Novel Methylpalladium(II) Complexes Bearing Tridentate Imidazole-Based Chelate Ligands: Synthesis, Structural Characterization, and Reactivity

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Novel methylpalladium(II) complexes of the general composition [PdCl(CH$_3$){N∧D∧N}] ({N∧D∧N} = (mim)$_3$COCH$_3$ (**1a**), (mim)$_2$CHCH$_2$C(O)Bu-*t* (**3a**)) were synthesized from [PdCl(CH$_3$)(COD)] and the respective *N*-methylimidazole (mim) ligands. The cationic derivatives [Pd$_2$(CH$_3$)$_2$({N∧D∧N}$_2$](BF$_4$)$_2$ (**1b**; {N∧D∧N} = (mim)$_3$COCH$_3$) and [Pd(CH$_3$){N∧D∧N)(CH$_3$CN)](BF$_4$) (**3b**; {N∧D∧N} = (mim)$_2$CHCH$_2$C(O)Bu-*t*) were obtained by halide abstraction with AgBF$_4$. The effect of varying the third donor moiety (D = "O", "N", "P") in the structurally very similar ligands on the coordination chemistry and reactivity of **1** and **3** and the previously reported [PdCl(CH$_3$){N∧D∧N}] (**2a**; {N∧D∧N} = (mim)$_2$CHCH$_2$PPh$_2$) was investigated in detail. Thus, a neutral monomeric and an ionic dimeric isomer were identified for **1a**, with the ligand adopting a σ^2-N∧N coordination mode in the former and a σ^3-N∧N∧N coordination mode in the latter. Exclusive formation of the ionic dimer occurs in methanol. Crystal structures are recorded for **1b** and [Pd$_2$Cl(CH$_3$){N∧N∧N}$_2$]Cl$_2$ (**1c**). Each complex has two square-planar N$_3$X (X = CH$_3$, Cl) coordinated Pd centers with the coordination planes in a quasi-parallel orientation but laterally displaced in projection. Two nitrogens from the three imidazole rings of one ligand chelate one Pd center, whereas the third is bridging to the neighboring Pd center. Complex **2a** displays σ^2-P∧N coordination and fluxional behavior of the ligand at room temperature. At lower temperatures, various isomers, possibly involving five-coordinate compounds, are observed in the NMR spectrum of **2a**. The predominant mode of coordination in complexes **3** is σ^2-N∧N; their NMR spectra provide evidence for weak O···Pd interactions. The complexes **1a**−**3a** readily insert CO, resulting in the formation of the respective Pd acyl complexes. The methylpalladium complexes give rise to active and stable catalysts for the Heck coupling reaction, with turnover numbers of up to 800 000 being obtained for **1b**.

Introduction

The synthesis and detailed investigation of palladium(II) complexes bearing nitrogen chelate ligands[1] have received considerable attention over the past decade. A number of these complexes have been found to be highly active catalysts for important reactions such as ethylene polymerization[2] and CO/ethylene copolymerization.[3] Complexes with various nitrogen chelate environments have also been successfully applied to studies providing information about intimate steps of catalytic reactions involving organopalladium compounds.[4]

In this context we recently became interested in the properties of palladium complexes containing functionalized chelating ligands derived from the heterocyclic imidazole unit. This class of ligands plays a key role in studies mimicking the binding sites of metalloproteins.[5] Other applications such as hydroamination and hydrosylilation have been described recently for rhodium complexes containing bis(imidazole) chelate ligands,[6] and in a previous article we reported the synthesis and catalytic behavior of several neutral and cationic

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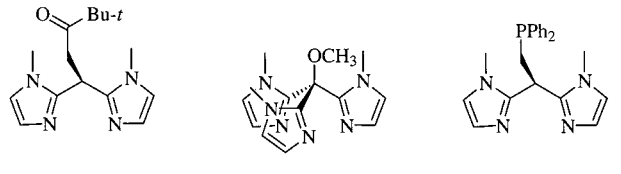

$(mim)_2CHCH_2C(O)Bu\text{-}t$ $(mim)_3COCH_3$ $(mim)_2CHCH_2PPh_2$

Figure 1. Ligands used in this work.

Pd(II) complexes bearing imidazole-based chelate ligands.[7] We demonstrated the effect of changing electronic and steric features of the ligand system on the behavior of the complexes in the Heck reaction and ethylene/CO copolymerization. More recently, we have found that chromium(III) complexes bearing a variety of donor-functionalized imidazole chelate ligands catalyze the oligomerization of ethylene in the presence of modified methylaluminoxane (MMAO).[8] We have now extended our investigations to palladium(II) complexes of the type $[PdCl(CH_3)(\sigma^2/\sigma^3\text{-}N\wedge D\wedge N)]$, containing tridentate ligands. The ligands shown in Figure 1 consist of a bridged bis-(1-methylimidazol-2-yl) framework and a third donor function varying from hard to soft. Thus, for complexes containing structurally closely related tridentate ligands, the effect of changing the donor properties of the third donor function on the coordination chemistry and reactivity on coordination to the soft palladium center (HSAB concept) can be studied.

Although less common than studies with bidentate ligands, methylpalladium(II) complexes containing symmetrical and unsymmetrical neutral tridentate nitrogen ligands have been reported by several groups. The coordination chemistry of tridentate N-ligands, some of them containing imidazole rings, in $[Pd(CH_3)_2\{N\wedge N\wedge N\}]$ and $[Pd\ I(CH_3)\{N\wedge N\wedge N\}]$ ($\{N\wedge N\wedge N\} = (py)_2(mim)CH$, $(py)(mim)_2CH$, $(pz)_2(mim)CH$, $(pz)_2(py)CH$, $(pz)_3CH$, $(py)_3CH$) has been studied in detail by Canty et al.[9] In a majority of these complexes the tridentate ligands display fluxional behavior, and those containing unsymmetrical ligands show isomerism, which is dependent on the nature of the different donor moieties present in the ligand system. A number of these complexes have played a key role in the development of organopalladium(IV) chemistry.[10] Fluxional behavior for the tridentate ligand system and the presence of coordination isomers have also been observed by Vrieze et al. for the complexes $[PdCl(CH_3)\{N\wedge N\wedge N\}]$, which contain neutral, N-heterocyclic based ligands ($\{N\wedge N\wedge N\}$ = 2,6-bis-(2-propanecarbaldimino)pyridine (*i*-Pr-DIP), 2,2′:6:2″-terpyridine (terpy), 2,6-bis(*N*-pyrazolyl)pyridine (bbp), 2-(2-(2′-pyridylmethylene)amino)ethyl)pyridine (MAP), 2-(2-(((6′-methyl-2-pyridyl)methylene)amino)ethyl)pyridine (6′-CH_3-MAP), 2-(2-(((1′-methyl-2′-imidazolyl)-methylene)amino)ethyl)pyridine) (MIMAP)).[11] Various isomers, involving cationic square-planar and five-coordinate complexes, have been identified in variable-temperature NMR experiments.

The insertion of unsaturated molecules into the Pd−carbon bond is a key step in numerous palladium-catalyzed organic reactions.[12] Among these, the Heck reaction[13] has received much attention in our group over the past few years. In particular, methylpalladium complexes carrying functionalized carbene ligands gave excellent TONs with good conversions.[14] Therefore, it was of interest for us to evaluate methylpalladium complexes bearing donor-functionalized bis(imidazole) ligands as catalysts for Heck-type coupling reactions. In this article we report the synthesis and properties of a number of new neutral and cationic methylpalladium complexes, containing (potentially) tridentate bis(imidazole) ligands carrying the additional donor functions O, N, and P, respectively. The carbonylation of these complexes has been investigated briefly and is shown

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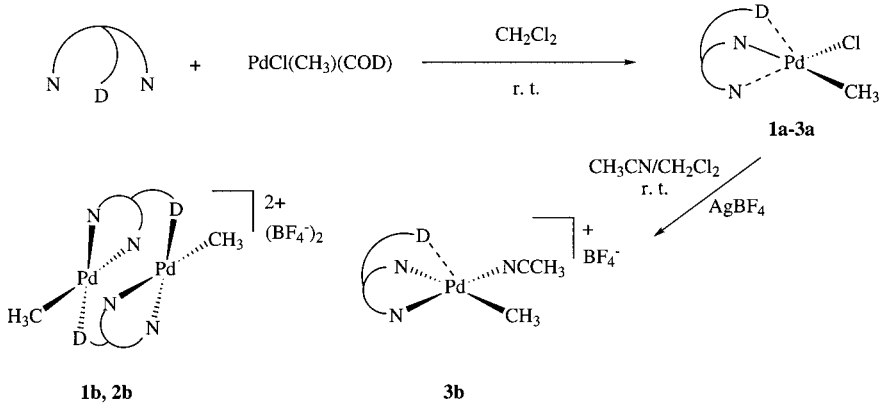
Scheme 1. General Synthesis of Complexes 1−3



to proceed rapidly. The new complexes have been tested as catalysts in the Heck coupling reaction.

Results and Discussion

The ligands employed in this work have been prepared according to published procedures.[5b,6b,c,15]

The novel complexes $[PdCl(CH_3)\{(mim)_3COCH_3\}]$ (**1a**), $[PdCl(CH_3)\{(mim)_2CHCH_2P\}]$ (**2a**),[7] and $[PdCl(CH_3)\{(mim)_2CHCH_2CO\}]$ (**3a**) have been prepared by substitution of the cyclooctadiene in $[PdCl(CH_3)(COD)]$ by the respective ligand in high yields (Scheme 1). The off-white or light yellow compounds are insoluble in hexane, Et_2O, and THF and partly soluble in acetone. They readily dissolve in CH_2Cl_2 and $CHCl_3$, but decomposition of the complexes occurs on prolonged standing in these solvents. Complex **3a** is significantly less stable in chloroform than **2a** and **1a.** Decomposition, which was accompanied by formation of palladium metal, was observed within hours at room temperature. All of the complexes are stable in the solid state at room temperature.

The ionic complexes $[Pd_2(CH_3)_2\{(mim)_3COCH_3\}_2](BF_4)_2$ (**1b**), $[Pd_2(CH_3)_2\{(mim)_2CHCH_2PPh_2\}_2](BF_4)_2$ (**2b**),[7] and $[Pd(CH_3)\{(mim)_2CHCH_2C(O)Bu\text{-}t\}(CH_3CN)]\ BF_4$ (**3b**) have been obtained by the reaction of **1a**−**3a** with $AgBF_4$ in CH_3CN/CH_2Cl_2 or CH_2Cl_2 (Scheme 1). Whereas **3b** is soluble in chlorinated solvents, **1b** is only slightly soluble in these solvents but readily dissolves in methanol. Complex **2b** is only soluble in hot DMSO. Complex **3b** appeared to be very unstable in chloroform even at −20 °C and in the solid state at ambient temperature (palladium metal), thus precluding a satisfactory elemental analysis for this compound.

Discussion of Individual Spectroscopic Data and Behavior of 1a−3a. According to the different donor sets present in the ligands, the NMR spectra of the complexes display particular features, which also reveal the presence of coordination isomers. Selected ^1H NMR data are presented in Table 1. Reactions of **1a** are illustrated in Scheme 2.

In contrast to many other palladium complexes bearing potentially tridentate ligands,[9a,b,11] complex **1a**, which contains the tris(imidazole) ligand $(mim)_3COCH_3$, does not display fluxional coordination behavior. The room-temperature ^1H NMR spectrum exhibits a sharp singlet for the Pd−CH_3 group at δ 0.92 ppm. Four sharp resonances for the methyl groups of the ligand system and four doublets and two singlets for the imidazole ring protons are observed, indicating the inequivalence of the three imidazole rings. Consistent with the coordination of two imidazole rings, two of the N−CH_3 resonances are found at 0.26 and 0.13 ppm downfield from the free ligand, whereas the third N−CH_3 resonance has a shift value similar to that of the free ligand. Static coordination of the ligand system was also observed in $Pd(CH_3)_2$ and $PdI(CH_3)$ complexes containing the closely related $(mim)_2(py)CH$, which is coordinated via the two imidazole rings.[9b] However, when we prepared **1a**, the formation of a second isomer **1a′** (Pd−CH_3: δ 0.07 ppm, $CDCl_3$) was observed in some cases, especially with prolonged reaction times. The isomer **1a′** was obtained exclusively when the reaction was carried out in the more polar solvent methanol. Formation of **1a′** also occurs when **1a** is dissolved in methanol. After 10 min at room temperature the ^1H NMR spectrum shows the presence of **1a** and **1a′** in an approximately 1:1 ratio and formation of **1a′** is complete after ca. 2.5 h. The ^1H NMR spectrum (CD_3OD) of **1a′** shows the signal pattern found for **1a**, but the Pd−CH_3 (δ −0.28 ppm) and one of the imidazole ring resonances (δ 5.59 ppm) are shifted to significantly lower ppm values. Reaction of **1a′** with $AgBF_4$ in MeOH gave the BF_4 salt **1b**, for which the ^1H NMR spectrum is almost identical with that of **1a′**. Cooling of a methanol solution of **1b** resulted in the precipitation of crystals suitable for X-ray diffraction (see discussion below). Complex **1b** is an ionic dimeric methylpalladium complex, with $(mim)_3COCH_3$ acting as a bridging ligand between the two metal centers (Figure 2).

Table 1. Selected ^1H NMR ($CDCl_3$) Data for Ligands and Complexes 1−3

compd	Pd−CH_3	N−CH_3
$(mim)_3COCH_3$[a]		3.46
$(mim)_2CHCH_2PPh_2$[a]		3.41
$(mim)_2CHCH_2C(O)$ Bu-t[a]		3.32
1a	0.91	3.67, 3.54, 3.38
1a′[b]	−0.28	4.37, 3.62, 3.59
1b[c]	−0.24	4.38, 3.62, 3.61
2a	0.61	3.28
2a′[b]	−0.35	3.89, 3.19
2b[d]	−0.55	3.92, 3.2
3a[e]	0.85	3.83, 3.71
3b	0.79	3.93, 3.83

[a] In $CDCl_3$. [b] In CD_3OD. [c] In CD_3CN. [d] In DMSO. [e] Major isomer.

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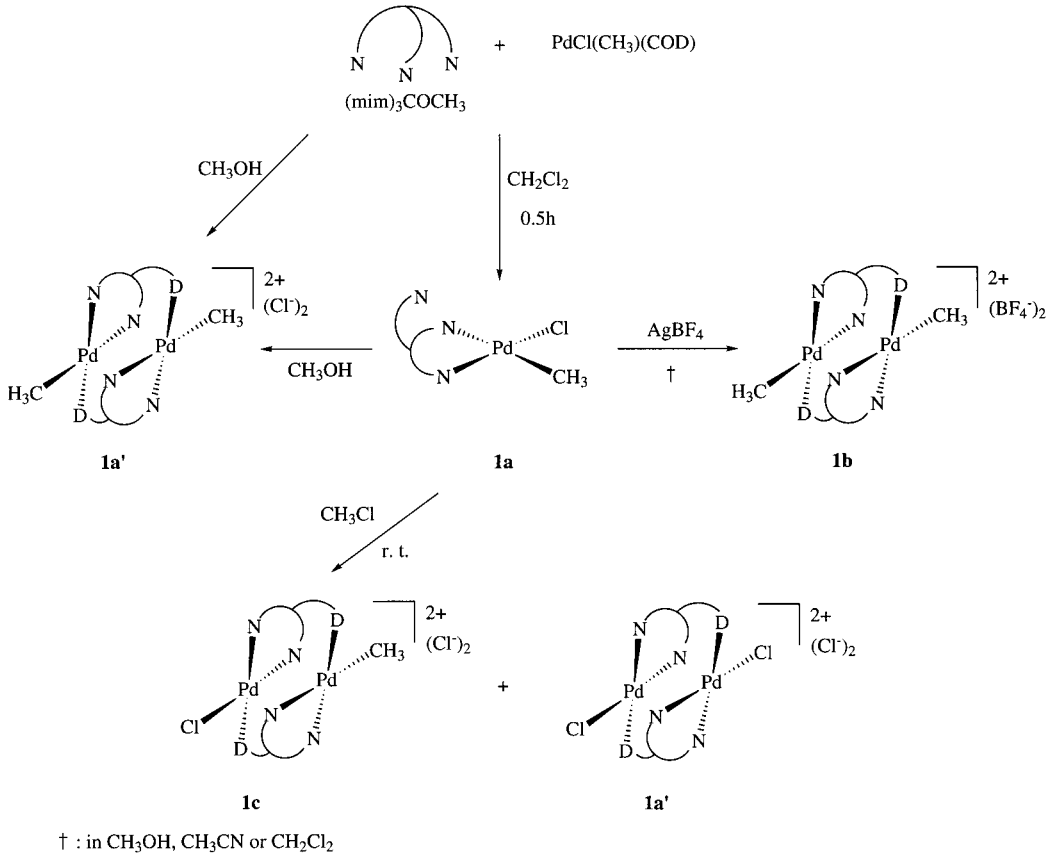
Scheme 2. Behavior and Reactions of 1a



Thus, on the basis of the dicationic molecular ion $[Pd_2(CH_3)_2\{(mim)_3COCH_3\}_2]^{2+}$ at *m/z* 814 observed for complex **1a′** in the mass spectrum (electrospray), and because of the similarity of the NMR spectrum to that for **1b**, we conclude that isomer **1a′** is also dimeric. NMR experiments (gCOSY, gHMQC, gHMBC) with **1a′** confirmed that, of the four methyl signals for the ligand system, the resonance at 2.77 ppm belongs to the OCH_3 group; the $N-CH_3$ groups give rise to signals at 3.59, 3.56, and 4.36 ppm, respectively. The exceptionally low ppm value for the $Pd-CH_3$ resonance is probably a result of the anisotropic shielding effect imposed by the bridging imidazole ring oriented perpendicular to the coordination plane (Figure 6a). The resonance with the relatively low value of 5.59 ppm can be assigned to an imidazole ring proton in the 4-position. In the imidazole ring cis to the perpendicular oriented ring, the 4-position lies in the shielding region of the latter, which causes the upfield shift of the respective proton resonance. A similar observation has been made for the ortho proton in the aryl-substituted bis(imine) ligand Ar-BIAN.[4b]

The complex **1a** undergoes a further transformation in chloroform solution, and loss of the $Pd-CH_3$ group is observed. One of the reaction products is the dimeric methyl chloro complex $[Pd_2Cl(CH_3)\{(mim)_3COCH_3\}_2]Cl_2$ (**1c**), which separated from the solution after 4 days at room temperature in the form of yellow needles suitable for X-ray diffraction (Figures 2 and 6b). The molecular structure of **1c** is discussed below. The ^1H NMR spectrum of crystalline **1c** in CD_3OD shows two sets of $N-CH_3$ and OCH_3 signals accounting for two inequivalent ligand environments; one ligand is coordinated (via two imidazole rings) to the $Pd-CH_3$ and the other to the Pd−Cl moiety. However, ^1H NMR analysis of the mother liquor suggests that scrambling between the two Pd moieties occurs in chloroform solution. Resonances for two different $N-CH_3$ environments in a 2:1 ratio and one $O-CH_3$ environment are found. After another 2 days in chloroform at room temperature an off-white solid precipitated, which is presumably a $PdCl_2$ complex, since no $Pd-CH_3$ signal was detected in the ^1H NMR spectrum. The spectrum displays the same signal pattern as observed for **1a′** and **1b** but with slightly higher ppm values, and hence, a dimeric structure with the composition $[Pd_2Cl_2\{(mim)_3COCH_3\}_2]Cl_2$ is very likely. Elimination of the $Pd-CH_3$ group and formation of the respective $PdCl_2$ complex in chloroform solution has been described previously for $[PdCl(Me)(mim)_2C{=}NPh\}]$.[7]

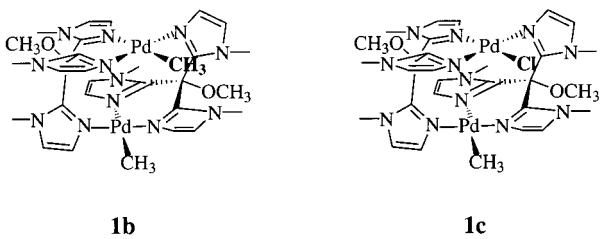


Figure 2. Coordination of $(mim)_3COCH_3$ in **1b**,**c**.

Complex **2a** had been described briefly in a previous article.[7] We now report the results of a detailed study of this complex, which displays a rich coordination chemistry. The ligand $(mim)_2CHCH_2PPh_2$ coordinates to the soft palladium center in a N∧P fashion. The coupling constant of $J_{PH} = 3.2$ Hz for the $Pd-CH_3$ doublet indicates a cis orientation of the P-donor and

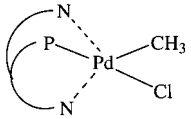
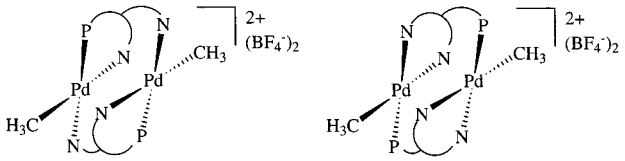


Figure 3. Fluxional coordination behavior of **2a** at ambient temperature.



2a'

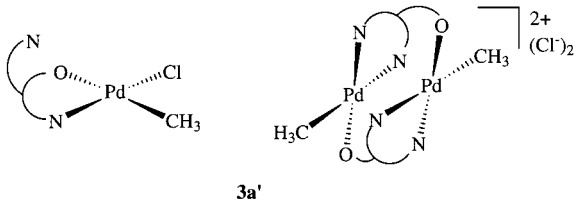
Figure 4. Possible isomers for **2a′**.

the methyl group.[7,16] However, all of the ^{1}H and ^{31}P NMR signals are broad at room temperature, and hence, the ligand is fluxional, in a process involving an on/off movement of the two imidazole rings with respect to the metal center (Figure 3). The signals sharpen on heating. Fluxional behavior involving exchange between coordinated and uncoordinated donor moieties has been observed for a number of other palladium(II) complexes containing unsymmetrical tridentate ligands.[9b,11a,b]

Sharp signals are observed in the room-temperature ^{1}H and ^{31}P NMR spectra when complex **2a** is dissolved in methanol. Similar to **1a′** and **1b**, the Pd−CH_3 group gives rise to a singlet at a relatively low chemical shift value (δ −0.34 ppm, J_{PH} = 3.3 Hz), and two inequivalent imidazole ring environments are observed (N−CH_3 signals at δ 3.89 and 3.19 ppm). Because of the similar behavior and NMR spectra of **2a** and **1a′**,**b**, we assume that **2a** forms the dicationic dimeric complex [Pd_2-$(CH_3)_2${$(mim)_2CHCH_2PPh_2$}$_2$]Cl_2 (**2a′**) when it is dissolved in methanol. The dimeric nature of **2a′** is also confirmed by the observation of a strong signal for the ion [$Pd_2(CH_3)_2${$(mim)_2CHCH_2PPh_2$}$_2$]Cl^+ at *m*/*z* 1025 in the mass spectrum (electrospray). As shown in Figure 4, two isomers are possible for **2a′**, involving either bridging of the two Pd centers through the PPh_2 group or one of the imidazole rings. However, the data obtained for **2a′** do not allow us to unambiguously decide which of the two isomers is formed.

The coordination chemistry of the ligand in **2a** has been further investigated by low-temperature ^{1}H and ^{31}P NMR spectroscopy. At 203 K three isomers are detected in the ^{1}H NMR spectrum in a ∼0.4:1:1 ratio, which by gradually raising the temperature resolve into the ambient-temperature structure. The isomers most likely involve five-coordinated species, as has been observed in other palladium(II) complexes containing potentially tridentate nitrogen ligands, which show fluxional behavior at ambient temperature.[11b,c] A figure showing relevant sections of the VT NMR study and a discussion of the NMR data are given in the Supporting Information.

The observation of one single C=O IR absorption (KBr: 1703 cm^{-1}) at a frequency almost identical with the value for the free ligand suggests N∧N coordination of the ligand $(mim)_2CHCH_2C(O)Bu$-*t* in complex **3a**.



3a'

Figure 5. Possible coordination isomers for **3a′**.

However, the ^{1}H NMR spectrum of **3a** shows the presence of two isomers in a ca. 3.5:1 ratio, with the resonances of the minor isomer, **3a′**, shifted to higher ppm values compared to those of the major isomer, **3a**. The two isomers do not interconvert upon heating. Similar to other palladium complexes with tridentate nitrogen ligands containing bridging CH_2 groups,[11b] the CH_2 protons are inequivalent and give rise to two resonances ($^2J_{HH}$ = 17.6 Hz) in both isomers. This indicates interaction of the $CH_2C(O)Bu$-*t* group with the palladium center in both isomers. A solution IR spectrum ($CHCl_3$) was recorded for **3a**. The somewhat broadened C=O absorption is slightly (1699 cm^{-1}) shifted to lower wavenumbers. We therefore conclude that the C=O palladium interaction in **3a** is only weak. Weak interaction between a Pd center and a carbonyl donor has also been observed in the structurally characterized complex [$Pd(CH_2CH_2COCH_3)(NC_5H_4CO_2CH_3)$-$(PPh_3)$]$BF_4$.[18] This interpretation is supported by an experiment in which we tried to achieve coordination of the oxygen donor in **3a** via chloride abstraction with $AgBF_4$ in absence of a coordinating solvent. The reaction resulted in the rapid formation of palladium metal and small amounts of dark brown unidentified products. No well-defined palladium complex could be isolated or detected spectroscopically. A similar observation has been made for oxygen-donor-functionalized carbene complexes of Pd.[14c] The exact nature of **3a′** is uncertain. The Pd−CH_3 signal of **3a′** is shifted downfield by 0.26 ppm compared to **3a**, suggesting that formation of an N∧O coordinated isomer might occur in solution (Figure 5).[19] Although, in contrast to **1a** and **2a**, treatment of **3a** with methanol had no effect on its ^{1}H NMR spectrum (CD_3OD), a dimeric σ^3-N∧O∧N structure in which the carbonyl function is coordinated to a neighboring palladium center is also to be considered for **3a′**, since the molecular ion [$Pd_2Cl(CH_3)_2${$(mim)_2CHCH_2C(O)Bu$-*t*}$_2$]$^+$ of low intensity is observed at *m*/*z* 825 in the mass spectrum (LSIMS). If formed, such a dimer can only be of limited stability because rapid decomposition was observed in methanol.

Discussion of X-ray Structure Determinations for Complexes 1b,c. The results of the two low-temperature single-crystal X-ray studies are neither totally straightforward or unambiguous; in each case the basis of the structure is consistent with a description in terms of stoichiometry and connectivity with the presence of a binuclear cation of the form [{$LPdX$}$_2$]$^{n+}$,

(16) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937.

(17) For a comparison of properties of im, pz, and py ligands see: Canty, A. J.; Lee, C. V. *Organometallics* **1982**, *1*, 1063.

(18) Green, M. J.; Britovsek, G. J. P.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1996**, 1563.

(19) (a) Britovsek, G. J. P.; Cavell, K. J.; Green, M. J.; Gerhards, F.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1997**, *533*, 201. (b) Green, M. J.; Britovsek, G. J. P.; Cavell, K. J.; Gerhards, F.; Yates, B. F.; Frankcombe, K.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1137.

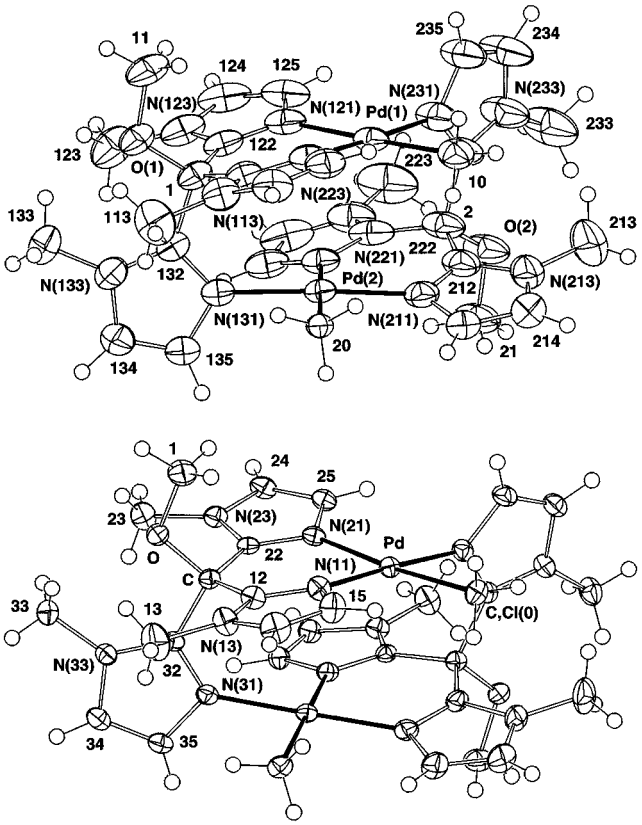


Figure 6. Projections of the cations of (a, top) **1b** and (b, bottom) **1c** in similar orientations. 50% probability amplitude displacement ellipsoids are shown for the nonhydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

L being tridentate and X unidentate, together with associated counterions and solvent molecules. In the presumed space groups, the cation of **1c** is disposed about a crystallographic 2-axis, while that of **1b** is devoid of crystallographic symmetry, having one half and one complete such cationic formula unit, respectively, with associated counterions and solvent, comprising the asymmetric unit of each structure. Of the pair, **1c** is the more readily apprehensible and we approach **1b** by consideration of **1c** first.

The model adopted for **1c** (Figures 2 and 6b; see Experimental Section) is $[\{LPd(Me/Cl)\}_2]Cl_2 \cdot 4CHCl_3$, methyl and chloride donors within the cation being scrambled within the unidentate site in the planar four-coordinate array about the metal. Bond lengths and angles (Table 2) are essentially as expected, interplanar dihedral angles quantifying deviations of individual ring components from the dominant pair of parallel planes, originating from the two metal atoms.

The cationic component of **1b** is based on a similar entity, which (see Experimental Section), in consequence of difference map components and high displacement parameters and the stoichiometric consequences of well-defined, presumptively anionic components, is modeled as a pair of cocrystallized species, the overall stoichiometry being $(5/6)[\{LPdMe\}_2](BF_4)_2 \cdot (1/6)[\{LPd(Me/OH_2)\}](BF_4)_3 \cdot (31/12)MeOH$ (Figures 2 and 6a). In this, the unidentate ligand in association with the disordered component of Pd(2) is modeled as (adventitious) water, the concomitant different trans effect impacting further afield on the location of the chelate components, and the different charge compensating the BF_4^- moiety at the site of $\bar{3}$ symmetry.

Table 2. Selected Cation Geometries[a]

atoms	param
Distances (Å)	
Pd−N(11)	2.021(3); 2.005(4), 2.025(4)
Pd−N(21)	2.049(2); 2.134(4), 2.097(4)
Pd−*N(31)*	2.016(2); 2.046(5), 2.031(4)
Pd−X	2.275(1); 2.082(5), 2.108(4)
N(11)...N(21)	2.829(3); 2.861(5), 2.865(5)
Angles (deg)	
X−Pd−N(11)	93.19(7); 93.0(2), 91.8(2)
X−Pd−N(21)	175.13(7); 178.5(2), 177.3(1)
X−Pd−*N(31)*	85.06(7); 86.9(2), 86.4(2)
N(11)−Pd−N(21)	88.10(9); 87.4(2), 88.0(2)
N(11)−Pd−*N(31)*	177.26(9); 177.5(2), 177.1(2)
N(21)−Pd−*N(31)*	93.83(9); 92.6(2), 93.7(2)
Pd−N(11)−C(12)	127.8(2); 127.5(3), 127.2(4)
Pd−N(11)−C(15)	124.7(2); 125.9(3), 125.2(4)
Pd−N(21)−C(22)	129.0(2); 127.5(4), 126.9(3)
Pd−N(21)−C(25)	124.0(2); 125.7(4), 125.0(4)
Pd−*N(31)*−*C(32)*	128.3(2); 132.4(3), 133.7(4)
Pd−*N(31)*−*C(35)*	123.1(2); 121.0(3), 119.1(3)
N(11)−C(12)−C	129.5(3); 130.9(5), 130.0(5)
N(21)−C(22)−C	128.7(2); 127.4(5), 127.7(5)
N(31)−C(22)−C	121.8(2); 120.6(4), 121.6(6)
C(12)−C−C(22)	113.7(2); 114.0(4), 114.7(5)
C(12)−C−C(32)	109.2(2); 109.5(5), 107.2(4)
C(22)−C−C(32)	110.4(2); 109.2(3), 111.8(5)
Interplanar Dihedral Angles (deg)	
N_3X/im(1)	13.0(1); 17.6(2), 17.1(2)
N_3X/im(2)	14.7(1); 16.7(2), 18.9(2)
N_3X/*im(3)*	80.4(1); 81.8(2), 85.0(2)
im(1)/im(2)	13.8(1); 14.2(2), 20.9(3)
im(1)/*im(3)*	88.5(1); 83.5(2), 87.3(2)
im(2)/*im(3)*	78.6(1); 77.7(3), 71.9(3)
δPd(im(1))	0.282(5); 0.286(1), 0.204(9)
δPd(im(2))	0.005(4); 0.231(9), 0.101(9)
δPd(*im*(3))	0.337(5); 0.057(10), 0.138(8)
N_3X/N_3X	10.83(5); 3.5(1)
Torsion Angles (deg)	
Pd−N(11)−C(12)−C	-16.7(4); −14.9(8), −10.6(6)
Pd−N(21)−C(22)−C	4.1(4); 11.9(6), 10.3(6)
N(11)−C(12)−C−C(22)	0.6(4); −4.6(7), −9.6(6)
N(21)−C(22)−C−C(12)	6.0(4); 5.5(6), 9.3(6)
N(21)−Pd−C(11)−C(12)	19.4(2); 22.9(4), 21.7(3)
N(11)−Pd−N(21)−C(22)	-13.7(2); −22.0(3), −21.8(4)

[a] The three values in each entry correspond to the value for the cation of **1c** and the halves of the cation of **1b**, respectively, (major Pd component for Pd(1)). X is the unidentate ligand. Italicized atoms are drawn from the other half of the cation. In **1b**, Pd(1′)−N(111,121,*231*) and Pd(1′)−C(10) are 2.362(5), 1.792(6), 1.765(6), and 2.479(6) Å. [b] δPd is the palladium atom deviation (Å).

In complexes **1b**,**c** the Pd−CH_3 distances are considerably longer and the Pd−N(11),N(31) distances slightly shorter than those found in other σ^2,σ^3 N-ligated Pd(II) complexes.[3a,7,11a,b,20] Whereas the Pd−N bond length trans to the methyl group in **1b** is in the range of those observed in other nitrogen-chelated Pd complexes,[3a,7,21] this distance is significantly shorter in **1c**. Relatively short Pd−N bond lengths trans to a methyl group have also been observed in $[PdCl(CH_3)(MAP)]$[11b] and $[PdCl(CH_3)(Terpy)]$.[11a]

(20) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1990**, *393*, 299.

(21) (a) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *J. Org. Chem.* **1993**, *58*, 7421. (b) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *Synlett* **1992**, 871. (c) van Asselt, R.; Elsevier, C. J. *Tetrahedron* **1994**, *50*, 323.

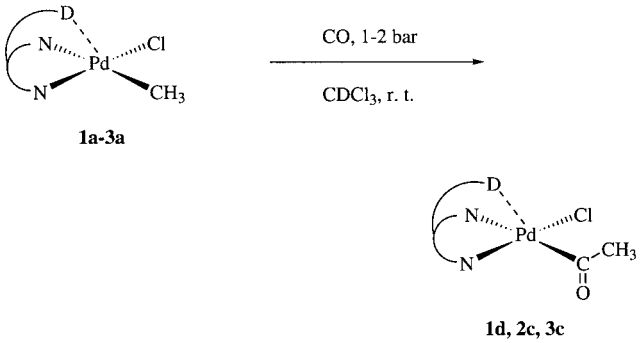
Halogen Abstraction Reactions in 1−3. Treatment of **3a** with $AgBF_4$ in CH_3CN/CH_2Cl_2 solution gave the expected cationic complex **3b**, as judged by its ^1H NMR spectrum. Coordination of CH_3CN is confirmed by the observation of a singlet at 0.37 ppm downfield from free CH_3CN. Similar to **3a**, the bridging CH_2 protons in **3b** are inequivalent and, hence, weak interactions between the carbonyl group and the palladium center might be present; the ν(C=O) absorption is observed at 1702 cm^{-1}. Complex **3b** is of very limited stability in solution even at −20 °C and in the solid state at room temperature (formation of palladium metal). A satisfactory elemental analysis could not be obtained for this complex. The presence of a singlet for uncoordinated CH_3CN suggests that **3b** decomposes via loss of the weakly coordinating solvent. Surprisingly, reaction of **1a** under the same reaction conditions (Scheme 2) did not result in the formation of the respective acetonitrile complex. Instead, the dimeric cationic complex **1b** was obtained. No signal for CH_3CN could be detected in the ^1H NMR spectrum, and the absence of CH_3CN is also confirmed by elemental analysis. A strong signal for a dimeric cationic cluster with *m*/*z* 814 is observed in the mass spectrum (electrospray) of the reaction product **1b**. Complex **1b** also forms upon reacting **1a** with $AgBF_4$ in CH_2Cl_2 only. However, under these conditions the reaction is accompanied by formation of significant amounts of palladium metal. The strong tendency of the third imidazole ring to become coordinated has also been found in a metathetical reaction in which CH_3CN has been replaced by the stronger donor pyridine (6-fold excess). Complex **1b** is the resulting product; no pyridine adduct could be detected.

As reported earlier, the metathetical reaction of **2a** in the presence of CH_3CN also resulted in the formation of a CH_3CN free cationic complex, but its structure remained uncertain: e.g., a monomeric pseudotetrahedral or dimeric square-planar structure.[7] On the basis of the similar ^1H NMR data obtained for this complex and for **2a′**, the reactivity observed for **1a**, and the molecular structure resolved for **1b**, we propose a dimeric structure of the composition $[Pd_2(CH_3)_2\{(mim)_2CHCH_2PPh_2\}_2](BF_4)_2$ for this complex.

The observations made for $[PdX(CH_3)\{N\wedge D\wedge N\}]$ (X = Cl, CH_3CN) amply demonstrate the effect of changing one of the donor moieties in the closely related ligand systems on their coordination behavior. In **3a**,**b** the (expected) preference of $(mim)_2CHCH_2C(O)Bu$-*t* to bind in an σ^2-N∧N fashion is found and interaction of the hard oxygen donor with the soft palladium center is only weak at best. The reluctance of the carbonyl donor to coordinate in these complexes is also reflected in the inability of **3a** to give a well-defined product upon halide abstraction in the absence of coordinating solvents.

In contrast, in **1a** and **2a** the ligand systems display a strong tendency to coordinate in a tridentate fashion, leading to the formation of dimeric complexes and/or fluxional behavior, respectively. Even when **1a** and **2a** are reacted under metathetical conditions in the presence of coordinating solvents, it is the third imidazole donor which occupies the vacated coordination site. These results demonstrate the strong σ-donor capacity

Scheme 3. Carbonylation of 1a−3a



of imidazole, and it is interesting to compare $[PdCl(CH_3)\{(mim)_3COCH_3\}]$ with $[PdX(CH_3)\{(mim)_2(py)CH\}]$ (X = I, CH_3),[9b] since both ligands are structurally very similar but differ in the third heterocycle linked to the central carbon. Whereas in the former case a dimeric isomer with σ^3-N∧N∧N coordination has been identified, σ^2-N∧N coordination via the two imidazole rings has been established in the latter. Neither fluxional behavior nor dimerization, involving the third pyridine donor, has been reported. The dimeric structures of **1a′**, **1b**, **2a′**, and **2b** can be partly explained by the arrangement of the donor moieties in the ligands, which does not allow the formation of square-planar $[Pd(CH_3)\{\sigma^3\text{-}N\wedge D\wedge N\}]X$ complexes as observed for other tridentate ligands.[11] Thus, the geometrical constraint and the strong σ-donor capacity of the imidazole ring leads to the formation of dimeric complexes. Interestingly, although these ligands are suitable for facial tripodal coordination, they do not impose tetrahedral four-coordination onto the palladium center in the ionic complexes **1b** and **2b**. However, facial tripodal coordination involving five-coordinated isomers is likely to occur in solutions of **2a** at low temperature. The fact that the $(mim)_2CHCH_2PPh_2$ ligand in **2a** displays fluxional behavior at room temperature and leads to presumably five-coordinated species at low temperature, whereas the $(mim)_3COCH_3$ ligand in **1a** coordinates in a (static) σ^2-fashion to one Pd center, can be explained by the relative flexibility of the former.

CO Insertion Reactions. Quantitative formation of the acyl complexes $[PdCl\{C(O)CH_3\}\{N\wedge D\wedge N\}]$ (**1d**, $\{N\wedge D\wedge N\}=(mim)_3COCH_3$; **2c**, $\{N\wedge D\wedge N\}=(mim)_2CHCH_2PPh_2$; **3c**, $\{N\wedge D\wedge N\} = (mim)_2CHCH_2C(O)Bu$-*t*) was achieved at 20 °C within a few minutes by bubbling CO into $CDCl_3$ solutions of the respective precursors in an NMR tube (Scheme 3). In the ^1H NMR spectrum, the $Pd-C(O)CH_3$ resonances were found at 2.0−2.6 ppm, which is the same as typically observed for related acylpalladium(II) complexes.[4a,c,j,11c] For **3a**, carbonylation was only observed for the major isomer, whereas the minor isomer **3a′** remained unaffected.

The insertion products **1d** and **3c** are not very stable in solution and decompose after a few hours at room temperature. The complex **2c** does not show any signs of decomposition in solution after 1 day at room temperature. It was isolated in almost quantitative yield and characterized by elemental analysis, IR, and MS. Surprisingly, the dimeric complex **1a′** did not react with CO, even with prolonged reaction times, and decomposition occurred even at −20 °C. Vrieze et al. have made a similar observation for the structurally related com-

Table 3. Heck Coupling Reactions[a]

entry	catalyst	amt (%)	time (h)	conversn[b] (%)	TON
1	**1a**	1.0×10^{-3}	24	92	92 000
2	**1b**[c]	1.0×10^{-3}	24	100	>100 000
3	**1b**	1.0×10^{-3}	7	76	75 960
4	**1b**	3.3×10^{-4}	24	82	273 600
5	**1b**	1.0×10^{-4}	72	81	808 000
6	**2a**	1.0×10^{-3}	24	31	30 940
7	**2a**	1.0×10^{-3}	72	83	82 572
8	**3a**	1.0×10^{-3}	24	59	59 389
9	**3a**	1.0×10^{-3}	48	84	84 177
10	**3b**	1.0×10^{-3}	24	73	73 400
11	**3b**	1.0×10^{-3}	14	71	70 700
12	*d*	1.0×10^{-3}	24	46	46 280
13	**1b**[e]	9.4×10^{-2}	24	31	334

[a] Coupling partner 4-bromoacetophenone/butyl acrylate; conditions for catalysis given in Experimental Section. [b] Conversions determined by GC. [c] Calculated per [Pd]. [d] Catalyst [PdCl(CH_3)-{$(mim)_2C{=}NPh$}].[7] [e] Coupling partners 4-chlorobenzaldehyde/butyl acrylate.

plexes [PdCl(CH_3){σ^2-*N*,*N*′-*i*-Pr-DIP}] and [Pd(CH_3){σ^3-*N*,*N*′,*N*″-*i*-Pr-DIP}]$^+$OTf$^-$.[11a] Whereas the former readily gives the respective acyl complex, the latter does not react with CO.

Despite the ability to rapidly insert CO, none of the methylpalladium complexes **1**−**3** catalyzed the copolymerization of ethylene and CO.

Heck Reaction. For comparison to the earlier reported methylpalladium complexes [PdCl(CH_3){N∧N}] containing bridged bis(imidazole) ligands (N∧N = $(mim)_2CO$, $(Bzmim)_2CO$, $(mim)_2CH_2$)[7] and in order to further establish the catalytic behavior of this class of palladium(II) complexes, we investigated the performance of **1**−**3** in the Heck reaction, using the coupling of 4′-bromoacetophenone with *n*-butyl acrylate as a test reaction. All of the complexes studied are active catalysts in this reaction and displayed good conversions at low catalyst concentrations ($\leq 1.0 \times 10^{-3}$ mol %). Turnover numbers and the conversions quoted were those obtained when the reactions were terminated after set times and do not necessarily represent maximum values, nor do they indicate that the catalyst had ceased to operate. The results of catalytic testing are summarized in Table 3.

We had observed earlier that the presence of electronegative groups on the ligand backbone of [PdCl(CH_3){N∧N}] significantly improved the catalytic activities of these complexes in the Heck reaction.[7] Consistent with this observation, we note that the activity of the related palladium complex [PdCl(CH_3)-{$(mim)_2C{=}NPh$}], containing the less electronegative imino function on the ligand backbone, is lower compared to the carbonyl derivative (entry 12). The interpretation of our previous results is further supported by the observations made for the new complexes **1**−**3** bearing tridentate ligands. Among these complexes **1a**,**b**, containing the electronegative OCH_3 group, display the highest activity (entries 1−5); the activity of **1a** is similar to that observed for [PdCl(CH_3){$(mim)_2$-CO}]. Interestingly, complexes **2** and **3**, although lacking a electronegative group in the bridge, are also active catalysts, whereas [PdCl(CH_3){$(mim)_2CH_2$}] had been found to be inactive. Thus, the third donor function present in these complexes appears to improve the catalyst performance. Analysis of the product from the reactions showed selective formation of *n*-butyl (*E*)-4-acetylcinnamate, with the *Z* isomer being present in less than 6% amounts. In general, the new complexes give catalysts with very good long-term stability (entries 3−5, 6, and 7). Comparisons of entries 1−5 and 9−11 demonstrate that the application of a cationic derivative of a given complex can have a positive effect on the overall activity of the catalyst.

An excellent TON of 808 000 with good conversion in a relatively short time was achieved with the dimeric complex **1b** at very low catalyst concentration. The activity of this complex is similar to that found for the donor-functionalized carbene complexes [PdCl(CH_3)-{3-methyl-1-(methylacetyl)imidazolin-2-ylidene)$_2$] and [PdCl(CH_3)(3-methyl-1-picolylimidazolin-2-ylidene)$_2$·0.7AgI], which gave one of the highest TONs so far reported for the Heck reaction.[14c] In addition these results clearly demonstrate that nitrogen-chelated Pd complexes, which have received surprisingly little attention in the Heck reaction,[7,21] can serve as highly active catalysts in this reaction. The high activity of **1b** prompted us to test this complex in the Heck coupling of 4-chlorobenzaldehyde with *n*-butyl acrylate to afford *n*-butyl (*E*)-4-formylcinnamate (entry 13) in the presence of tetrapropylammonium bromide as cocatalyst. Moderate conversion (31.5%) was obtained.

Concluding Remarks

New methylpalladium(II) complexes containing donor-functionalized imidazole ligands and their cationic counterparts have been synthesized and studied in detail. The potentially tridentate ligands present in the complexes give rise to a rich and interesting coordination chemistry. Depending on the third donor moiety linked to the bridging carbon of the bis(imidazole) framework, bidentate coordination, fluxional behavior, and/or dimerization involving σ^3-N∧D∧N coordination are observed in these complexes. The formation of dimeric complexes in which one of the donor moieties of the tridentate ligand system is bridging to a neighboring Pd center was confirmed by resolving X-ray structures for two of the compounds.

The novel nitrogen-chelated methylpalladium complexes also give active catalysts for the Heck reaction, and TONs as high as ∼800 000 could be achieved. More generally, this approach provides a new entry to the development of non-phosphine-based late-metal homogeneous catalysis.

Experimental Section

General Comments. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox (Innovative Technology Inc.). All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. Complex **2a** has been reported previously,[7] and its NMR data are given here for convenience. Elemental analysis, MS, and GC-MS were carried out by the Central Science Laboratory (CSL), University of Tasmania.

General Procedure for the Preparation of Neutral Complexes. One equivalent of the ligand was added to a solution of [PdCl(CH_3)(COD)] in CH_2Cl_2, and the reaction mixture was stirred for 1−2 h (0.5 h for **1a**). The solution was filtered through a small bed of Celite and the solvent removed in vacuo. The crude product was washed with Et_2O (3 × ca. 5 mL) and dried under vacuum. Yields for all complexes were >90%.

[PdCl(CH$_3$){σ^2(*N,N*)-tris(*N*-methylimidazol-2-yl)methoxymethane}] (1a). Anal. Calcd for $C_{15}H_{21}N_6OClPd$: C, 40.64; H, 4.78; N, 18.96. Found: C, 40.43; H, 4.59; N, 18.94. MS (LSIMS): *m/z* 407, [M − Cl]$^+$ (34%); 392 [M − Cl, CH$_3$]$^+$ (71%); 255 [Ligand − OCH$_3$]$^+$ (100%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.96 (d, J = 1.4 Hz, 1H, Imd *H*), 7.30 (d, J = 1.6 Hz, 1H, Imd *H*), 7.06 (s, 1H, Imd *H*), 6.99 (d, J = 1.6 Hz, 1H, Imd *H*), 6.92 (d, J = 1.4 Hz, 1H, Imd *H*), 6.84 (s, 1H, Imd *H*), 3.67 (s, 3H, NC*H*$_3$), 3.54 (s, 3H, NC*H*$_3$), 3.38 (s, 3H, NC*H*$_3$), 3.06 (s, 3H, OC*H*$_3$), 0.91 (s, 3H, Pd(*CH*$_3$)).

[Pd(CH$_3$){σ^3(*N,N,N*)-tris(*N*-methylimidazol-2-yl)methoxymethane}]$_2$[Cl]$_2$ (1a′). This complex was prepared in a manner analogous to that described for **1a**, using 42.8 mg (0.161 mmol) of [PdCl(CH$_3$)(COD)] and 46.2 mg (0.161 mmol) of (mim)COCH$_3$ in methanol. The resulting slightly yellow solid was washed with CH_2Cl_2 (3 × 1.5 mL) and dried under vacuum. Yield: 65 mg (92%).

Alternatively, **1a′** can be prepared by dissolving **1a** (7 mg) in CH_3OH (1.5 mL). After the mixture was stirred for ca. 3 h at room temperature, the solvent was removed in vacuo and the remaining solid washed with Et_2O (2 × 1.5 mL). Drying under vacuum afforded an off-white solid. Yield: 7 mg (100%).

Anal. Calcd for $C_{30}H_{42}N_{12}O_2Cl_2Pd_2{\cdot}CH_2Cl_2$: C, 38.32; H, 4.57; N, 17.31. Found: C, 38.68; H, 4.60; N, 17.69. MS (electrospray): *m/z* 849, [M − Cl]$^+$ (14%); 814, [M − 2Cl]$^{2+}$ (100%). ^{1}H NMR (400 MHz, CD_3OD): δ 7.65 (d, J = 1.6 Hz, 1H, Imd *H*), 7.53 (d, J = 1.6 Hz, 1H, Imd *H*), 7.33 (d, J = 1.6 Hz, 1H, Imd *H*), 7.13 (d, J = 1.6 Hz, 1H, Imd *H*), 6.99 (d, J = 1.3 Hz, 1H, Imd *H*), 5.59 (d, J = 1.3 Hz, 1H, Imd *H*), 4.37 (s, 3H, NC*H*$_3$), 3.62 (s, 3H, NC*H*$_3$), 3.59 (s, 3H, NC*H*$_3$), 2.77 (s, 3H, OC*H*$_3$), −0.28 (s, 3H, Pd(C*H*$_3$)). ^{13}C NMR (400 MHz, CD_3OD): δ 142.7 (ring 3), 142.2 (ring 2), 140.0 (ring 1) (*C*═N); 132.0 (ring 2), 127.2 (ring 3), 124.5 (ring 1) (*C4*); 128.0 (ring 2), 127.9 (ring 1), 126.8 (ring 3) (*C5*); 81.3 (*C*OCH$_3$); 52.8 (CO*C*H$_3$); 39.9 (ring 2), 36.0 (ring 3), 35.5 (ring 1) (N−*C*H$_3$); −3.1 (Pd−*C*H$_3$).

[PdCl(CH$_3$){σ^2(*N,P*)-2-[2-(diphenylphosphino)-1-(1-methylimidazol-2-yl)ethyl]-1-methylimidazole}] (2a).[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s (br), 2H, phenyl) 7.57 (s (br, 2H, phenyl), 7.4 (s (br), 7H, 6 phenyl + 1 Imd *H*), 6.88 (s (br), 2H, Im*H*), 6.42 (s (br), 1H, Im *H*), 5.46 (m (br), 1H, *CH*), 3.60 (m (br), 1H, C*H*$_2$), 3.28 (s (br), 3H, N−C*H*$_3$), 3.16 (s (br), 3H, N−C*H*$_3$), 2.95 (m (br), 1H, C*H*$_2$), 0.61 (d (br), 3H, $^3J_{P-H}$ = 3.2 Hz, Pd-C*H*$_3$). ^{31}P NMR (400 MHz, CD_2Cl_2): δ 29.4 (s (br).

[Pd(CH$_3$){σ^3(*N,N,P*)-2-[2-(diphenylphosphino)-1-(1-methylimidazol-2-yl)ethyl]-1-methylimidazole}]$_2$[Cl]$_2$ (2a′). ^{1}H NMR (200 MHz, CD_3OD): δ 7.58 (m, 4H, phenyl), 7.48 (m, 7H, 6 phenyl + 1 Imd *H*), 7.0 (d, J = 1.5 Hz, 1H, Imd *H*), 4.63 (m, 1H, C*H*), 3.89 (s, 3H, NC*H*$_3$), 3.24 (m, 2H, C*H*$_2$), 3.19 (s, 3H, NC*H*$_3$), −0.35 (d, ^3J = 3.3 Hz, 3H, Pd−C*H*$_3$). ^{31}P NMR (400 MHz, CD_3OD): δ 31.4 ppm.

[PdCl(CH$_3$){σ^2(*N,N*)-4,4-dimethyl-1,1-bis(1-methylimidazol-2-yl)pentan-3-one}] (3a). Anal. Calcd for $C_{16}H_{25}N_4OClPd$: C, 44.55; H, 5.85; N, 12.99. Found: C, 44.53; H, 5.88; N, 12.74. MS (LSIMS): *m/z* 825, [2M − Cl]$^+$ (19%); 669, [(Ligand)$_2$Pd(CH$_3$)]$^+$ (19%); 395, [M − Cl]$^+$ (17%); 380, [M − CH$_3$ −Cl]$^+$ (80%); 295, [M − Cl − CH$_3$ − *t*-BuCO]$^+$ (71%); 275, [LigandH]$^+$ (90%); 189, [Ligand − *t*-BuCO]$^+$ (100%). ^{1}H NMR (400 MHz, $CDCl_3$; two isomers in a ca. 3.5:1 ratio (A:B)): δ 7.87 (d, J = 1.6 Hz, 1H, Imd H_B), 7.37 (d, J = 1.2 Hz, 1H, Imd H_A), 7.31 (d, J = 1.6 Hz, 1H, Imd H_B), 7.03 (d, J = 1.6 Hz, 1H, Imd H_A), 6.84 (d, J = 1.6 Hz, 1H, Imd H_B), 6.77 (d, J = 1.2 Hz, 1H, Imd H_A), 6.74 (d, J = 1.6 Hz, 1H, Imd H_A), 6.73 (d, J = 1.6 Hz, 1H, Imd H_B), 4.80 (d/d, ^3J = 9/5 Hz, 1H, CH_B), 4.75 (d/d, ^3J = 9/5.2 Hz, 1H, CH_A), 4.41 (d/d, ^2J = 17.6 Hz, ^3J = 9 Hz, 1H, C(H_A)$_2$), 4.22 (d/d, ^2J = 17.6 Hz, ^3J = 9 Hz, 1H, C(H_B)$_2$), 3.87 (s, 3H, NC(H_B)$_3$), 3.83 (s, 3H, NC(H_A)$_3$), 3.74 (s, 3H, NC(H_B)$_3$), 3.71 (s, 3H, NC(H_A)$_3$), 3.68 (d/d, ^2J = 17.6 Hz, ^3J = 5.2 Hz, 1H, C(H_B)$_2$), 3.34 (d/d, ^2J = 17.6 Hz, ^3J = 5.2 Hz, 1H, C(H_A)$_2$), 1.11 (s, 3H, Pd(CH_3)$_B$), 1.10 (s, 9H, t-Bu), 1.05 (s, 9H, *t*-Bu$_A$), 0.85 (s, 9H, Pd(CH_3)$_A$). IR (KBr): 1703 (ν_{CO}).

[Pd(CH$_3$){σ^3(*N,N,N*)-tris(1-methylimidazol-2-yl)methoxymethane}]$_2$[BF$_4$]$_2$ (1b). **1a** (84 mg, 0.19 mmol) and $AgBF_4$ (36.9 mg, 0.19 mmol) were mixed as solids, and a 1:1 mixture of CH_3CN and CH_2Cl_2 (5 mL) was added with stirring. A white precipitate (AgCl) formed. The mixture was stirred for 1 h, after which time it was filtered through a small bed of Celite. The solvent was removed in vacuo, and the residue was washed with Et_2O (2 × 4 mL) and dried in vacuo to afford an off-white solid. Yield: 89.3 mg (95%). Anal. Calcd for $C_{30}H_{42}N_{12}B_2F_8Pd_2$: C, 36.42; H, 4.29; N, 16.99. Found: C, 35.96; H, 4.56; N, 16.84. MS (electrospray): *m/z* 901, [M − BF$_4$]$^+$ (38%); 814, [M − 2BF$_4$]$^{2+}$ (100%). ^{1}H NMR (200 MHz, CD_3CN): δ 7.67 (d, J = 1.6 Hz, 1H, Imd *H*), 7.50 (d, J = 1.6 Hz, 1H, Imd *H*), 7.28 (d, J = 1.6 Hz, 1H, Imd *H*), 7.18 (d, J = 1.6 Hz, 1H, Imd *H*), 6.93 (d, J = 1.4 Hz, 1H, Imd *H*), 5.58 (d, J = 1.4 Hz, 1H, Imd *H*), 4.38 (s, 3H, NC*H*$_3$), 3.62 (s, 3H, NC*H*$_3$), 3.61 (s, 3H, NC*H*$_3$), 2.82 (s, 3H, OC*H*$_3$), −0.24 (s, 3H, Pd(C*H*$_3$)).

[Pd(CH$_3$){σ^2(*N,N*)-4,4-dimethyl-1,1-bis(1-methylimidazol-2-yl)pentan-3-one}(CH$_3$CN)][BF$_4$] (3b). This complex was prepared in a manner analogous to that described for **1b**, using 56.6 mg (0.108 mmol) of **3a** and 21 mg (0.108 mmol) of $AgBF_4$. A light yellow solid was obtained. Yield: 54 mg (95%). Anal. Calcd for $C_{18}H_{28}N_5OBF_4Pd$: C, 41.28; H, 5.40; N, 13.38. Found: C, 38.95; H, 5.89; N, 12.23. MS (LSIMS): *m/z* 901, [M − BF$_4$]$^+$ (19%); 395, [(Ligand)Pd(CH$_3$)]$^+$ (39%); 380, [(Ligand)-Pd]$^+$ (100%); 361, [(Ligand)Pd − OCH$_3$]$^+$ (52%); 275, [Ligand + H]$^+$ (94%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.95 (s, 1H, Imd *H*), 6.93 (s, 1H, Imd *H*), 6.88 (s, 1H, Imd *H*), 6.85 (s, 1H, Imd *H*), 4.86 (d/d, ^3J = 8.3/5.5 Hz, 1H, C*H*), 4.12 (d/d, ^2J = 18 Hz, ^3J = 8.3 Hz, 1H, CH$_2$), 3.93 (s, 3H, NC*H*$_3$), 3.83 (s, 3H, NC*H*$_3$), 3.42 (d/d, ^2J = 18 Hz, ^3J = 5.5 Hz, 1H, CH$_2$), 2.47 (s, 3 H, *CH*$_3$CN), 1.08 (s, 9H, *t*-Bu), 0.79 (s, 3H, Pd(C*H*$_3$)). IR (KBr): 1702 (ν_{CO}).

X-ray Data Collection and Structure Refinement for Complexes 1b,c. Crystals of **1b** suitable for X-ray diffraction have been obtained by cooling a CD_3OD solution of the crude reaction product at −20 °C. Crystals of **1c** suitable for X-ray diffraction formed when a $CDCl_3$ solution of **1a** was allowed to stand for 4 days at room temperature.

Full spheres of CCD area-detector diffractometer data were measured (T ca. 153 K; ω-scans; monochromatic Mo Kα radiation, λ = 0.710 7$_3$ Å; Bruker AXS instrument), yielding $N_{(total)}$ reflections, merging to N_{unique} (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software). N_o ($F > 4\sigma(F)$) were used in the full-matrix least-squares refinements, refining non-hydrogen atom anisotropic displacement parameter forms and (x, y, z, U_{iso})$_H$ constrained at estimated values. Conventional residuals R and R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted at convergence. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[22] Pertinent results are given below and in Figure 6 and Table 2, individual difficulties, variations in procedure, and abnormalities being described as "variata". In the figures, 50% amplitude displacement envelopes are shown for the non-hydrogen atoms, hydrogen atoms as shown having arbitrary radii of 0.1 Å.

[{LPd(Me/Cl)}$_2$]Cl$_2$·4CHCl$_3$ (1c): $C_{33}H_{43}Cl_{15}N_{12}O_2Pd_2$, M_r = 1384.4, monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), a = 14.3524(8) Å, b = 13.5720(8) Å, c = 26.310(2) Å, β = 91.765(1)°, V = 5123 Å^3, D_c(Z = 4 dimers) = 1.79$_5$ g cm^{-3}, μ_{Mo} 15.3 cm^{-1}, specimen 0.14 × 0.19 × 0.05 mm, "T"$_{min,max}$ = 0.76, 0.89, $2\theta_{max}$ = 75°, N_t = 49 468, N = 12 932 (R_{int} = 0.053), N_o = 8344, R = 0.049, R_w = 0.052, $|\Delta\rho_{max}|$ = 1.5(1) e Å^{-3}. Variata: as modeled in space group $C2/c$, the halves of the dimer are related by a crystallographic 2-axis, implying scrambling of the chloride and methyl entities between the two sites at the two palladium atoms, attempted refinement

(22) *The Xtal 3.7 System*; Hall, S. R., du Boulay, D. J., Olthof-Hazekamp, R., Eds.; University of Western Australia: Nedlands, WA, Australia, 2000.

of an ordered model in lower symmetry being (inherently) unfruitful. One of the chloroform molecules was modeled as rotationally disordered about the C−H bond, the chlorine atom being disposed over two sets of sites set at equal occupancy after trial refinement.

"(5/6[{LPdMe}$_2$](BF$_4$)$_2$·(1/6)[{LPd(Me/OH$_2$)}$_2$](BF$_4$)$_3$·(31/12)MeOH" (1b): $C_{32.417}H_{52.167}B_{2.167}F_{8.667}N_{12}O_{4.75}Pd_2$, M_r = 1086.9, rhombohedral, space group $R\bar{3}c$ (D^6_{3d}, No. 167), a = 25.829(2) Å, c = 69.505(4) Å, V = 40157 Å^3 (hexagonal setting). $D_c(Z = 36) = 1.61_6$ g cm^{-3}, μ_{Mo} 8.9 cm^{-1}, specimen 0.35 × 0.30 × 0.24 mm, "T"$_{min,max}$ = 0.51, 0.80, $2\theta_{max}$ = 58°, N_t = 257 680, N = 12 035 (R_{int} = 0.066), N_o = 8609, R = 0.054, R_w = 0.072, $|\Delta\rho_{max}|$ = 1.61(3) e Å^{-3}. Variata: extensive disorder was found among the "solvent" (S) component of the structure, modeled in terms of methanol molecules with weightings refined to values close to and constrained at 0.25 (S02), 0.5 (S03,5), or 0.33 (S04; symmetry constraint). The oxygen component was assigned tentatively on the basis of refinement behavior, and the hydrogen stoichiometry was not defined. Beyond possible ambiguity here, the anion component appears well-defined, albeit with anion 2 disordered about a general position (pairs of atom components refining to and constrained at 0.5 site occupancy) and anion 3 with a pair of fluorine components disposed about the boron, which is located on a site of $\bar{3}$ symmetry, one fluorine on the axis and one off. Displacement amplitudes are high throughout the single independent binuclear cation, with a substantial difference map residue (Pd(1′)) close to Pd(1) (distant 0.511(4) Å), ultimately modeled as a disordered pair with populations totaling unity and with the occupancy of the major fragment refined to $^5/_6$, at which it was constrained, with that of Pd(1′) complementary ($^1/_6$). The high displacement parameters, disordered palladium, and charge balance are rationalized in terms of occupancy of the unidentate site at Pd(1′) by a water molecule rather than a methyl group. Within the extended ligand atom envelopes, disordered components were not resolved. Analysis of residual crystals showed no silver content.

In Situ CO Insertion Experiments. In a typical experiment the complex was placed in a nitrogen flushed NMR tube and dissolved in $CDCl_3$. CO was bubbled into the solution at ambient pressure for ca. 1 min and the spectrum recorded.

[PdCl{C(O)CH$_3$}{σ^2(*N*,*P*)-2-[2-(diphenylphosphino)-1-(1-methylimidazol-2-yl)ethyl]-1-methylimidazole}] (2c). In a preparative-scale reaction, **2a** (10 mg, 0.019 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and CO was bubbled into the solution for ca. 1 min. Stirring at room temperature was continued for 1 h, after which time the product was precipitated from the solution by the addition of petroleum ether (40/60) and cooling to −20 °C. The solvents were decanted, and the off-white solid was dried under vacuum. Yield: 10.4 mg (97%). Anal. Calcd for $C_{24}H_{26}N_4OClPPd$: C, 51.53; H, 4.69; N, 10.02. Found: C, 51.77; H, 4.55; N, 10.13. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (m (br), 4H, phenyl), 7.45 (m (br), 8H, phenyl + Imd *H*), 6.69 (s (br), 2H, Imd *H*), 4.52 (m (br), 1H, C*H*), 3.14 (m (br), 2H, CH_2), 3.02 (s, NCH_3), 2.04 (d, ^4J = 1.3 Hz, 3H, Pd−C(O)CH_3). ^{31}P NMR (400 MHz, $CDCl_3$): δ 10.4 ppm. IR (KBr): 1681, 1654 (ν_{CO}).

[PdCl{C(O)CH$_3$}{σ^2(*N*,*N*)-tris(1-methylimidazol-2-yl)-methoxymethane}] (1d). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.74 (s (br), 1H, Imd *H*), 7.06 (s (br), 1H, Imd *H*), 6.96 (s (br), 1H, Imd *H*), 6.91 (s (br), 2H, Imd *H*), 6.84 (s (br), 1H, Imd *H*), 3.65 (s, 3H, NCH_3), 3.54 (s, 3H, NCH_3), *3*.36 (s, 3H, NCH_3), 3.08 (s, 3H, OCH_3), 2.63 (s, 3H, Pd−C(O)CH_3).

[PdCl{C(O)CH$_3$}{σ^2(*N*,*N*)-4,4-dimethyl-1,1-bis(1-methylimidazol-2-yl)pentan-3-one}] (3c). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18 (s (br), 1H, Imd *H*), 7.07 (s (br), 1H, Imd *H*), 6.78 (s (br), 1H, Imd *H*), 6.76 (s (br), 2H, Imd *H*), 4.72 (m, 1H, C*H*), 4.35 (m, 1H, CH_2), *3*.85 (s, 3H, NCH_3), 3.73 (s, 3H, NCH_3), 3.40 (m, 1H, CH_2), 2.59 (s, 3H, Pd−C(O)CH_3).

Catalytic Heck Coupling of *n*-Butyl Acrylate and 4-Bromoacetophenone. In a typical run, a 100 mL Schlenk flask was charged with 4-bromoacetophenone (4.98 g, 25 mmol) and anhydrous sodium acetate (2.29 g, 27.92 mmol), and degassed by successive vacuum−nitrogen cycles. *N*,*N*-Dimethylacetamide (25 mL) and *n*-butyl acrylate (5 mL, 27.5 mmol) were then added. The complex (2.5×10^{-5} mmol) was dissolved in *N*,*N*-dimethylacetamide (10 mL) and 0.1 mL of this solution injected into the reaction mixture, which was then heated to 120 °C. After a set time, the mixture was cooled and bis(ethylene glycol) butyl ether (500 μL) added. A sample of the solution (500 μL) was taken, injected into a sample vial containing 5% HCl (5 mL), and extracted with 2.5 mL of CH_2Cl_2. The CH_2Cl_2 extracts were analyzed by gas chromatography.

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Supporting Information Available: An illustration (Figure 7 and 8) of sections of the low-temperature NMR study, a discussion of the data, and complete listings of crystallographic data for compounds **1b**,**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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