pd_2\cdot 2CHCl_3$: C, 49.60; H, 3.30; N, 2.41. Found: C, 49.91; H, 3.37; N, 2.46.

X-ray crystal structure data for **7a**: formula $C_{97}H_{81}Cl_9N_4O_5P_4Pd_4$, triclinic system, space group $P\bar{1}$, a = 13.7810(2) Å, b = 18.3740(2) Å, c = 19.3370 Å, α = 92.7680(5)°, β = 90.2160(6)°, γ = 91.0030(5)°, V = 4889.85 Å^3, Z = 2, crystal dimensions 0.27 × 0.25 × 0.20 mm^3, Mo Kα radiation, 293(2) K, 11 939 reflections, 11 939 independent reflections (μ = 1.088 mm^{-1}), refinement (on F^2) with SHELXTL (version 6.1), 1100 parameters, 0 restraints, R1 = 0.0914 ($I > 2\sigma$) and wR2 (all data) = 0.2607, GOF=1.148, maximum/minimum residual electron density 2.147/−2.369 e Å^{-3}.

Preparation of $Pd_2[(C_6H_4)PPh_2]_2(N,O)_2$ (8, N,O = Acetanilidate). Acetanilide (38 mg, 0.280 mmol) was added to a suspension of sodium hydride (60% in mineral oil, 12 mg, 0.300 mmol) in dry tetrahydrofuran under an argon atmosphere. When the emission of hydrogen ceased, a solution of **2** (60 mg, 0.070 mmol) in dry dichloromethane was added. After it was stirred for 15 min, the solution was evaporated to dryness. The yellow crude product obtained was extracted with dichloromethane, filtered over a short plug of silica, and precipitated by addition of hexane to give a yellow microcrystalline powder, which was collected by filtration and washed with hexane. Yield: 51 mg, 72%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.96 (s, 6H, $-CH_3$), 6.47−6.52 (m, 6H, ar), 6.56−6.64 (m, 6H, ar), 6.70−6.73 (m, 4H, ar), 6.86−6.95 (m, 6H, ar), 7.03−7.07 (m, 4H, ar), 7.10−7.14 (m, 2H, ar), 7.40−7.48 (m, 6H, ar), 7.70−7.75 (m, 4H, ar). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.5 (s). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 21.2 (s, $-CH_3$), 120−150 (ar), 164.4 (m, metalated), 174.4 (m, $OC(CH_3)N$).

Typical Catalytic β-Diboration, Subsequent Suzuki Reaction, and Oxidative Workup. Bis(catecholato)diboron (0.4 mmol) was added to a solution of the catalyst (5 mol %, 0.01 mmol Pd) and sodium acetate (0.2 mmol) in tetrahydrofuran (2 mL) under nitrogen. The solution was stirred for 5 min, the substrate (0.2 mmol) was added, and stirring was continued for 4 h at room temperature. The diboration conversions were determined by ^{1}H NMR spectroscopy of 0.1 mL aliquots of the reaction mixtures. After the reaction mixture was heated to reflux, cesium carbonate (0.6 mmol), 4-nitrobromobenzene (0.4 mmol), and water (degassed, 0.2 mL) were added and the reaction mixture was stirred for 15 h. After the mixture was cooled to room temperature, NaOH(aq) (3 M, 1 mL) and H_2O_2 (30%, 1 mL) were added carefully and stirring was continued for 2 h. The oxidation was quenched by adding a saturated aqueous solution of sodium thiosulfate (1 mL) and NaOH(aq) (1 M, 10 mL). Then the reaction mixture was extracted with ethyl acetate (3 × 20 mL) and the united organic phases were washed with brine (20 mL), dried over magnesium sulfate, and dried under reduced pressure. The products obtained were analyzed by ^{1}H NMR spectroscopy[51] to determine the degree of conversion and the nature of the reaction products.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Text, tables, and figures giving computational details and CIF files giving full crystallographic data for **3a**−**c** and **5a**−**7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553.
(2) Soderberg, B. C. G. *Coord. Chem. Rev.* **2004**, *248*, 1085.
(3) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400.
(4) Mueller, J. A.; Goller, C. P.; Sigman, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9724.
(5) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442.
(6) Jain, V. K.; Jain, L. *Coord. Chem. Rev.* **2005**, *249*, 3075.
(7) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(8) Garcia-Ruano, J. L.; Gonzalez, A. M.; Lopez-Solera, I.; Masaguer, J. R.; Navarro-Ranninger, C.; Raithby, P. R.; Rodríguez, J. H. *Angew. Chem., Int. Ed.* **1995**, *34*, 1351.
(9) Masciocchi, N.; Ragaini, F.; Sironi, A. *Organometallics* **2002**, *21*, 3489.
(10) Tian, G.; Boyle, P. D.; Novak, B. M. *Organometallics* **2002**, *21*, 1462.
(11) Vicente, J.; Arcas, A.; Fernandez-Hernandez, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767.
(12) Ruíz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P.; Hitchcock, P. B. *Organometallics* **2001**, *20*, 1973.
(13) Nakatsu, K.; Kafuku, K.; Yamaoka, H.; Isobe, K.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chim. Acta* **1981**, *54*, L69.
(14) Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9330.
(15) Ruiz, J.; Rodriguez, V.; Lopez, G.; Casabo, J.; Molins, E.; Miravitlles, C. *Organometallics* **1999**, *18*, 1177.
(16) Takani, M.; Masuda, M.; Yamauchi, O. *Inorg. Chim. Acta* **1995**, *235*, 367.
(17) Lenarda, M.; Nardin, G.; Pellizer, G.; Braye, E.; Graziani, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1536.
(18) Canty, A. J.; Minchin, N. J.; Engelhardt, L. M.; White, A. H. *Inorg. Chim. Acta* **1985**, *102*, L29.
(19) Cera, M.; Cerrada, E.; Laguna, M.; Mata, J. A.; Teruel, H. *Organometallics* **2002**, *21*, 121.
(20) Cotton, F. A.; Matusz, M.; Poli, R. *Inorg. Chem.* **1987**, *26*, 1472.
(21) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144.
(22) Yao, C. L.; He, L. P.; Korp, J. D.; Bear, J. L. *Inorg. Chem.* **1988**, *27*, 4389.
(23) Abul-Haj, M.; Quiros, M.; Salas, J. M. *Polyhedron* **2004**, *23*, 2373.
(24) Berry, J. F.; Cotton, F. A.; Ibragimov, S. A.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2005**, *44*, 6129.
(25) Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 13280.
(26) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 1015.
(27) Aarif, A. M.; Estevan, F.; García-Bernabé, A.; Lahuerta, P.; Sanaú, M.; Úbeda, M. A. *Inorg. Chem.* **1997**, *36*, 6472.
(28) Estevan, F.; García-Bernabé, A.; Lahuerta, P.; Sanaú, M.; Úbeda, M. A.; Ramirez de Arellano, M. C. *Inorg. Chem.* **2000**, *39*, 5964.
(29) Koshevoy, I. O.; Lahuerta, P.; Sanaú, M.; Úbeda, M. A.; Doménech, A. *Dalton Trans.* **2006**, 5536.
(30) Umakoshi, K.; Ichimura, A.; Kinoshita, I.; Ooi, S. *Inorg. Chem.* **1990**, *29*, 4005.
(31) Bond, A. M.; Canty, A. J.; Cooper, J. B.; Tedesco, V.; Traill, P. R.; Way, D. M. *Inorg. Chim. Acta* **1996**, *251*, 185.
(32) Cotton, F. A.; Koshevoy, I. O.; Lahuerta, P.; Murillo, C. A.; Sanaú, M.; Úbeda, M. A.; Zhao, Q. *J. Am. Chem. Soc.* **2006**, *128*, 13674.
(33) Lillo, V.; Mas-Marzá, E.; Segarra, A. M.; Carbó, J. J.; Bo, C.; Fernández, E. *Chem. Commun.* **2007**, 338.
(34) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742.
(35) Sakaki, S.; Kikuno, T. *Inorg. Chem.* **1997**, *36*, 22.
(36) Penno, D.; Lillo, V.; Koshevoy, I. O.; Sanaú, M.; Úbeda, M. A.; Lahuerta, P.; Fernández, E. *Chem. Eur. J.* **2008**, *14*, 10648.
(37) (a) Powers, D. C.; Ritter, T. *Nat. Chem.* **2009**, *1*, 302. (b) Powers, D. C.; Geibel, M. A. L.; Klein, E. M. N.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 17050.
(38) Bonet, A.; Gulyás, H.; Koshevoy, I. O.; Estevan, F.; Sanaú, M.; Úbeda, M. A.; Fernández, E. *Chem. Eur. J.* **2010**, *16*, 6382.
(39) Archibald, S. J.; Alcock, N. W.; Busch, D. H.; Whitcomb, D. R. *Inorg. Chem.* **1999**, *38*, 5571.
(40) Green, N. J.; Xiang, J.; Chen, J.; Chen, L.; Davies, A. M.; Erbe, D.; Tam, S.; Tobin, J. F. *Bioorg. Med. Chem.* **2003**, *11*, 2991.
(41) Esteban, J.; Hirva, P.; Lahuerta, P.; Martínez, M. *Inorg. Chem.* **2006**, *45*, 8776.
(42) Imao, D.; Glasspoole, B. W.; Laberge, V. S.; Crudden, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 5024.
(43) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, U.K., 1980.
(44) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422.
(45) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* **1942**, *22*, 69.
(46) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134.
(47) *SHELXTL (Version 6.10)*; Bruker, 2000.
(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.;

Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision C.02*; Gaussian, Inc., Wallingford, CT, 2004.

(49) Becke, A. D. J. *Chem. Phys.* **1993**, *98*, 5648.

(50) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(51) Miller, S. P.; Morgan, J. B.; Nepveux, F. J.; Morken, J. P. *Org. Lett.* **2004**, *6*, 131.