Silver(I) and Palladium(II) Complexes of an Ether-Functionalized Quasi-pincer Bis-carbene Ligand and Its Alkyl Analogue

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Silver and palladium complexes of bis-NHC ligands bearing a weakly coordinating ether functionality have been prepared as counterparts to the well-studied pyridine-functionalized bis-NHC pincer ligands. The Ag(I) complex of bis[2-(3-methylimidazolin-2-yliden-1-yl)ethyl] ether ($_{Me}$COC) was prepared through the reaction of the corresponding bis-imidazolium salt with Ag_2O and crystallographically characterized as the triflate salt. The structure reveals a dinuclear $[Ag_2(_{Me}COC)_2](OTf)_2$ formulation and the presence of two separate forms in the crystal lattice arising from varying conformations of the ether bridging groups. The related pentamethylene-bridged bis-NHC ligand 1,5-bis(3-methylimidazolin-2-yliden-1-yl)-pentane was analogously complexed to Ag(I) and crystallized as the $[AgBr_2]^-$ salt. A single-crystal X-ray study of the pentamethylene-bridged complex revealed continuous ladders of quasi-planar dinuclear cations linked by $[AgBr_2]^-$ anions; the divergent metal−ligand associations in the two Ag(I) compounds are attributed to the influence of the coordinating $[AgBr_2]^-$ anions rather than any effect of the ether functionality of $_{Me}$COC. Transmetalation of the bis-NHC ligand from $[Ag_2(_{Me}COC)_2](BF_4)_2$ to Pd(II) gave the structurally characterized complex $[PdCl(MeCN)(_{Me}COC)](BF_4)$, in which the NHC groups adopt a *cis* configuration with the oxygen atom remaining uncoordinated. This Pd^{II}(NHC) complex exhibited good activity in a model Heck coupling reaction.

Introduction

Nucleophilic heterocyclic carbene (NHC) ligands have enjoyed wide applicability as ligands for transition metals in a variety of catalytic transformations since they were first isolated in 1991.[1] The provision of hemilabile donor functional groups to complement the strongly binding NHCs[2] has led to impressively high turnover numbers (TONs), when combined with Pd, for catalytic C−C couplings such as the Heck and Suzuki reactions.[3] The concept of two NHC groups separated by a pyridine functionality has been explored by several groups, yielding Pd(II) pincer complexes of both the methylene-bridged ligands **I**[4−7] and the planar examples **II**[7−10] (R = various alkyl/aryl; these ligands are highly “tunable”). The resulting complexes $[PdX(\mathbf{I}/\mathbf{II})]^+$ (X = halogen, methyl) are active precatalysts for C−C coupling reactions and exhibit excellent thermal stability and resistance to degradation reactions such as the reductive elimination of 2-methylimidazolium species from complexes containing PdMe(NHC) moieties.[4,7,8,10,11] Replacement of pyridine with benzene gives the cyclometalated analogue, where the ligand may be viewed as a bis-NHC ligand bearing a strongly bound third donor group;[5] however, the incorporation of less strongly nucleophilic functional groups into potentially tridentate bis-NHC ligands and their subsequent complexation to transition metals has not been reported. Despite, at best, transient coordination, the presence of weakly binding oxygen-donor groups in isolated complexes of polydentate ligands can significantly increase the catalytic performance of these systems.[12] Compared to the configurations of **I** and **II**, a more flexible ligand bearing a weakly nucleophilic oxygen-containing donor group might be expected to aid catalytic processes by the ready provision of vacant sites at the metal center. At the same time the robust NHC “anchors” and the hemilabile donor group are available to stabilize intermediates in the catalytic cycle against decomposition processes. A palladium(II) complex **III** of an amido-functionalized bis-NHC

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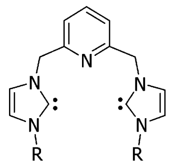
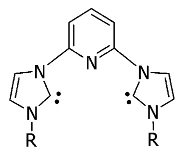
ligand has been reported,[13] but catalytic applications have not been documented.



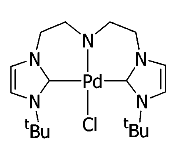
I

($_{R}$C^N^C)



II

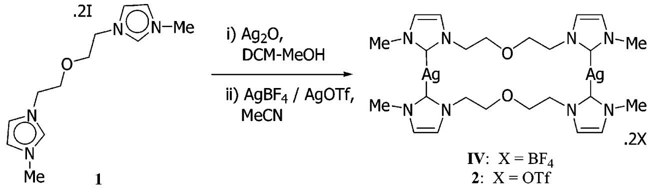
($_{R}$CNC)



III

Ag^{I}(NHC) complexes have been shown to be facile reagents for the transmetalation of a variety of functionalized NHC ligands to Pd(II),[14,15] including those of type **I**[7,10,16] and **II**;[4,6,7,16,17] they are readily accessed through the reaction of an imidazolium salt with Ag$_2$O by the method of Wang and Lin.[18] In recent years the number of crystallographically characterized Ag^{I}(NHC) complexes has increased considerably with a rich structural diversity revealed, especially when halide ions are present in the compound.[15,19,20] The capacity of Ag(I) to form complex anions [AgX$_2$]$^-$ (X = halogen), coordinate to either one or two NHC moieties, and engage in Ag(I)···Ag(I) interactions in the solid state contribute to this structural variety; the presence of additional functional groups on the NHC ligand appears to have little structural influence, as these typically remain uncoordinated.[4,15,17,21−24] In the absence of halide ions, most crystallographically characterized examples show Ag(I) quasi-linearly ligated by two NHC moieties;[18,19,23−26] dinuclear [Ag$_2$(bis-NHC)$_2$]$^{2+}$ structures are frequently observed when bis-NHC ligands are employed.[4,22,24,26,27] Several notable exceptions have resulted from syntheses conducted in the presence of excess Ag$_2$O or Ag$^+$ where products incorporating additional bridging silver ions that participate in metal−metal interactions are obtained.[23,28]

Scheme 1. Synthesis of Ag(I) Complexes of the $_{Me}$COC Ligand



1

IV: X = BF$_4$
2: X = OTf

Results and Discussion

Preparation of the tetrafluoroborate salt of the Ag(I) complex of bis[2-(3-methylimidazolin-2-yliden-1-yl)ethyl] ether ($_{Me}$COC), **IV**, was reported previously,[29] but a crystalline sample was not obtained. Nonetheless, LSIMS data suggested a dinuclear structure analogous to crystallographically characterized Ag(I) complexes of pyridine-, thiophene-, and furan-functionalized bis-NHC ligands.[4,24] An analogous synthesis entailing reaction of the ether-functionalized bis-imidazolium iodide **1** with Ag$_2$O, followed by anion substitution with Ag(OTf) (OTf = triflate, OSO$_2$CF$_3$), yielded complex **2** as a colorless crystalline solid suitable for X-ray crystallography (Scheme 1).

Complex **2** crystallizes with two structurally distinct [Ag$_2$($_{Me}$COC)$_2$]$^{2+}$ cations, modeled with an overall formulation of $\mathbf{2}{\cdot}{}^{2}/_{3}$MeCN. The two cations are present in a 2:1 ratio in the crystal lattice and are readily distinguished by the "crossed" and "parallel" arrangements of the two C−Ag−C strings in each (Figure 1a and b, respectively). The cation containing Ag(1,2) is devoid of crystallographic symmetry, and that containing Ag(3) is disposed about a crystallographic inversion center. Both the "crossed" and "parallel" molecular conformations present in $\mathbf{2}{\cdot}{}^{2}/_{3}$MeCN have recently been described in the *N*-(1-naphthylmethylene) and *N*-(9-anthracenylmethylene), respectively, substituted analogues of **2**.[26] See the Supporting Information for a detailed discussion of the crystal structures described in this work.

The two cations of $\mathbf{2}{\cdot}{}^{2}/_{3}$MeCN are related by a notional rotation by 180° of one NHC group per $_{Me}$COC ligand about an $_{im}$N$_1$−CH$_2$ bond, concomitant with a conformational change in the ether linkages in the $_{Me}$COC ligands (Table 1). The structure of the "helical" cation results in a decreased Ag(1)···Ag(2) distance of 3.5402(8) Å, cf. Ag(3)···Ag(3′) = 4.2927(9) Å; the slight deviation of Ag(1) toward Ag(2) is apparent (Figure 1a). The Ag(1)···Ag(2) distance approaches the sum of the van der Waals radii (3.40 Å[30]) and the "helical" conformation is perhaps stabilized by a very weak silver···silver interaction. The modest steric requirements of the N-Me substituents appear crucial to the stability of the "helical" conformation as these closely approach the NHC rings of the second $_{Me}$COC ligand, N(13)···H(231a′) ca. 2.6 Å; the corresponding N-Me···NHC distances are significantly greater in the "parallel" structure. In both cations of $\mathbf{2}{\cdot}{}^{2}/_{3}$MeCN the silver atom

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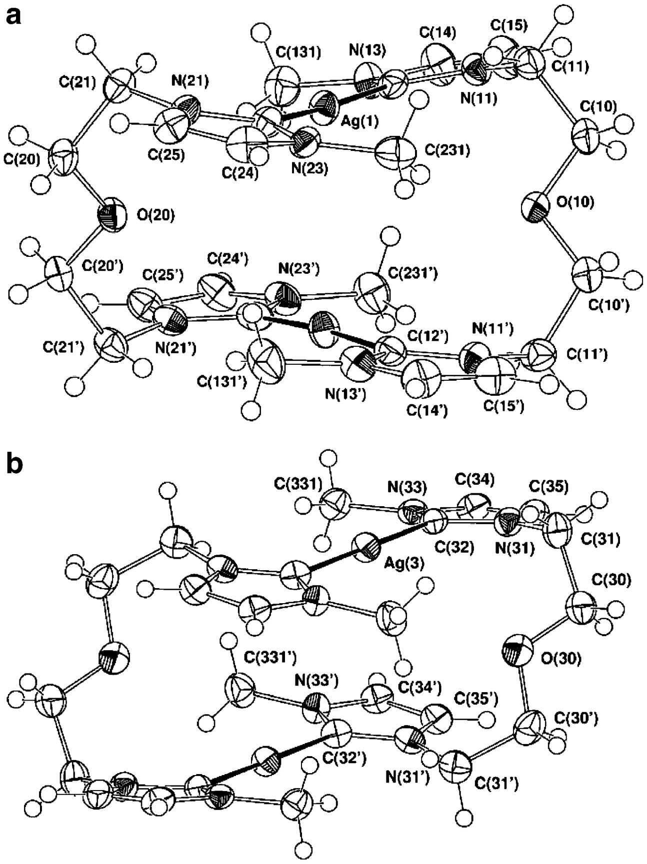
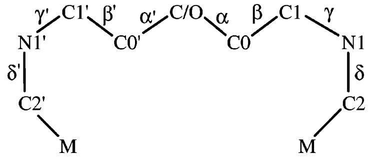


Figure 1. (a) Projection of the non-centrosymmetric "crossed" or "helical" cation of $\mathbf{2}\cdot{}^{2}/_{3}$MeCN perpendicular to the Ag(1)−Ag(2) and O(10)−O(20) axes. (b) Projection of the centrosymmetric "parallel" cation of $\mathbf{2}\cdot{}^{2}/_{3}$MeCN oblique to the Ag(3)···Ag(3′) axis.

Table 1. Intraligand Torsion Angles in (Ag/Pd)($_{\mathrm{Me}}$COC) and Ag($_{\mathrm{Me}}$(CH$_2$)$_5$C) Complexes



torsion angle (deg)	$\mathbf{2}\cdot{}^{2}/_{3}$MeCN string 1	string 2	string 3	**4**	**5**
α	−172.4(5)	−168.4(5)	163.6(4)	−172(2)	−91.4(2)
α′	−165.6(5)	−167.2(5)	−161.4(4)	176(2)	94.6(2)
β	−68.8(6)	−66.6(6)	−65.4(6)	176(2)	−59.5(3)
β′	−69.7(7)	−64.8(6)	56.8(6)	−174(2)	53.4(2)
γ	105.9(5)	103.8(5)	95.5(7)	140(2)	122.5(2)
γ′	105.4(6)	109.2(6)	−143.9(5)	−139(2)	−116.6(2)
δ	−3.9(6)	−1.1(7)	−9.8(7)	−6(2)	−8.9(3)
δ′	−2.4(7)	−8.0(7)	−2.2(7)	−1(3)	−2.8(3)

environments are closely similar and the Ag(I) ions approach linear ligation between the NHC moieties with typical Ag−$_{\mathrm{im}}$C$_2$ bond lengths (Table 2). The oxygen atoms do not contact the silver ions nor any other atom. The results presented here, together with those of Wang et al.,[26] suggest that the overall molecular conformation in this class of compounds is readily influenced by crystal-packing forces and weak intra- and intermolecular forces.

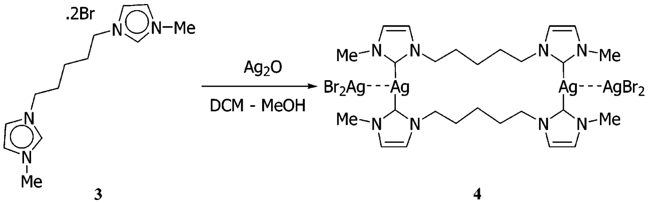
The ^{1}H NMR spectrum of **2** and its tetrafluoroborate analogue **IV** are identical and show a single $_{\mathrm{Me}}$COC ligand environment, with broadened signals observed for the ether linkage protons. The ^{13}C NMR spectrum of **IV**[29] is similarly straightforward, with the absence of an $_{\mathrm{im}}C_2$ resonance ascribed to fluxional behavior in solution.[18,31] The solution NMR data support a flexible cation structure for **2**, with the observed structural diversity in $\mathbf{2}\cdot{}^{2}/_{3}$MeCN a consequence of crystal-packing forces. Aside from the expected absence of the $_{\mathrm{im}}$C$_2$-*H* signal in **2** and **IV**, the ^{1}H NMR spectra of the complexes closely resemble the precursor imidazolium salt **1**, the greatest divergence being a shift of the $_{\mathrm{im}}$C$_{4,5}$-*H* signals to higher field by approximately 0.3 ppm in the Ag$^{\mathrm{I}}$(NHC) complexes.

Table 2. Bond Distances and Angles about the $_{\mathrm{Im}}$C$_2$−M−$_{\mathrm{Im}}$C$_2$′ (M = Ag, Pd) Units of Complexes $\mathbf{2}\cdot{}^{2}/_{3}$MeCN, 4, and 5

complex		M−($_{\mathrm{im}}$C$_2$, $_{\mathrm{im}}$C$_2$′) distance (Å)	$_{\mathrm{im}}$C$_2$−M−$_{\mathrm{im}}$C$_2$′ angle (deg)
$\mathbf{2}\cdot{}^{2}/_{3}$MeCN	[Ag$_2$($_{\mathrm{Me}}$COC)$_2$](OTf)$_2$[a,b]	2.097(6), 2.078(6)	172.5(2)
$\mathbf{2}\cdot{}^{2}/_{3}$MeCN		2.066(6), 2.070(7)	176.2(2)
$\mathbf{2}\cdot{}^{2}/_{3}$MeCN		2.094(6), 2.085(6)	177.6(2)
4	[Ag$_2$($_{\mathrm{Me}}$C(CH$_2$)$_5$C)$_2$][AgBr$_2$]$_2$	2.04(1), 2.09(1)	173.8(6)
5	[PdCl(MeCN)($_{\mathrm{Me}}$COC)]BF$_4$	1.970(2), 1.999(2)	88.38(8)

[a] Solvent of crystallization omitted. [b] Data for Ag(1,2,3), respectively.

Scheme 2. Preparation of Ag$^{\mathrm{I}}$(NHC) Complex 4



The pentamethylene-linked 1,5-bis(3-methylimidazolium-1-yl)pentane dibromide, **3**, was investigated as precursor to a Ag$^{\mathrm{I}}$(NHC) complex analogous to **2**. Structurally, substitution of the oxygen atom in **1** with a methylene group could be expected to have limited impact in resultant metal complexes unless there was direct interaction of the oxygen atom with the metal center. Bis-imidazolium **3** was prepared in high yield as a deliquescent white powder from the reaction of 1,5-dibromopentane with *N*-methylimidazole in refluxing THF; **3** exhibits straightforward ^{1}H and ^{13}C NMR spectra consistent with the proposed structure and gave a satisfactory high-resolution MS determination for the [M − Br]$^+$ ion. The reaction of **3** with Ag$_2$O in DCM−MeOH gave [Ag$_2$($_{\mathrm{Me}}$C(CH$_2$)$_5$C)$_2$][AgBr$_2$]$_2$ ($_{\mathrm{Me}}$C(CH$_2$)$_5$C = 1,5-bis(3-methylimidazolin-2-yliden-1-yl)pentane), **4**, as a low yield of white solid (Scheme 2) that rapidly darkened to a dark cream color on initial exposure to light; however, no further evidence of decomposition was apparent on storage under air at room temperature. Elemental analysis of discolored **4** returned uniformly low C, H, and N percentages of the correct ratio for the bis-NHC ligand derived from **3**, suggesting contamination of the product with inorganic silver compounds.

The ^{1}H and ^{13}C NMR spectra of **4** showed a single set of signals attributable to a symmetrical Ag$^{\mathrm{I}}$(NHC) complex, with the $_{\mathrm{im}}C_2$ signal observed as a singlet at δ 180.0 devoid of ^{13}C−^{107,109}Ag coupling. Electrospray MS (ESMS) data show two clusters for dinuclear [Ag$_2$($_{\mathrm{Me}}$C(CH$_2$)$_5$C)$_2$]$^{2+}$ species at *m/z* = 946.3 and 760.6 corresponding to [M + AgBr$_2$]$^+$ and [M + Br]$^+$, respectively. Additional clusters due to mononuclear [Ag($_{\mathrm{Me}}$C(CH$_2$)$_5$C)]$^+$ species were observed at *m/z* = 421.0 for [M/2 + Br + H]$^+$ and 339.3 and 341.2 for [M/2]$^+$.

The improved solubility of **4** relative to the analogous ether-functionalized complex allowed crystals to be grown by diffusion of Et$_2$O into a DCM−MeCN−DMSO solution. Although

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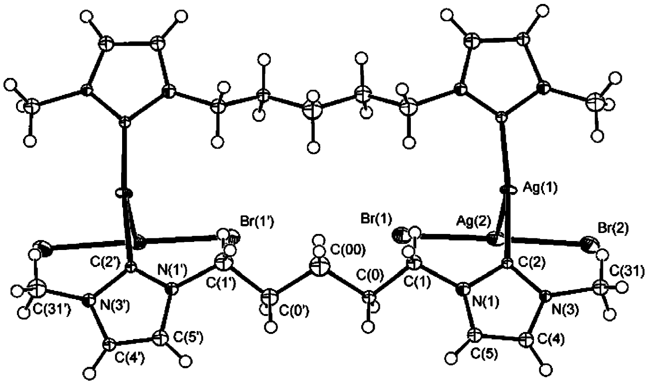


Figure 2. Projection of dinuclear **4** showing the interaction between the dimetallacyclic cation and $[AgBr_2]^-$ anions.

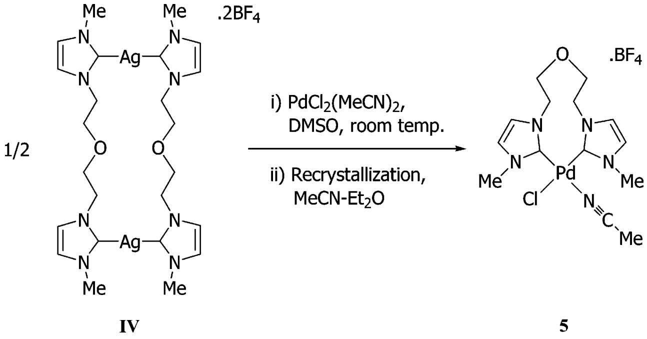
these proved to be of relatively poor quality and yielded a solution of less than optimal precision, with only the Ag and Br displacement parameters refined anisotropically, the structure obtained is of relevance and interest, as it demonstrates the influence of a coordinating anion, in this case $[AgBr_2]^-$, on the molecular geometry of a $[Ag_2(bis\text{-}NHC)_2]^{2+}$ complex (Figure 2).

Each cation of **4** forms a 20-membered dimetallacycle encompassing a crystallographic 2-axis. Within each $_{Me}C(CH_2)_5C$ ligand the NHC rings show a small interplanar dihedral angle of 13.5(7)°, resulting in a slightly bowed structure. The $[AgBr_2]^-$ anions of **4** are closely associated with the NHC-ligated Ag(1,1′) atoms, with the Br(1)−Ag(2)−Br(2) and C(2)−Ag(1)−C(2′) strings quasi-perpendicular in typical fashion;[18,19,31,32] infinite chains of Ag atoms are closely aligned along *b* in the solid state. Despite the disparity in the bis-(NHC) ligand conformations and the anions present, the coordination environment about Ag(1) of **4** is similar to that found for Ag(1,2,3) in **2**·$^2/_3$MeCN (Table 2).

The shortcomings of the $Pd(OAc)_2$ route to Pd(NHC) complexes, especially as applied to bis-imidazolium salts, have been elaborated previously;[4,33] nevertheless, in several instances careful control of reaction temperature has yielded desired products with good specificity.[5,34] However, attempts to synthesize Pd(II) complexes of the $_{Me}$COC ligand via reaction of imidazolium salt **1** with $Pd(OAc)_2$[35] gave a mixture of poorly soluble Pd^{II}(NHC) complexes that could not be satisfactorily separated by chromatography on silica. NHC ligand transmetalation from Ag(I) to Pd(II) has proved useful in the synthesis of complexes of pyridine-functionalized **I** and **II**.[4,10] Correspondingly, reaction of **IV** with $PdCl_2(MeCN)_2$ in DMSO and subsequent recrystallization from $MeCN-Et_2O$ gave X-ray quality crystals of $[PdCl(_{Me}COC)(MeCN)]BF_4$, **5** (Scheme 3).

The proposed formulation of **5** was confirmed by a single-crystal X-ray study (Figure 3), with the NHC moieties of the $_{Me}$COC ligand adopting a chelating *cis* configuration and the remaining coordination sites occupied by a chloride ion and an MeCN molecule. The environment about Pd in **5** is puckered square planar and the 10-membered $Pd(_{Me}COC)$ metallacycle shows quasi-*m* symmetry with Pd−C(2,2′) = 1.970(2), 1.999(2) Å, differing only slightly despite the different *trans* ligands

Scheme 3. Transmetalation of $_{Me}$COC from Ag(I) to Pd(II) Yielding Complex 5



(Table 2). The unprimed and primed NHC ring planes make dihedral angles to the Pd coordination plane of 82.45(7)° and 80.58(7)°, respectively. The oxygen atom of the ether functionality is well removed from the Pd center (ca. 4.3 Å) but contacts H(4′) of an adjacent molecule in the crystal lattice (O(0)···H(4′) ca. 2.6 Å). Notably, the *cis* chelation of the $_{Me}$COC ligand of **5** brings the N-Me groups into relatively close proximity to each other (C(31)−C(31′) ca. 3.5 Å) and would allow little space for incorporation of the catalytically interesting N-Mes and N-dipp (Mes = mesityl, dipp = 2,6-di(isopropyl)phenyl) groups with retention of the observed ligand conformation.

The ^1H and ^{13}C NMR spectra of **5** in d_6-DMSO indicate displacement of the MeCN ligand by the stronger d_6-DMSO donor;[36] the solution NMR measurements discussed below thus relate to $[PdCl(d_6\text{-DMSO})(_{Me}COC)]^+$. The ^1H NMR spectrum of **5** shows significantly broadened signals for the $_{Me}$COC ligand, indicating restricted flexibility in the metallacycle. Correspondingly, a total of four signals are observed for the eight methylene protons, comprising two triplets at δ 5.30 and 4.15 together with two doublets at δ 4.03 and 3.84. Assignment of the latter pair as an AB coupling pattern is hampered by the coincident N-*Me* peak at δ 4.06. The pair of triplets are tentatively assigned to the OCH_2 protons given that their position downfield of the AB pattern is consistent with the relative positions of these signals in the Ag^I(NHC) complexes **2** and **IV**; the AB pattern is thus attributed to the NCH_2 protons. The extent of geminal coupling apparent between the methylene groups in the ^1H NMR spectrum of **5** can be compared to that seen in several complexes bearing ligands of similar geometry. The ^1H NMR spectrum of *cis*-*N*,*N*′-$PdCl_2$(NON) (NON = ether-bridged bis-pyrazol-1-yl analogue of $_{Me}$COC) shows only a pair of triplets, with this equivalency of the ether bridge methylene groups retained at 183 K.[37] While *cis*-$PdCl_2$(NSN) (NSN = thioether-bridged bis-pyrazol-1-yl analogue of $_{Me}$COC) shows extremely broad ^1H NMR signals due to *N*,*S*-*N*,*N*′-*S*,*N*′ hemilability, the spectrum of cationic [*N*,*S*,*N*′-PdCl(NSN)]BF_4 shows well-defined geminal coupling of the diastereotopic methylene protons due to the rigid conformation of the NSN ligand induced by S coordination to Pd.[38] Notably, the ^1H NMR coupling pattern in the ether linkage of **5** is intermediate of the extremes defined by *cis*-*N*,*N*′-$PdCl_2$(NON) and [*N*,*S*,*N*′-PdCl(NSN)]BF_4, consistent with some "locking" of the flexible $_{Me}$COC ligand into the conformation observed in the solid state.[39] The ^{13}C NMR spectrum of **5** is consistent with the ^1H NMR spectrum, with signals due to $_{im}C_{4,5}$

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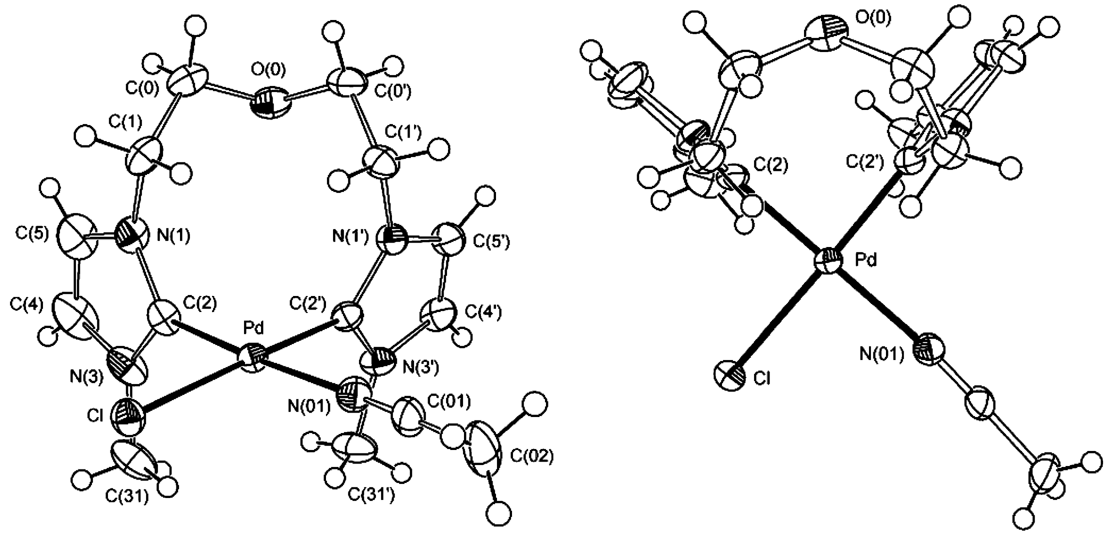
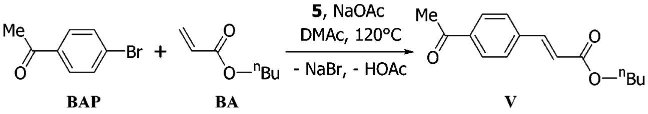


Figure 3. Projections of the cation of **5** oblique (left) and perpendicular (right) to the Pd coordination plane.

Table 3. Results of the Heck Coupling of 4-Bromoacetophenone and *n*-Butyl Acrylate[a] Catalyzed by Complex 5



entry	precatalyst	loading (mmol %)	additive[b]	time (h)[c]	conversion (%, GC)[d]	TON[e]	TOF[f]
1	**5**	1.0		20	23	22 600	1130
2	**5**	0.84	$^{n}Bu_4NBr$	20	88	104 800	5240

[a] Conditions as described in the Experimental Section. [b] 0.2 equiv of $^{n}Bu_4NBr$ relative to BAP added to reaction. [c] Reactions halted after arbitrary time period. [d] Total yield of coupled products. [e] mol(product)/mol(Pd). [f] mol(product)/mol(Pd)/h.

and N*C*H_2 observed as pairs of closely separated peaks near δ 125, 122, and 52, respectively; a single peak was observed for each of the two N-*Me* and O*C*H_2 nuclei; the $_{im}C_2$ signal for **5** could not be distinguished and suggests some fluctionality of the $_{Me}$COC ligand.

The available spectroscopic and crystallographic evidence suggests that, despite the availability of a solvent-occupied vacant site at Pd, the oxygen atom in **5** does not appear to ligate Pd to any significant extent.

Heck Reaction. The Heck coupling of the activated aryl bromide 4-bromoacetophenone (BAP) with *n*-butyl acrylate (BA) under conditions previously described[4] for [Pd(Cl,Me)($_{Me}$C^N^C)]BF_4 complexes was selected to test the activity of **5**. Under standard conditions (*N*,*N*-dimethylacetamide (DMAc), 120 °C, 20 h, 1.0 mmol % loading of **5**) a 23% conversion to the Heck coupling product **V** was obtained, corresponding to a modest TON of 22 600 (Table 3, entry 1). The addition of tetraalkylammonium bromide salts has been observed to yield increased activities in Heck coupling reactions due to presumed catalyst stabilization effects;[40] $^{n}Bu_4NBr$ has been found to be a significantly more effective additive than hydrazine hydrate in combination with Pd^{II}(NHC) precatalysts.[4] Accordingly, addition of 0.2 equiv of $^{n}Bu_4NBr$ relative to BAP gave a ca. 4-fold increase in coupling activity, yielding ultimate TONs and TOFs of 104 800 and 5240 h^{-1} respectively (entry 2). While the activity in entry 2 is approximately 50% higher than that obtained using N-Me-substituted [PdX(**I**/**II**)]$^+$ complexes,[4] it is still well short of some of the activities recorded using Pd(II) complexes of the sterically hindered N-Mes- and N-dipp-substituted variants of **I** and **II**, albeit at the higher temperature of 140 °C.[16]

Conclusions

Silver(I) and Pd(II) complexes of two bis-NHC ligands bearing five-membered sp^3-hybridized linkages have been described; the Ag(I) complexes show variable solid state geometries attributed predominantly to the coordinating ability of the counterion. Complex **4**, bearing a pentamethylene-linked bis-NHC ligand, is the first reported $[Ag_2(\text{bis-NHC})_2]^{2+}$ complex that has been structurally characterized in the presence of the coordinating $[AgBr_2]^-$ ion. In contrast to the report of Simons et al.,[17] the reported structure of **4** demonstrates that dinuclear $[Ag_2(\text{bis-NHC})_2]^{2+}$ geometries may be formed in the presence of halide ions.

Transmetalation of the ether-bridged bis-NHC $_{Me}$COC ligand from Ag(I) to Pd(II) yielded complex **5**. The solid state structure of **5** shows catalytically favorable attributes in the form of a coordination site occupied by a labile solvent molecule and a relatively flexible ligand bearing two strong donor NHC groups and a weak hemilabile oxygen donor.

Complex **5** performed satisfactorily as a precatalyst in a model Heck coupling reaction, with significantly increased activity obtained in the presence of $^{n}Bu_4NBr$. Given the observed activity trends in [PdX(**I**/**II**)]$^+$ complexes in the Heck reaction, replacement of the methyl substituents of the $_{Me}$COC ligand of **5** with the bulkier Mes or dipp groups could result in increased catalytic activity for this system; however, the observed solid state structure of **5** may not be flexible enough to accept such large N-substituents.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry dinitrogen or argon using standard Schlenk

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(39) A reviewer suggests that the chemical shift of the signal at δ 5.30 is sufficiently anomalous to that of the precursor imidazolium salt and the Ag(I) complex to cast doubt on our assignment of the broad triplets at δ 5.30 and 4.15. An alternative suggestion is that the Ha−Hc vicinal coupling in the N−C(Ha)(Hb)−C(Hc)(Hd)−O unit could be large, giving rise to the observed triplets, while the smaller vicinal coupling of the Hb−Hd protons would give rise to the pair of doublets at δ 4.03 and 3.84. We thank the reviewer for the comments.

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techniques; solvents were purified and dried by usual methods,[41] unless otherwise indicated. Imidazolium salt **1** was prepared as reported;[29] all other reagents were used as received. ^1H and ^{13}C (proton decoupled) NMR spectra were run on Varian Gemini 200 or Unity Inova 400 instruments at ambient temperature and referenced to residual solvent signals.[36] Elemental analyses (Carlo Erba EA1108 or ThermoFinnigan Flash 1112 Series EA), liquid secondary ion mass spectrometry (LSIMS, Kratos Concept ISQ), and electrospray mass spectrometry (ESMS, Finnigan MAT LCQ) were performed by the Central Science Laboratory, University of Tasmania. All reactions involving silver compounds were performed with the exclusion of light.

$[Ag_2({}_{Me}COC)_2](OTf)_2$ ($_{Me}$COC = *C,C′*-bis[2-(3-methylimidazolin-2-yliden-1-yl)ethyl] ether) (2). This compound was prepared in 92% yield in a manner analogous to **IV**.[29] X-ray diffraction quality crystals were grown by the diffusion of Et_2O into an MeCN solution of **2**. ^1H NMR (199.98 MHz, d_6-DMSO, δ): identical to **IV**.[29]

1,5-Bis(3-methylimidazolium-1-yl)pentane dibromide (3) ≡ $[{}_{Me}C(CH_2)_5C](HBr)_2$. *N*-Methylimidazole (2.5 mL, 31.4 mmol) was added to 1,5-dibromopentane (2.0 mL, 14.7 mmol) in THF (60 mL) and refluxed for 24 h. The resultant white solid was filtered on a glass frit, washed with Et_2O (2 × 10 mL), and dried in vacuo, yielding **3** (4.70 g, 81%) as a deliquescent white powder that was handled and stored in a glovebox. **3** proved too hygroscopic for successful elemental analysis. MS (LSIMS): *m/z* 313.2 and 315.2 $[M - Br]^+$ (70%), 233.2 $[M - 2Br - H]^+$ (20%). HRMS, $[M - Br]^+$: 313.10265 (−0.44 ppm from calc). ^1H NMR (199.98 MHz, d_6-DMSO, δ): 9.20 (s, 2H, $_{im}C_2$-*H*), 7.80 and 7.73 (d of t, $J = 1.8$ Hz, each 2H, $_{im}C_{4,5}$-*H*), 4.18 (t, $J = 7.2$ Hz, 4H, NCH_2), 3.86 (s, 6H, N-*Me*), 1.82 (quintet, $J = 7.4$ Hz, 4H, NCH$_2$CH_2), 1.21 (br quintet, $J = 7$ Hz, 2H, N(CH$_2$)$_2$CH_2). ^{13}C NMR (50.289 MHz, d_6-DMSO, δ): 136.6 ($_{im}C_2$), 123.6 and 122.3 ($_{im}C_{4,5}$), 48.4 (NCH$_2$), 35.8 (N-*Me*), 28.7 (NCH$_2$CH$_2$), 22.0 (N(CH$_2$)$_2$CH$_2$).

$[Ag_2({}_{Me}C(CH_2)_5C)_2][AgBr_2]_2$ ($_{Me}C(CH_2)_5C$ = *C,C′*-1,5-bis(3-methylimidazolin-2-yliden-1-yl)pentane) (4). **3** (0.500 g, 1.27 mmol) was dissolved in 5:1 DCM−MeOH (60 mL) and Ag_2O (0.2882 g, 1.24 mmol) added. The resulting suspension was stirred at room temperature for 6 h, yielding a gray precipitate and colorless solution. The supernatant was separated and stripped in vacuo and the sticky white residue washed with MeOH (5 × 5 mL). The resultant white powder was dried in vacuo but rapidly discolored, giving **4** (0.20 g, 27%) as a dark cream powder that showed no further signs of decomposition at room temperature. X-ray diffraction quality crystals of **4** were grown by vapor diffusion of Et_2O into a DCM−MeCN−DMSO solution. Elemental analysis gave consistently low results of correct ratio for the presence of the $_{Me}C(CH_2)_5C$ ligand. MS (ESMS): *m/z* 946.3 $[M + AgBr_2]^+$ (25%), 760.6 $[M + Br]^+$ (15%), 421.0 $[M/2 + Br + H]^+$ (15%), 339.3 and 341.2 $[M/2]^+$ (100%). ^1H NMR (399.70 MHz, d_6-DMSO, δ): 7.47 and 7.42 (d × 2, $J = 1.8$ Hz, each 4H, $_{im}C_{4,5}$-*H*), 4.08 (t, $J = 6.8$ Hz, 8H, NCH_2), 3.73 (s, 12H, N-*Me*), 1.79 (br quintet, $J = 7.2$ Hz, 8H, NCH$_2$CH_2), 1.20 (br quintet, $J = 7.0$ Hz, 4H, N(CH$_2$)$_2$CH_2). ^{13}C NMR (100.51 MHz, d_6-DMSO, δ): 180.0 ($_{im}C_2$), 123.1 and 121.6 ($_{im}C_{4,5}$), 50.5 (NCH$_2$), 38.1 and 38.0 (N-*Me*), 30.3 (NCH$_2$CH$_2$), 22.9 (N(CH$_2$)$_2$CH$_2$).

$[PdCl(MeCN)({}_{Me}COC)]BF_4$ ($_{Me}$COC = *C,C′*-bis-[2-(3-methylimidazolin-2-yliden-1-yl)ethyl] ether) (5). **IV** (0.1056 g, 0.246 mmol) was dissolved in DMSO (4 mL) at room temperature and $PdCl_2(MeCN)_2$ (0.0650 g, 0.251 mmol) added. The resulting yellow solution lightened and became turbid over a period of 10 min. After 1 h the reaction was filtered and the filtrate stripped in vacuo. The residue was taken up in MeCN (3 mL), centrifuged to remove AgCl, and concentrated to one-third volume. The crude product was precipitated by the addition of Et_2O (5 mL), washed with Et_2O (2 × 5 mL), then extracted into MeCN (2 mL). Diffusion of Et_2O into this extract gave **5** (0.08 g, 63%) as pale yellow X-ray-quality crystals. Anal. Calcd for $C_{14}H_{21}N_5ClOPdBF_4$: C, 33.36; H, 4.20; N, 13.89. Found: C, 33.16; H, 4.09; N, 13.82. MS (LSIMS): *m/z* 375.0 & 377.0 $[M - MeCN - BF_4]^+$ (30%), 339.0 $[M - Cl - MeCN - BF_4]^+$ (100%). ^1H NMR (399.70 MHz, d_6-DMSO, δ): 7.55 and 7.50 (br d × 2, $J = 13.4$ Hz, each 2H, $_{im}C_{4,5}$-*H*), 5.30 (br t, $J = 12.4$ Hz, 2H) and 4.15 (br t, $J = 12.8$ Hz, 2H, OCH_2), 4.06 (s, 6H, N-*Me*), 4.03 (d, $J = 10.0$ Hz, 2H) and 3.84 (d, $J = 12.0$ Hz, 2H, NCH_2), 2.07 (s, 3H, *Me*CN). ^{13}C NMR (100.51 MHz, d_6-DMSO, δ): 125.3 and 125.1 and 122.4 and 122.0 ($_{im}C_{4,5}$), 71.9 (OCH$_2$), 52.0 and 52.1 (NCH$_2$), 38.0 (N-*Me*), 1.2 (*Me*CN), $_{im}C_2$ and Me*C*N not observed.

Catalysis. To an oven-dried Schlenk flask under a dinitrogen atmosphere were added BAP (0.995 g, 5.00 mmol), NaOAc (0.459 g, 5.60 mmol), $^nBu_4NBr$ (0.322 g, 1.00 mmol, if required), DMAc (5 mL), BA (1.1 mL, 7.7 mmol), and **5** (0.05 mmol, solution in DMAc). The mixture was immediately sealed and put into an oil bath preheated to 120 °C. After stirring for 20 h the reaction was cooled to room temperature and diethyleneglycol mono-*n*-butyl ether (200 μL) added as internal standard, followed by DCM (25 mL) to precipitate inorganic salts. The resulting suspension was filtered and the filtrate analyzed by GC. Product identities were confirmed by ^1H NMR and GC-MS.

Structure Determination. Full spheres of low-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; *T* ca. 153 K), yielding $N_{t(otal)}$ reflections, these merging to *N* unique (R_{int} cited) after empirical/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered observed and used in the full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimates. Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.00n_wF^2)^{-1}$) on $|F|$ at convergence are cited; neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[42] Pertinent results are given below and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Individual diversions in procedure are mentioned as *variata*. CCDC #'s 609339−609341.

Crystal/Refinement Data. 2·$^2/_3$MeCN ≡ $[Ag_2({}_{Me}COC)_2](OTf)_2$·$^2/_3$MeCN ≡ $C_{27\,1/3}H_{38}Ag_2F_6N_{8\,2/3}O_8S_2$, $M = 1009.9$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $Z = 3$ (dimeric f.u.), $a = 11.896(2)$ Å, $b = 12.275(2)$ Å, $c = 22.478(4)$ Å, $\alpha = 86.183(3)°$, $\beta = 89.019(3)°$, $\gamma = 61.050(3)°$, $V = 2865$ Å^3. $D_c = 1.756$ g cm^{-3}. $\mu_{Mo} = 1.22$ mm^{-1}; specimen: 0.36 × 0.23 × 0.11 mm; $T_{min/max} = 0.75$; $2\theta_{max} = 62°$; $N_t = 33112$, $N = 14\,999$ ($R_{int} = 0.055$), $N_o = 10\,936$; $R = 0.051$, R_w ($n_w = 1$) = 0.065.

4 ≡ $[Ag_2({}_{Me}C(CH_2)_5C)_2][AgBr_2]_2$ ≡ $C_{26}H_{40}Ag_4Br_4N_8$, $M = 1215.8$. Monoclinic, space group $C2$ (C_2^3, No. 5), $Z = 2$ (dimeric f.u.), $a = 15.999(3)$ Å, $b = 6.435(1)$ Å, $c = 17.479(3)$ Å, $\beta = 99.433(4)°$, $V = 1731$ Å^3. $D_c = 2.333$ g cm^{-3}. $\mu_{Mo} = 6.9$ mm^{-1}; specimen: 0.20 × 0.12 × 0.05 mm; $T_{min/max} = 0.64$; $N_t = 17175$, $N = 2505$ ($R_{int} = 0.074$), $N_o = 2277$; $R = 0.077$, R_w ($n_w = 7$) = 0.12. *Variata*: Initially, Friedel data were retained distinct, but refinement of x_{abs} being nondefinitive of chirality, data were merged in the final stages of refinement. Caveat: geometries should be treated circumspectly in view of the lack of assignment of absolute configuration of the crystal. Weak data support meaningful anisotropic displacement parameter form refinement for Ag, Br only.

5 ≡ $[PdCl(MeCN)({}_{Me}COC)]BF_4$ ≡ $C_{14}H_{21}BClF_4N_5OPd$, $M = 504.0$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $Z = 4$, $a = 11.6850(9)$ Å, $b = 11.8826(9)$ Å, $c = 13.559(1)$ Å, $\beta = 93.115(2)°$, $V = 1880$ Å^3. $D_c = 1.781$ g cm^{-3}. $\mu_{Mo} = 1.8$ cm^{-1};

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specimen: 0.12 × 0.09 × 0.08 mm, colorless plate; $T_{\mathrm{min/max}} = 0.87$. $N_t = 39102$, $N = 9802$ ($R_{\mathrm{int}} = 0.051$), $N_o = 6662$; $R = 0.036$, R_w ($n_w = 0.4$) $= 0.034$. *Variata*: All $(x, y, z, U_{\mathrm{iso}})_H$ refined throughout.

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Supporting Information Available: Detailed crystallographic discussions and data files in CIF format for complexes **2**·$^2/_3$MeCN, **4**, and **5** are available free of charge at http://pubs.acs.org.

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