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Competition between Carbene and Pseudo η^3-Allyl Bonding Modes in a Palladium(II) Complex of a Functionalized Bis(imidazolium) Ligand

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The reaction of the functionalized bis(imidazolium) salt 1,3-bis(1-methylimidazolium-3-yl)propan-2-one diiodide with palladium(II) acetate gave as the sole product the unexpected complex *cis*-$I_2Pd[(CHR)_2C(O)]$ (R = 1-methylimidazolium-3-yl). Single-crystal X-ray crystallography and infrared spectroscopy revealed a highly puckered palladacyclobutan-3-one ring with an η^3-allylic (η^3-oxodimethylenemethane) bonding disposition of Pd(II) to the $[C-C(O)-C]^{2-}$ fragment. No imidazolin-2-ylidene formation was evident. The neutral complex may be viewed as zwitterionic, with the negatively charged ligands at the Pd(II) center balanced by the positive charges on the pendant imidazolium groups.

Introduction

A new wave of interest in catalytic C−C coupling reactions has been driven by the discovery that nucleophilic heterocyclic carbenes (NHC)[1] can give highly active, stable catalyst systems for a variety of these useful reactions when coordinated to transition metals such as palladium[2,3] and nickel.[4,5] Recent advances in ligand design have included substitution of one[6−9] or both[8,10,11] of the N-substituents on the imidazolin-2-ylidene ring with functional groups capable of coordination to transition-metal centers. The presence of the electronegative, nucleophilic, functional groups desirable for hemilabile coordination to transition metals has been reported to complicate the isolation of the free carbene[6] and to interfere with other routes to NHC complexes that utilize strong, somewhat indiscriminate, bases. The sodium hydride in liquid ammonia route to free heterocyclic carbenes has been reported as being more appropriate for functionalized NHCs,[8] although the authors surmised that this method failed for the 1,1′-(methylene)-3,3′-dimethylimidazolium ion due to deprotonation of the methylene bridge situated α to two heteroatoms. A recent report by Danopoulos et al.[7] showed that 3-R-1-(2-pyridyl)imidazolium bromide (where R is the bulky Bu^t or mesityl group) could be deprotonated using lithium diisopropylamide ($LiNPr_2^i$) in tetrahydrofuran at low temperature, and the free carbene was subsequently trapped with PdBrMe(1,5-cyclooctadiene). An earlier report by McGuinness and Cavell[6] on the synthesis of complexes employing similarly functionalized carbene ligands found that transmetalation from the Ag(I) carbene, prepared using the milder Ag_2O as base,[12] to Pd(II) precursor complexes was necessary.

Most of the donor-functionalized NHC complexes thus far reported have shown excellent catalytic activities under the basic conditions of the Heck reaction.[6,7] However, their stability when exposed to stronger bases such as triethylamine (NEt_3) used in the addition of arylamines to olefins (the “amination reaction”) has been variably reported as good[7] or poor,[6] depending on the exact structure of the catalyst precursor.

Results and Discussion

The reaction of the imidazolium salt **1** with 1 equiv of $Pd(OAc)_2$ in dimethyl sulfoxide (DMSO) (Scheme 1) gave exclusively the palladacyclobutan-3-one **2**, nominally formed by coordination of the neutral zwitterionic $[(CHR)_2CO]$ (R = 1-methylimidazolium-3-yl) fragment to PdI_2. Complex **2** could also be obtained by reaction of imidazolium salt **1** with Ag_2O and $PdCl_2(MeCN)_2$,

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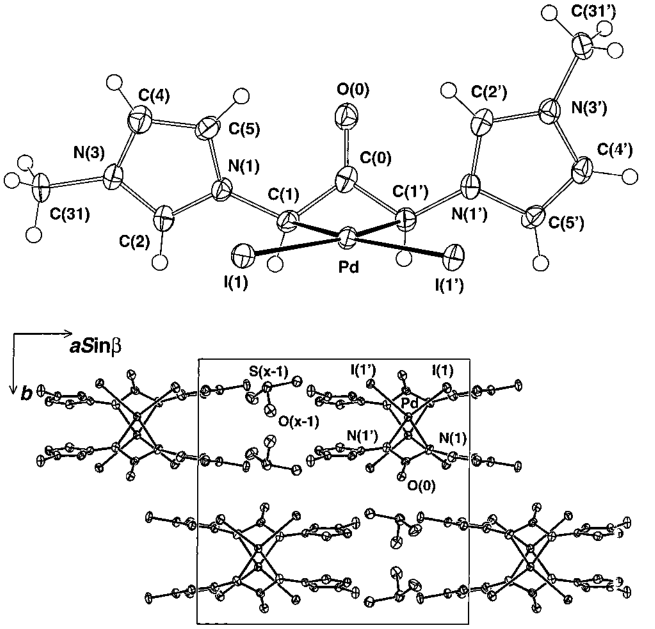


Figure 1. (a, top) Molecular projection of complex **2** oblique to the coordination plane, showing the inclination of it to the C_3O moiety. 50% displacement ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. The atom labeling scheme is also shown. (b, bottom) Unit cell contents of **2**·DMSO projected down *c*, showing the molecular stacking up that axis.

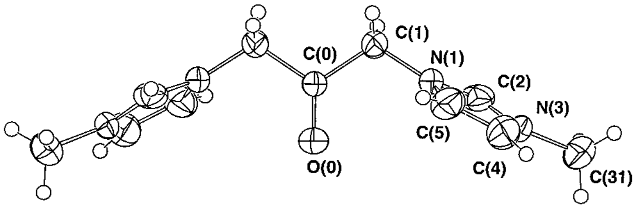


Figure 2. The ligand cation of **1**, projected normal to the central C_3O plane and the 2-fold axis, showing the atom-labeling scheme.

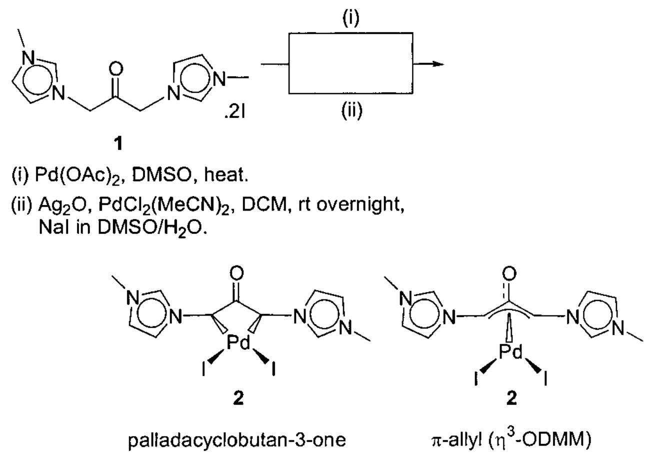
followed by treatment with sodium iodide in aqueous DMSO (Scheme 1). In the solid state **2** is stable toward brief exposures to air and moisture and decomposes slowly in solutions exposed to humid air over a period of months at room temperature.

Low-temperature single-crystal X-ray structure determinations were carried out for both complex **2** and the precursor imidazolium salt **1**. The results of these determinations are presented below and in Figures 1 and 2, respectively, with selected parameters collected in Tables 1 and 2.

Figure 1b shows the crystal packing of the DMSO solvate of **2** (**2**·DMSO); one formula unit devoid of any crystallographic symmetry comprises the asymmetric unit of the structure. The molecules of **2** pack in stacks up *c*, successive members within each stack generated by the crystallographic glide plane (x, $^1/_2 - y$, $z - ^1/_2$) (i) and separated by ca. $c/2$ (4.75 Å). The most notable contacts between successive molecules of **2** are $I\cdots H(1^i) = 3.0_5$ Å and $I'\cdots H(5'^i) = 3.3_0$ Å (estimated). The DMSO oxygens contact hydrogens at the periphery of the stacks ($O(1)\cdots H(4')$ ($1 + x$, $^1/_2 - y$, $z - ^1/_2$) at 2.3_6 Å (estimated)).

The $[I_2Pd(C_3O)]^{2-}$ molecular core of **2** may be described in terms of two planes: (a) the $C(1,1')I_2$ array, which does not deviate significantly from planarity, with the palladium atom closely coplanar and (b) the C_3O array, which is somewhat less rigorously planar, with the central carbon showing a small but significant pyramidal deviation away from the palladium atom (χ^2 C_3O 239; δC(1,1′,0)O; Pd −0.024(7) (×2), 0.083(6); −0.017(5); −1.566(5) Å). This deviation is common to previously described systems[13,14] and may also be viewed as a distortion of O(0) out of the plane of C(0,1,1′) toward Pd.

Scheme 1. Preparation of 2, Showing Possible Pd–Ligand Bonding Interactions



The hydrogen atoms at C(1,1′) lie cis to the C_3O plane, so that the array about Pd is a good approximation to *m* symmetry, the mirror plane containing Pd, C(0), and O(0). This symmetry carries through with diminishing rigor to the 1-methylimidazolium-3-yl (MeIm) substituents, with the C_3N_2 planes making dihedral angles to the C_3O and coordination planes which differ by nearly 10° within each pair (MeIm(1,2)/C_3O 42.5(2), 32.7(2)°; MeIm(1,2)/$C(1,1')I_2$ 76.0(2), 85.6(2)°). More significantly, the symmetry is broken by the rotation of the MeIm rings by nearly 180° about the C–N (pendant) bond relative to each other. These differences are presumably consequent on inter- rather than intramolecular interactions, since the exocyclic angles about the pendant nitrogen atoms are in a narrow range (124.7(5)–126.2(5)°); $H(5,2')\cdots O(0)$ distances are 2.6_5, 2.4_2 Å (estimated). The single peak at δ 9.42 observed for the imidazolium C_2–H protons in the ^1H NMR of **2** suggests that in solution the MeIm rings are equivalent on the NMR time scale, resulting from their being symmetrically oriented or able to undergo relatively unhindered rotation about the pendant C–N bond.

Several palladacyclobutan-3-one systems similar to **2** have previously been structurally described. Selected parameters from these complexes are presented comparatively with those of **2** in Table 1, together with corresponding parameters for the ligand precursor **1**. Kemmit and other workers[13–16] have shown that metallacyclobutan-3-one complexes with structural similari-

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Table 1. Selected Geometries for 1, 2·DMSO, and Related Compounds of the Form $[X_2Pd(\eta^3\text{-}(CHR)_2CO)]^{x+}$ [a]

	R (disposition)					
			CO_2Me (trans)[d]			
X_2	MeIm[b]	MeIm (cis)[c] $(I)_2$	$(PhP_3)_2$[d]	$(Ph_3As)_2$[d]	2,2′-bipyridyl[d]	Ph_3P (cis)[e,f] $(\mu\text{-}Cl)_2$
			Distances (Å)			
Pd−X		2.6746(6), 2.6691(6)	2.316(2), 2.343(1)	2.404(2), 2.437(1)	2.106(4), 2.076(3)	2.372(3), 2.389(3); 2.389(3), 2.390(3)
Pd−C(1)		2.085(6), 2.090(6)	2.135(6), 2.165(7)	2.125(5), 2.152(5)	2.103(3), 2.085(3)	2.06(1), 2.05(1);
Pd−C(0)		2.362(6)	2.389(7)	2.384(6)	2.374(3)	2.39(1); 2.38(1)
C(0)−O(0)	1.21(2)	1.261(7)	1.224(8)	1.231(7)	1.242(4)	1.24(2); 1.23(2)
C(0)−C(1)	1.51(1)	1.446(8), 1.458(8)	1.467(9), 1.492(8)	1.482(7), 1.473(6)	1.471(5), 1.471(5)	1.47(2), 1.47(2); 1.46(2), 1.47(2)
			Angles (deg)			
X−Pd−X′		100.90(2)	102.2(1)	100.38(7)	79.0(2)	87.5(1); 87.1(1)
C(1)−Pd−C(1′)		66.8(2)	68.4(2)	68.7(2)	68.8(1)	68.8(4); 68.0(5)
C(1)−Pd−X		96.5(2), 95.7(2)	98.9(2), 91.1(1)	98.4(1), 92.9(1)	108.2(1), 104.3(1)	101.0(3), 102.6(3); 101.1(3), 103.9(3)
C(1)−Pd−X′		162.5(2), 163.4(2)	158.2(2), 165.8(3)	160.7(2), 166.3(1)	172.0(2), 175.6(1)	171.1(3), 169.2(3); 171.4(3), 169.0(3)
Pd−C(1)−C(0)		81.8(3), 81.4(3)	80.8(3), 79.2(4)	80.6(3), 79.9(3)	81.2(2), 81.8(2)	83.4(7), 83.6(7); 83.4(8), 82.5(7)
Pd−C(1)−R		122.4(3), 122.3(4)	125.9(5), 105.8(5)	125.2(4), 105.0(4)	122.0(3), 105.7(2)	125.1(6), 123.8(6); 126.5(7), 128.5(6)
C(0)−C(1)−R	112.5(8)	117.8(5), 118.0(5)	116.8(6), 119.6(4)	115.7(5), 120.8(4)	122.2(3), 122.9(3)	117.0(9), 117.3(9); 119.8(9), 118.2(9)
O(0)−C(0)−C(1)	123.9(5)	127.5(7), 125.8(5)	126.0(6), 122.6(5)	125.3(4), 123.7(4)	126.9(3), 124.1(3)	126(1), 127(1); 128(1), 126(1)
C(1)−C(0)−C(1′)	112(1)	104.7(5)	109.5(6)	109.5(5)	107.1(3)	105(1); 104(1)
			Interplanar Dihedral Angles θ (deg) and Atom Deviations δ (Å)			
$\theta(OC_3/C(1,1')Pd)$		62.2(2)	53.3(2)	52.3(4)	51.3(3)	57.0(5); 57.6(4)
$\delta(Pd(C_3O))$		1.556(5)	1.569(6)	1.536(5)	1.512(4)	1.45(1); 1.47(1)
χ^2 (C(1,1′)X,X′)		29	1.0×10^3	1.0×10^3	6.1×10^2	11; 19
$\delta(Pd(C_2X_2))$		0.015(2)	0.007(2)	0.009(2)	0.004(1)	0.046(4); 0.028(4)

[a] Where two values are found for an entry, they are for the unprimed and primed portions of the molecule on either side of the plane drawn through Pd, C(O), and O. The dispositions of the η^3-oxodimethylenemethane ligand substituents relative to the C_3O ligand plane are indicated. [b] Data for **1**. [c] Data for **2**·DMSO. [d] Reference 13; the Pt/EPh_3 analogues are reported in refs 19 and 20. [e] Reference 14. [f] Data for Pd(1); Pd(2).

ties to **2** exhibit a significant η^3-allyl Pd−C_3O bonding component and may be viewed as complexes of η^3-oxodimethylenemethane (η^3-ODMM) ligands. Adoption of this ligand bonding mode leads to an increase in the C−C(O) bond order and a decrease in the C−O bond order when compared to the free ligand precursor. In the transition-metal complexes these changes are manifested by a shortening of the ligand C−C(O) bonds and a lengthening of the C−O bond, with an associated decrease in the energy of ν_{CO}.[13,14]

Comparison of the carbonyl group stretching frequency and selected structural data in Table 1 for **1** and **2**·DMSO indicates that the palladium−ligand interaction in **2** is indeed pseudo η^3-allylic in nature. The merged ν_{CO} absorptions for **2** (1585 and 1564 cm^{-1}) are reduced in energy from 1749 cm^{-1} in the free ligand **1**. Pd−C(0) is 2.362(6) Å, compared to 2.085(6) and 2.090(6) Å for Pd−C(1,1′), while C(0)−C(1) distances are 1.446(8) and 1.458(8) Å, decreased from 1.51(1) Å in **1**. The C(0)−O(0) (1.261(7) Å in **2**) distance has increased from 1.21(2) Å in **1**. All of these measurements show a marked reduction in the C−O bond order due to electron delocalization across the C_3O^{2-} moiety and indicate a significant component of η^3-ODMM bonding.

A consistent feature of previously reported Pd(II)−η^3-ODMM complexes is a highly puckered four-membered palladacyclobutan-3-one ring. The fold angles (ring pucker) between the PdC(1,1′) and C_3O planes in these complexes fall between 51.3(3) and 57.6(4)° (Table 1), significantly more than required purely for steric reasons,[16] but somewhat less than in truly η^3-allyl Pd(II) complexes, where typical values range from 61 to 72°.[16] The tilt of the C_3O plane relative to the Pd coordination plane in **2** is notably larger than in previously described complexes of this type, with a dihedral angle between the PdC(1,1′) and C_3O planes of 62.2(2)°. Data presented in Table 1 indicate that the C−O bond length in **2** is the longest yet observed in a Pd-η^3-ODMM complex, and the C−C(O) bond lengths are the shortest. In addition, the C(1)−C(0)−C(1′) angle for **2** (104.7(5)°, diminished from 112(1)° in **1**) is among

Table 2. Comparison of Internal and External Bond Lengths and Angles in the MeIm Groups of 1 and 2·DMSO

		2·DMSO	
	1	unprimed	primed
	Bond Lengths (Å)		
N(1)−C(2)	1.35(1)	1.329(7)	1.333(7)
C(2)−N(3)	1.36(1)	1.334(8)	1.336(7)
N(3)−C(4)	1.32(1)	1.379(8)	1.374(8)
C(4)−C(5)	1.33(2)	1.344(9)	1.353(8)
C(5)−N(1)	1.41(1)	1.374(7)	1.386(7)
N(3)−C(31)	1.50(1)	1.477(8)	1.471(8)
N(1)−C(1)	1.45(1)	1.448(7)	1.430(7)
	Bond Angles (deg)		
N(1)−C(2)−N(3)	104.4(9)	108.1(5)	108.7(5)
C(2)−N(3)−C(4)	113.2(9)	108.5(5)	108.8(5)
N(3)−C(4)−C(5)	106(1)	107.3(5)	107.1(5)
C(4)−C(5)−N(1)	108(1)	107.0(5)	107.3(5)
C(5)−N(1)−C(2)	107.9(9)	109.1(5)	108.1(5)
C(1)−N(1)−C(2)	130.3(9)	124.7(5)	126.2(5)
C(1)−N(1)−C(5)	121.7(8)	125.9(5)	125.4(5)
C(31)−N(3)−C(2)	119.5(9)	126.5(5)	125.3(5)
C(31)−N(3)−C(4)	127(1)	125.0(5)	125.9(5)

the tightest yet observed, although a lack of precision in other measurements obscures the comparison somewhat. The increased homogeneity of the C−O and C−C(0) bond lengths suggests that a greater charge delocalization across the C_3O^{2-} fragment exists in **2** relative to the previously described complexes. This would presume that the η^3-allylic contribution to the Pd−ligand interaction in **2** is significantly greater than in previously reported Pd−η^3-ODMM complexes and is reflected in the increased fold angle of **2**.

In the chloro-bridged dimer $[LPd(\mu\text{-Cl})_2PdL]^{2+}$ (L = η^3-[(CH(PPh$_3$))$_2$CO]) described by Falvello et al.,[14] the pendant Ph_3P ylide groups are arranged cis to the ligand C_3O core plane, as in **2**, although the (μ-Cl)$_2$ bridge comprises a ligand pair of significantly diminished bite compared to the iodide ligands of **2**. In the remainder of described systems[13] the pendant methoxycarbonyl groups are disposed trans to either side of the C_3O core plane. In these examples when bulky PPh_3 or $AsPh_3$ ligands fill the remaining coordination sites on Pd, X−Pd−X (X = P, As) angles of the order found in **2** are observed. When X = 2,2′-bipyridyl, a significantly smaller bite angle opposite the C_3O ligand is found, but the effect of this on the bond distances and angles in the Pd−C_3O fragment appears small. The effect of the trans arrangement of the ligand substituents may perhaps be most evident in the deviant dispositions to either side of the PdX_2 (X = P, As, N) coordination plane of the coordinated carbon atoms (0.203(9) and −0.160(8), 0.144(7) and −0.147(6), and 0.123(6) and −0.112(6) Å, respectively), resulting in significant nonplanarity of the C_2X_2 array about the palladium.

The minor variations in Pd−C(1,1′) bond lengths of the complexes in Table 1 may be seen to reflect the relative trans influences of the supporting ligands at Pd. Pd−C(1,1′) distances are significantly longer in the cases of $\{L_2Pd[\eta^3\text{-(CH(CO}_2\text{Me))}_2\text{CO}]\}^{2+}$ (L = PPh_3, $AsPh_3$) than the relatively similar values found in $I_2Pd[\eta^3\text{-(CH(MeIm))}_2\text{CO}]$ (**2**) and the (μ-Cl)$_2$ dimer.

The bond lengths and angles of the MeIm groups in **2** are more uniform than in the bis(imidazolium) salt **1** (Table 2), suggesting that the electron delocalization across the η^3-ODMM core of the ligand in **2** also leads to an increase in the π-electron delocalization (aromaticity) in the heterocyclic rings of the ligand.[17] The possibility of an extended electronic interaction (delocalization) across the entire zwitterionic ligand in **2** may explain the enhanced Pd−η^3-allylic interaction over that seen in previous Pd−η^3-ODMM complexes. However, the absence of any change in the C(1,1′)−N(1,1′) bond lengths on formation of **2** may argue against such a far-reaching electronic delocalization, and the observed increase in C(0)−C(1,1′)−N(1,1′) angles on formation of **2** (117.8(5) and 118.0(5)° from 112.5(8)° in **1**) is similar to that in other Pd−η^3-ODMM complexes.[13]

Crystallographic data for a series of platinum complexes analogous to some of those presented in Table 1 are available[15,18−20] but are not tabulated in detail as they are of inherently lower precision due to domination of the scattering by the heavy Pt atom. The Pt−η^3-(C_3O^{2-}) core dimensions resemble those of their Pd counterparts, although the platinacyclobutan-3-one complexes encompass a wider range of fold angles (42(1)−56.7°),[15,19] suggesting that the Pt−η^3-ODMM interaction may be more subject to influence from the C(1,1′) substituents and supporting ligands at the metal. It should be noted that among the four reported comparable M/EPh_3 (M = Pd, Pt; E = P, As) combinations, the notably divergent Pt/$AsPh_3$ adduct[15] is not isomorphous with the other three, suggesting that in that case unduly irregular lattice forces may be responsible for the fold angle difference.

Octahedral complexes of η^3-ODMM ligands have also been structurally defined for Ru[21] and Ir,[22] the fold angles of the metallocyclobutan-3-one fragments of these two complexes being quoted as 45.6(5) and 41°, respectively. Our calculation of the fold angle for the Ir complex[22] using the deposited data is 48.0(4)°.

Complex **2** proved to be inert toward the insertion of carbon monoxide (CO) at atmospheric pressure. Bubbling CO through a d_6-DMSO solution of **2**, both at room temperature and 80 °C, caused a small amount of Pd black to be deposited, but no products resulting from the coordination of CO to Pd or insertion into the Pd−C bonds could be detected using ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, and **2** was recovered unchanged. Previous attempts to react Pt−η^3-ODMM complexes with CO have also been unsuccessful in isolating an insertion intermediate or liberated insertion product, even under forcing conditions.[19] These observations are not entirely inconsistent with previous results for conventional Pd−η^3-allyl complexes, where significant variability in reactivity toward CO is encountered, even between relatively similar systems.[23]

The $Pd[\eta^3\text{-(CH(MeIm))}_2\text{CO}]^{2+}$ moiety is also generated by the in situ reaction of **1** with Ag_2O and $PdCl_2(MeCN)_2$ in dichloromethane (DCM). The infrared spectrum of the crude product of this reaction exhibits a broad, intense carbonyl absorption centered on 1566 cm^{-1}, with a weak band at 1750 cm^{-1} attributable to unreacted **1**. ^{1}H NMR and mass spectrometry results suggest that the chloro analogue of **2** is the major product of the above reaction. It is likely that this reaction involves transmetalation from an unidentified Ag^I complex of **1** to a Pd^{II} complex. It is noteworthy that the impure product isolated from the reaction of Ag_2O and **1** in DCM/methanol shows the presence of a strong carbonyl peak at 1738 cm^{-1}. The energy of this absorption is largely unchanged from that of **1** (1749 cm^{-1}) and is consistent with the formation of a Ag^I−imidazolin-2-ylidene complex of **1**, where the carbonyl group is relatively unaffected, rather than a Ag−η^3-ODMM complex. A possible, although less likely in our opinion, explanation for this observation is that the ligand is again deprotonated at the methylene groups but that

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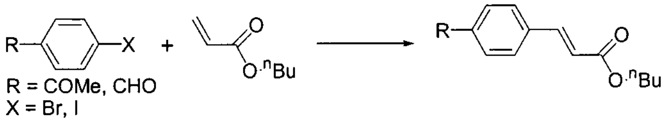
Table 3. Heck Coupling Reactions[a] Catalyzed by Complex 2



run[b]	amt of **2** (mol %)	aryl halide	time (h)	conversn[c] (%)	TON[d]	TOF[e]
1	9.9×10^{-3}	4-bromoacetophenone	20	100	10 080	504
2[f]	5.1×10^{-4}	4-bromoacetophenone	20	31	60 750	3040
3[f]	1.03×10^{-2}	4-chlorobenzaldehyde	64.5	10	940	15

[a] The coupling partner in all cases is *n*-butyl acrylate. [b] Conditions as described in the Experimental Section. Hydrazine hydrate (50 μL) was added to each run. [c] Conversion determined by GC. [d] In units of mol of product/(mol of Pd). [e] In units of mol of product/((mol of Pd)/h). [f] Reactions purposely halted before complete conversion.

the extent of charge delocalization across the C_3O^{2-} core is substantially reduced such that the η^3-ODMM interaction is an insignificant component of the bonding in the resultant argentocyclobutan-3-one, when compared to **2**. We have been unable to completely characterize the Ag^I−**1** complex due to its poor solubility and the presence of AgI impurities. The formation of a Ag^I−imidazolin-2-ylidene complex of **1** would imply that a mechanism exists for conversion to the η^3-ODMM bonding mode in the presence of Pd(II), through a mechanism that results in a hydrogen shift from the methylene group to C_2 of the imidazolin-2-ylidene. Such a mechanism is likely to be promoted by the additional stabilization to be gained on adoption of the Pd−η^3-ODMM interaction in **2**.

Palladacylobutan-3-ones have been implicated as intermediates in catalytic cycloaddition cycles,[24,25] but no report on their activity in C−C coupling reactions was available. Table 3 summarizes the results of catalytic tests using **2** as precatalyst in the Heck reaction. Complex **2** was found to be very active in the Heck coupling of 4-bromoacetophenone and *n*-butyl acrylate at loadings of 0.0099 mol %, converting 100% of the aryl bromide within 20 h at 120 °C. A decrease in catalyst loading to 5.1×10^{-4} mol % increased the turnover number (TON) to 60 750 mol of product/(mol of Pd) at the expense of yield and longer reaction times. When **2** was tested in the coupling of 4-chlorobenzaldehyde and *n*-butyl acrylate, poor activity was found. The stability of **2** under the basic conditions (sodium acetate) of the Heck reaction suggests that the MeIm groups and remaining protons α to the carbonyl group are not sufficiently acidic to be abstracted under these conditions, although the exact nature of the catalytic cycle involving **2** has not yet been determined.

Conclusions

It was found that the acidity of the protons on the methylene groups α to the carbonyl group of the functionalized imidazolium salt **1** was sufficiently enhanced by the presence of the functional group to facilitate their abstraction by reaction with $Pd(OAc)_2$, although apparently not by Ag_2O in the absence of Pd(II). X-ray crystallographic and infrared data indicate that the resulting Pd(II) complex **2** contains a palladacyclobutan-3-one ring with a pseudo π-allyl (η^3-ODMM) interaction between Pd and the ligand. The Pd−η^3-ODMM interaction provides a low-energy bonding mode which generates a thermodynamically stable end product, rather than undefined decomposition products. The large fold angle in the palladacyclobutan-3-one ring suggests that the Pd−η^3-ODMM π-allylic interaction may be greater in **2** than in similar examples, where relatively consistent Pd−C_3O geometries are found. Among functionalized imidazolium ligands, however, this ability to stabilize the deprotonated methylene groups α to the functional group is a rather special case due to the potential for delocalization of charge across the C_3O^{2-} core of the zwitterionic ligand derived from **1**, and possibly through an extended interaction of the core and MeIm groups. Complex **2** performed well as a Heck coupling precatalyst for activated aryl bromides at moderate to low catalyst loadings, suggesting that it forms a stable catalytic species under the basic conditions of this reaction. It is evident from this study that efforts to prepare transition-metal complexes of functionalized NHC ligands, which necessarily involves the deprotonation of functionalized imidazolium salts, may produce unexpected outcomes due to the acidity of the protons α to the functional group.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques, and solvents were dried by usual means,[26] unless otherwise indicated. All other reagents were used as received. NMR spectra were run at ambient temperature and referenced to residual solvent signals. Melting points were performed in glass capillaries under air and are uncorrected. Infrared spectra were run as KBr disks on a Bruker IFS66. Elemental analysis and mass spectrometry were performed by the Central Science Laboratory, University of Tasmania.

Synthesis of 1,3-Bis(1-methylimidazolium-3-yl)propan-2-one Diiodide (1). To a stirred solution of NaI (12.11 g, 80.8 mmol) in acetone (50 mL) at 0 °C was added 1,3-dichloroacetone (5.00 g, 39.4 mmol). The resulting thick yellow suspension was warmed to room temperature over the course of 30 min and was then filtered through Celite. The volume of the orange filtrate was reduced in vacuo to approximately 40 mL and then cooled in ice prior to the slow addition of 1-methylimidazole (6.9 mL, 86.6 mmol) over the course of 5 min. The solution darkened and became cloudy as an oily brown precipitate formed. After 30 min of stirring, diethyl ether (50 mL) was added to precipitate the crude product as a sticky brown solid. The supernatant was decanted off and the crude product washed with diethyl ether (2 × 10 mL) and then extracted with ethanol (2 × 400 mL) at 70 °C. The extracts

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were treated with activated charcoal to remove highly colored impurities and filtered through Celite, and then their volume was reduced under reduced pressure at 60 °C until crystallization began. Cooling to −20 °C gave **1** as X-ray-quality tan crystals that were washed with cold ethanol and then dried in vacuo. A second crop was obtained from the combined filtrates, giving a total yield of 5.02 g (27%). Anal. Calcd for $C_{11}H_{16}I_2N_4O$: C, 27.87; H, 3.40; N, 11.82. Found: C, 27.88; H, 3.38; N, 11.77. MS (LSIMS): m/z 347.0 $[M - I]^+$ (10%), 219.1 $[M - I - HI]^+$ (100%). ^1H NMR (399.7 MHz, DMSO-d_6): δ 9.01 (s, 2H, NC(H)N), 7.76 (t, $J = 1.8$ Hz, 2H, HCCH), 7.61 (t, $J = 1.8$ Hz, 2H, HCCH), 5.51 (s, 4H, NCH_2C(O)), 3.93 (s, 6H, NCH_3). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 195.0 (CO), 137.5 (NCN), 123.6 and 123.5 (NCCN), 55.3 (CH$_2$), 36.1 (NCH$_3$). IR (KBr disk, cm^{-1}): 1749 (ν_{CO}). Mp: 221−222 °C.

Synthesis of *cis*-$I_2Pd[\eta^3$-(CH(MeIm))$_2$CO] (2). **1** (0.51 g, 1.1 mmol) was dissolved in DMSO (10 mL), and Pd(OAc)$_2$ (0.23 g, 1.0 mmol) was added with stirring. The resulting red-brown solution was heated to 65 °C for 2.5 h, after which time a small amount of orange solid had formed. The temperature was gradually increased to 90 °C over the course of 1 h and maintained there for a further 1 h, with 1−2 mL of solvent removed in vacuo every $^1/_2$ h to remove the acetic acid formed by the reaction. The remaining DMSO was removed in vacuo to leave a sticky orange solid that was washed with methanol (3 × 2.5 mL) to give an orange powder. Recrystallization from DMSO/acetonitrile (MeCN) gave 0.41 g (71%) of **2** as a yellow powder that strongly retains residual DMSO. Crystals suitable for the X-ray work were grown by diffusion of MeCN into a saturated DMSO solution of **2** and gave a satisfactory analysis for **2**·DMSO. Anal. Calcd for $C_{11}H_{14}I_2N_4OPd$·DMSO: C, 23.78; H, 3.07; N, 8.53. Found: C, 23.65; H, 3.18; N, 8.57. MS (LSIMS): m/z 450.9 $[M - I]^+$ (100%), 577.9 $[M]^+$ (20%), 1030.5 $[2\ M - I]^+$ (10%). ^1H NMR (399.7 MHz, DMSO-d_6): δ 9.42 (s, 2H, NC(H)N), 7.89 (t, $J = 1.6$ Hz, 2H, HCCH), 7.63 (t, $J = 1.6$ Hz, 2H, HCCH), 5.59 (s, 2H, NPdC(H)C(O)), 3.86 (s, 6H, NCH_3). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 136.1 (NCN), 123.0 and 121.8 (NCCN), 66.6 (NPdCC(O)), 35.7 (NCH$_3$), no signal was observed for CO. IR (KBr disk, cm^{-1}): 1585, 1564 (ν_{CO}).

Catalysis. Heck reactions were carried out using aryl halide (25 mmol), n-butyl acrylate (5.0 mL, 35 mmol), and sodium acetate (2.23 g, 28 mmol), at 120 °C in N,N-dimethylacetamide (DMAc), with di(ethylene glycol) n-butyl ether as internal standard. An appropriate amount of catalyst was injected in DMAc solution when the operating temperature was reached, followed by hydrazine hydrate (50 μL). Coupling product yields were calculated by GC on the basis of residual aryl halide, and the product identity confirmed by NMR and GC-MS.

Structure Determination. Full spheres of CCD area-detector data were measured at ca. 153 K (Bruker AXS instrument, ω-scans, $2\theta_{max} = 58°$, monochromatic Mo Kα radiation, $\lambda = 0.710\ 7_3$ Å) yielding N_t (total) reflections; these were merged to N (unique) (R_{int} quoted) after “empirical”/multiscan absorption correction, N_o with $F > 4\sigma(F)$ being considered “observed” and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals at convergence R and R_w (weights: $(\sigma^2(F) + 0.0004\ F^2)^{-1}$) are quoted, neutral atom complex scattering factors being employed within the Xtal 3.4 program system.[27]

Crystal/Refinement Data for 1: $[CH_2(MeIm)]_2CO\cdot 2I \equiv C_{11}H_{16}I_2N_4O$, $M_r = 474.1$; orthorhombic, space group $Fdd2$ (C_{2v}^{19}, No. 43); $a = 19.187(2)$ Å, $b = 19.921(4)$ Å, $c = 8.513(4)$ Å, $V = 3254(2)$ Å^3; $D_c(Z = 8) = 1.93_5$ g cm^{-3}; $\mu_{Mo} = 39$ cm^{-1}; crystal dimensions 0.32 × 0.30 × 0.27 mm; $T_{min,max} = 0.62, 0.78$; $N_t = 15\ 581$; $N = 1069$ ($R_{int} = 0.017$), $N_o = 1013$; $|\Delta\rho_{max}| = 1.22(3)$ e Å^{-3}; $x_{abs} = 0.41(8)$.

Crystal/Refinement Data for 2·DMSO: $I_2Pd[\eta^3$-(CH(MeIm))$_2$CO]·DMSO $\equiv C_{13}H_{20}I_2N_4O_2PdS$, $M_r = 656.6$; monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14); $a = 14.396(1)$ Å, $b = 14.049(2)$ Å, $c = 9.525(2)$ Å, $\beta = 90.335(2)°$, $V = 1926.4(5)$ Å^3; $D_c(Z = 4) = 2.26_4$ g cm^{-3}; $\mu_{Mo} = 43$ cm^{-1}; crystal dimensions 0.2 × 0.07 × 0.06 mm; $T_{min,max} = 0.50, 0.86$; $N_t = 19\ 124$, $N = 4881$ ($R_{int} = 0.055$), $N_o = 3659$; $R = 0.038$, $R_w = 0.041$; $|\Delta\rho_{max}| = 2.8(2)$ e Å^{-3}.

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Supporting Information Available: Tables of atomic parameters and molecular geometries for **1** and **2**·DMSO. This material is available free of charge via the Internet at http://pubs.acs.org.

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