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Tripodal N-Heterocyclic Carbene Complexes of Palladium and Copper: Syntheses, Characterization, and Catalytic Activity

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The tris-palladium tripodal N-heterocyclic carbene (NHC) complexes (timteb^{tBu}){Pd(ICy)I$_2$}$_3$ (**4a**), (timteb^{tBu}){Pd(PPh$_3$)I$_2$}$_3$ (**5a**), and (timteb^{dipp}){Pd(PPh$_3$)I$_2$}$_3$ (**5b**) (timteb^{tBu} = 1,3,5-{tris(*tert*-butylimidazol-2-ylidene)methyl}-2,4,6-triethylbenzene, **3a**; ICy = 1,3-dicyclohexylimidazol-2-ylidene; timteb^{dipp} = 1,3,5-{tris({2,6-diisopropylphenyl}imidazol-2-ylidene)methyl}-2,4,6-triethylbenzene, **3b**) were prepared by reaction of Pd(II) precursors with either the free carbenes or imidazolium salts. Treatment of [Cu(NCMe)$_4$]X (X = PF$_6$, BF$_4$) with **3a** or **3b** produced the tris-copper(I) bridged complexes [(timteb^R)Cu$_3$(μ_3-O)]X (R = ^{t}Bu, X = PF$_6$, **6a**; R = dipp, X = BF$_4$, **6b**). Complexes **4a**, **5a**, and **6a** were structurally characterized. The palladium complexes were tested as catalysts for Suzuki−Miyaura and Sonogashira coupling reactions and the copper species also employed for the Sonogashira reaction, as well as for the Ullmann-type arylation of imidazoles and phenols.

Introduction

Polydentate N-heterocyclic carbene (NHC) ligands represent a small subset of the vast array of NHCs now present in the literature.[1] Of the tripodal NHCs, ligand **1**, reported by Fehlhammer and Smith,[2,3] and **2**, prepared by Meyer,[4] have received the most attention (Scheme 1). The presence of a small central linker atom or group gives **1** and **2** the ability to bind a selection of single metal atoms, such as Mn, Fe, Co, Ni, and Cu, within the ligand coordination sphere, whereas the much larger central arene group in the tris-carbene ligand **3** (abbreviated timteb^R)[5] restricts the extent to which a single metal ion can be accommodated between the three carbene arms to only the very large thallium atom.[6,7] As a result, the chemistry of **3** has largely been overlooked.

An alternative mode of coordination for timteb^R involves the three arms anchoring more than one metal center.[8,9] Such an approach has very recently been reported by Hahn and co-workers using **3c** to afford a supramolecular structure based on a [Ag$_3$(**3c**)$_2$]$^{3+}$ framework.[10] We now describe the use of the *tert*-butyl and 2, 6-diisopropylphenyl (abbreviated to dipp)-substituted ligands **3a** and **3b** to form Pd$_3$ and Cu$_3$ complexes. The catalytic activity of both sets of compounds for C−C and C−N coupling reactions has been investigated.

Results and Discussion

Synthesis and Characterization of Palladium timteb^{tBu} and timteb^{dipp} Complexes. The reaction of **3a** with 3 equiv of the

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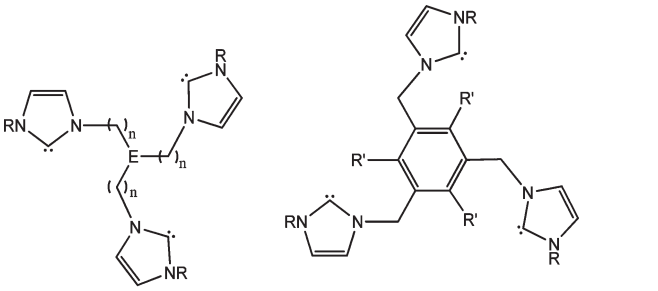
mixed NHC-phosphine complex *trans*-Pd(ICy)(PPh_3)I_2 (ICy = 1,3-dicyclohexylimidazol-2-ylidene)[11] in THF at 70 °C for 4 h allowed the isolation of the Pd_3 complex (timteb^{tBu}){Pd(ICy)I_2}$_3$ (**4a**) as a yellow, air-stable microcrystalline solid in 68% yield (Scheme 2). The ^{1}H NMR spectrum of **4a** provided little in the way of confirmation for the structure, as only minimal differences were seen in the chemical shifts of the compound relative to the free carbene **3a**. This was also the case for the $^{13}C\{^1H\}$ spectrum, apart from at high frequency, where two new singlets at δ 167.6 and 164.9 were observed corresponding to the two types of Pd−C_{NHC} groups.

The molecular structure of **4a** was elucidated by X-ray crystallography, as shown in Figure 1. The compound adopts an idealized C_3-symmetrical arrangement with the three Pd(ICy)I_2 fragments pointing out on the opposite side of the central arene ring to the three ethyl substituents. Each palladium center has a *trans*-timteb^{tBu}-Pd-ICy geometry with the dihedral angles between the planes of the imidazole ring pairs bonded to each palladium ranging from 9.6° to 25.8°. All six

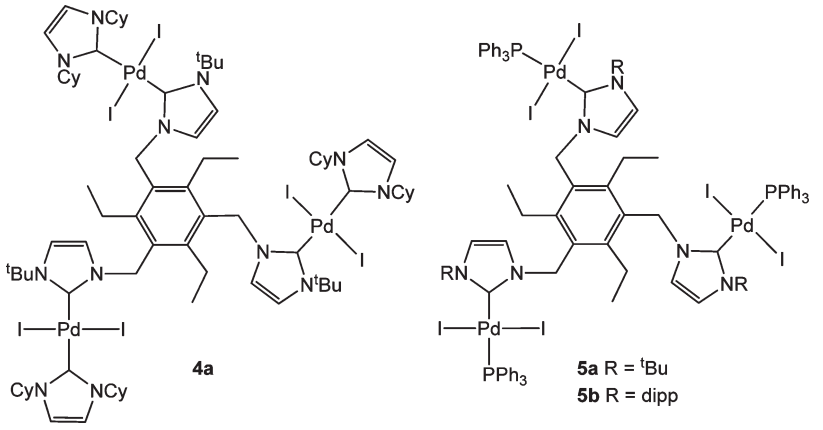
Scheme 1



1 E = BH, BPh, n = 0
2 E = CMe, n = 1; E = N; n = 2

3a R = ^{t}Bu, R' = Et
3b R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (dipp), R' = Et
3c R = Et, R' = H

Scheme 2



4a

5a R = ^{t}Bu
5b R = dipp

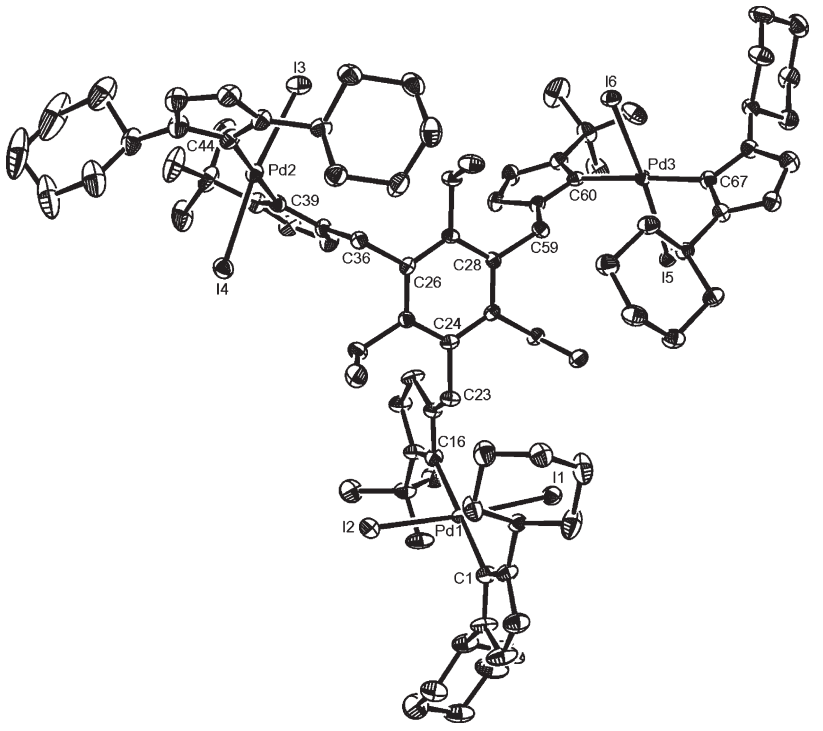


Figure 1. Molecular structure of **4a**. Thermal ellipsoids are represented at 30% probability. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) 2.013(9), Pd(1)−C(16) 2.024(8), Pd(2)−C(39) 2.030(8), Pd(2)−C(44) 2.033(8), Pd(3)−C(60) 2.031(8), Pd(3)−C(67) 2.049(8), C(1)−Pd(1)−C(16) 177.5(3), C(39)−Pd(2)−C(44) 178.0(3), C(60)−Pd(3)−C(67) 175.5(3).

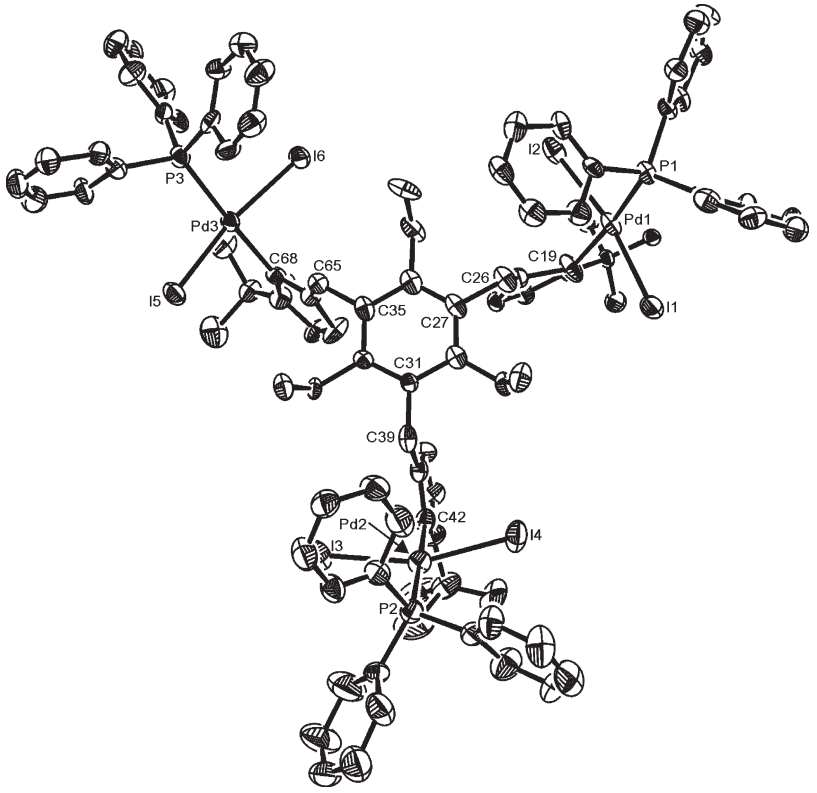
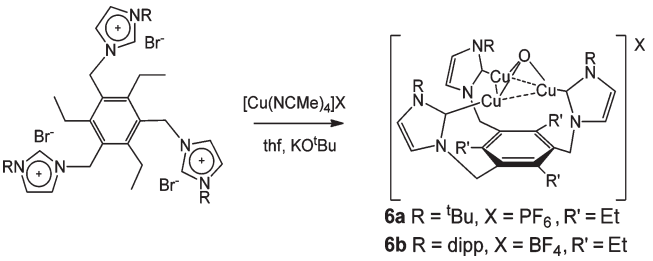


Figure 2. Molecular structure of **5a**. Thermal ellipsoids are represented at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(19) 1.994(18), Pd(2)−C(42) 2.050(18), Pd(3)−C(68) 2.037(16), Pd(1)−P(1) 2.309(5), Pd(2)−P(2) 2.319(5), Pd(3)−P(3) 2.324(5), C(19)−Pd(1)−P(1) 169.4(5).

Pd−C_{NHC} bond lengths range between 2.013(9) and 2.049(8) Å and are unexceptional for Pd^{II}−NHC complexes.[12]

A number of reports have detailed the higher catalytic activity of NHC-Pd-phosphine complexes relative to their bis-carbene analogues.[13,14] This prompted us to synthesize the corresponding timteb^{tBu} and timteb^{dipp} palladium phosphine species **5a** and **5b** (Scheme 2). Both compounds were prepared using a two-step procedure, the first of which involved reaction of $Pd(OAc)_2$ with the corresponding tris-imidazolium salt in the presence of NaI and KO^{t}Bu. Orange solids were formed, which we believe to be the bis-timteb^R complexes $(timteb^R)_2\{PdI_2\}_3$, although the lack of both definitive NMR information (cf. **4a**) and X-ray quality crystals prevented unambiguous characterization of these species.[15] Nevertheless, reaction of both species with PPh_3 in a second step gave the desired products **5a** and **5b**, which were isolated in low yields as a yellow-orange air-stable solids.[16] The high-frequency region of the $^{13}C\{^1H\}$ NMR spectrum again proved to be most informative in terms of spectroscopic characterization, showing doublet carbene resonances at δ 155.0 (**5a**) and δ 163.2 (**5b**) with large trans $^2J_{CP}$ couplings of 192 and 196 Hz, respectively.

Scheme 3



The molecular structure of **5a** was confirmed by X-ray crystallography, as shown in Figure 2. Crystals of only moderate quality could be grown (see Experimental Section), ruling out any detailed comparison of the bond lengths and angles in **5a** versus **4a**.

Formation of Tris-Cu(I) Complexes of timteb^R. Treatment of $[Cu(NCMe)_4]X$ (X = PF_6, BF_4) and 0.33 equiv of the tris-imidazolium salts 1,3,5-{tris(3-*tert*-butylimidazolium)-methyl}-2,4,6-triethylbenzene tribromide or 1,3,5-{tris(2,6-diisopropylphenyl)imidazolium)methyl}-2,4,6-triethylbenzene tribromide with NaO^{t}Bu in thf at room temperature gave, after workup, pale yellow solids, which upon extraction with CH_2Cl_2 afforded the unexpected tris-copper(I) μ_3-oxo complexes $[(timteb^R)Cu_3(\mu_3\text{-}O)]X$ (R = ^{t}Bu, X = PF_6, **6a**; R = dipp, X = BF_4, **6b**) in good to excellent isolated yields (Scheme 3).

The structure of **6a** was established by X-ray crystallography, and the cation is shown in Figure 3. The complex

(11) As reported in the Experimental Section, *trans*-Pd(ICy)(PPh_3)I_2 was prepared by addition of PPh_3 to the dimer $[Pd(ICy)I_2]_2$. The X-ray crystal structure of the dimer is given in the Supporting Information.

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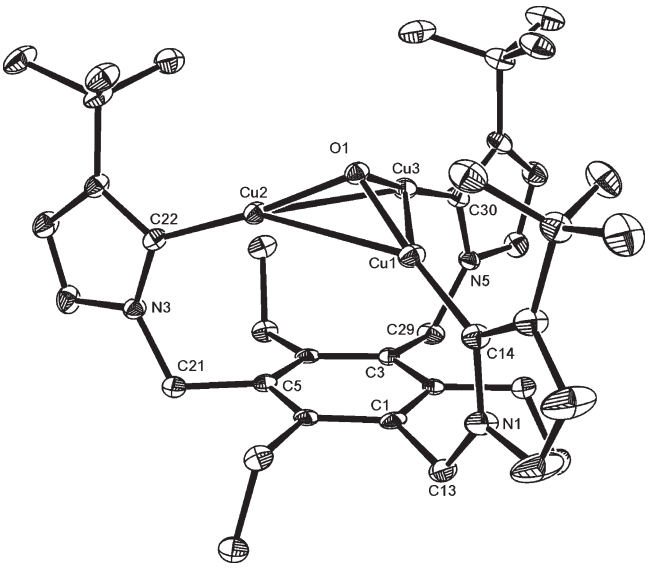

Figure 3. Molecular structure of one of the cations in the asymmetric unit of **6a**. Thermal ellipsoids are represented at 30% probability. Hydrogen atoms, counterions, and solvent moieties are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(14) 1.860(3), Cu(2)−C(22) 1.868(3), Cu(3)−C(30) 1.869(3), Cu(1)−O(1) 1.807(2), Cu(2)−O(1) 1.812(2), Cu(3)−O(1) 1.821(2), O(1)−Cu(1)−C(14) 174.17(13), Cu(1)−O(1)−Cu(2) 106.93(12).

displays pseudo-C_3 symmetry with an axis running through the μ_3-O ligand, the center of the plane defined by the three Cu atoms, and the centroid of the anchoring arene ring. The bridging oxygen lies 0.8 Å above the plane of the three copper atoms, which themselves are located 3 Å above the arene ring of the carbene. The Cu−O distance of 1.81 Å is comparable to the values found in $Cu^{I}_4(\mu_4\text{-O})$ reported by Hakansson and Meyer.[17] The $Cu-C_{NHC}$ bond length in **6a** (1.86 Å) is noticeably shorter than found in other Cu(I)-NHC species,[8,18] while the Cu···Cu separations range from 2.7557(6) to 2.9078(5) Å, outside of the generally accepted range for $d^{10}-d^{10}$ interactions.[19] In contrast to the structures of **4a** and **5a**, in the structure of **6a** only two of the ethyl groups at the tripodal ligand core are directed toward the same side of the central aryl moiety. This reflects, in part, an opening of the pocket created by the presence of the Cu_3O scaffold, which can accommodate a twist of the third ethyl group in the latter structure and is evidenced by the average of the $C_{aryl}-C_{H2}-N_{imidazole}$ angles across all three structures, which register at 112° (**4a**), 111° (**5a**), and 116° (**6a**).

As for the Pd complexes above, the proton NMR spectra of **6a** and **6b** were similar to the spectra of the free ligands. However, the $^{13}C\{^1H\}$ spectra exhibited characteristic high-frequency carbenic resonances at δ 169.2 (**6a**) and δ 177.6 (**6b**).

Table 1. Suzuki−Miyaura and Sonogashira Reactions Catalyzed by 4a, 5a, and 5b

entry	Ph-X	substrate	cat.	*T*/°C	*t*/h	% conv[c]
1[a]	I	$PhB(OH)_2$	**4a**	80	2	73
				120	2	80
2[a]	I	$PhB(OH)_2$	**5a**	80	2	75
				120	2	100
3[a]	I	$PhB(OH)^2$	**5b**	80	2	86
4[a]	Br	$PhB(OH)_2$	**4a**	80	2	3
				120	2	48
5[a]	Br	$PhB(OH)_2$	**5a**	80	3	62
				120	2	100
6[a]	Br	$PhB(OH)_2$	**5b**	80	2	70
7[a]	Cl	$PhB(OH)_2$	**5a**	120	3	21
8[a]	Cl	$PhB(OH)_2$	**5b**	120	3	16
10[b]	I	PhC≡CH	**4a**	80	2	20 (3)[d]
				120	2	28(3)[d]
11[b]	I	PhC≡CH	**5a**	80	2	24
				120	2	54 (3)[d]
12[b]	I	PhC≡CH	**5b**	80	2	7 (3)[d]
				120	2	13 (2)[d]
13[b]	Br	PhC≡CH	**5a**	120	2	4 (3)[d]
14[b]	Br	PhC≡CH	**6a**	120	2	0

[a] 0.5 mmol of aryl halide, 0.75 mmol of phenylboronic acid, 1 mmol of Cs_2CO_3, 0.83 mol % **4a** or **5a**, 1.5 mL of dioxane. [b] 0.5 mmol of aryl halide, 0.7 mmol of PhC≡CH, 1 mmol of Cs_2CO_3, 2 mol % CuI, 1.0 mol % **4a** or **5a**, 1.5 mL of dioxane. [c] Yields were detemined by GC. [d] Yields in parentheses are for the oxidative dimerization product, 1,4-diphenylbutadiyne.

The oxo ligand appears to originate from both the base (NaO^tBu) and the solvent (thf). Thus, **6a** was still formed when the base was changed to $KN(SiMe_3)_2$, but in a lower yield. Replacing thf by MeCN also afforded a lower yield of **6a**, along with a number of other unknown products.

Catalytic Activity of Pd_3 and Cu_3 timteb^R Complexes. The activity of **4a**, **5a**, and **5b** in Suzuki−Miyaura and Sonogashira coupling reactions was investigated, and the results are summarized in Table 1.[20,21] As the focus of the study was essentially to demonstrate the potential of timteb^R as supporting ligands, catalytic activities were not optimized. A comparsion of the Suzuki−Miyaura coupling of $PhB(OH)_2$ with iodo- and bromobenzene (entries 1−6) showed that mixed timteb^R-PPh_3 complexes **5a** and **5b** were more active than the bis-carbene species **4a**. Chlorobenzene proved to be the most unreactive of the aryl halides (entries 7, 8), even with the bulkier timteb^{dipp} containing catalyst.[22] Sonogashira coupling was probed in light of the relatively little impact

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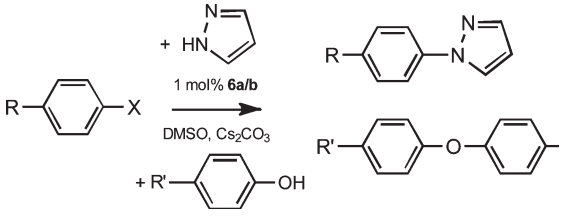
Table 2. Sonogashira Coupling of Aryl Halides and PhC≡CH Catalyzed by 6a and 6b

entry	aryl halide	*t*/h	% conv (**6a**)[a,b]	% conv (**6b**)[a,b]
1	*p*-MeC(O)C_6H_4I	24	96	86
2	*p*-MeC(O)C_6H_4Br	24	83	72
3	*p*-MeC_6H_4I	24	86	91

[a] Reaction conditions: 1 mol % catalyst, aryl halide (0.5 mmol), phenylacetylene (0.6 mmol), Cs_2CO_3 (1.2 equiv), DMSO (1.5 mL), 120 °C. [b] Yields determined by NMR.[24]

Table 3. Catalytic Arylation of Azoles and Phenols with 6a and 6b



entry	aryl halide	phenol	*t*/h	% conv (**6a**)[a]	% conv (**6b**)[a]
1	R = COMe, X = I		24	90[b]	91[b]
2	R = COMe, X = Br		24	65[b]	68[b]
3	R = Me, X = I		24	21[b]	39[b]
4	R = Me, X = Cl		48	0[b]	nd
5	R = Me, X = Cl		24	0[c]	nd
6	R = MeCO, X = I	R′ = Me	24	76[d]	90[d]
7	R = MeCO, X = Br	R′ = Me	24	52[d]	nd
8	R = Me, X = I	R′ = Me	24	52[d]	nd

[a] Yields determined by NMR.[26] [b] 1 mol % catalyst, aryl halide (1.0 mmol), azole (1.5 mmol), Cs_2CO_3 (2 equiv), DMSO (1.5 mL), 100 °C. [c] 6 mol % catalyst, 150 °C. [d] 3 mol % catalyst, aryl halide (1.0 mmol), phenol (1.5 mmol), Cs_2CO_3 (2.0 equiv), DMSO (1.5 mL), 100 °C. nd = not determined.

that Pd-NHCs have made on this class of coupling reaction.[21,23] Catalytic activity was restricted to the coupling of PhC≡CH with iodobenzene (entries 10−12) and necessitated a temperature of 120 °C in order for even moderate conversion to be recorded for the most active catalyst **5a**.

Biffis and co-workers have recently reported the use of trinuclear Cu(I) complexes of the borate-carbene ligand **1** in Sonogashira coupling.[3b] Employing their same reaction conditions, we investigated the activity of **6a** and **6b** for the coupling of phenylacetylene with aryl iodides and bromides as summarized in Table 2. Both complexes showed good activity toward *p*-iodoacetophenone and *p*-iodotoluene, as well as the more challenging *p*-bromoacetophenone.

The catalytic activity of **6a** and **6b** was also tested in Ullmann-type arylation reactions of azoles and phenols (Table 3).[25] Again, the optimum conditions employed by Biffis and co-workers were used.[3] The two complexes showed equivalent activity for the N-arylation of imidazole with *p*-iodo and *p*-bromoacetophenone (entries 1 and 2). Coupling of imidazole with *p*-iodotoluene was more challenging, with **6b** proving to be somewhat more active. Biffis also reported a significant drop in activity on going from *p*-iodoacetophenone to *p*-iodotoluene using $[Cu_3(\mathbf{1})_2]^+$ bearing *N*-Me-substituted **1**, although they noted that upon changing to *N*-benzyl-substituted **1**, *p*-iodotoluene was the more reactive substrate. Disappointingly, **6a** showed no reactivity toward *p*-chloroacetophenone, even at higher temperature and with double the catalyst loading (entries 4 and 5). The *o*-arylation of phenols was briefly investigated, and activities were found to be in line with those for the C−N coupling of imidazole (entries 6−8).

Summary

Tris-palladium and tris-copper complexes of the tripodal N-heterocyclic carbenes 1,3,5-{tris(*tert*-butylimidazol-2-ylidene)methyl}-2,4,6-triethylbenzene (**3a**) and 1,3,5-{tris-({2,6-diisopropylphenyl}imidazol-2-ylidene)methyl}-2,4,6-triethylbenzene (**3b**) have been prepared, fully characterized, and employed in C−X (X = C, N, O) coupling reactions.

The palladium(II) compounds show activity for Suzuki−Miyaura and Sonogashira coupling of aryl iodides and bromides. As expected, higher levels of conversion are observed with the mixed NHC-phosphine species than with the bis-carbene complexes. In the case of the copper, the reaction conditions employed afford copper(I) complexes with an unusual $Cu_3(\mu\text{-O})$ motif that proves active in both Sonogashira and Ullmann arylation reactions. Further modifications to the tripodal NHC substituents may allow higher levels of catalytic performance to be induced. Similarly, it will be of interest to see if **3a** and **3b** can support other metal centers, thus broadening the scope of these unusual NHC ligands.

Experimental Section

All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques using dried and degassed solvents, unless otherwise stated. NMR spectra were recorded on Bruker Avance 300, 400, and 500 MHz NMR spectrometers and referenced to residual solvent signals for ^{1}H and ^{13}C spectra for $CDCl_3$ (δ 7.24, 77.2) and CD_2Cl_2 (δ 5.32, 54.0). Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, UK, or the Elemental Analysis Service, London Metropolitan University, London, UK. 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene, 1-*tert*-butylimidazole, and 2,6-diisopropylphenylimidazole were prepared according to literature methods.[27,28]

[Pd(ICy)I_2]$_2$. The synthesis was based on that for the analogous I^{t}Bu dimer.[13] $Pd(OAc)_2$ (336 mg, 1.5 mmol), NaI (900 mg, 6.0 mmol), KO^{t}Bu (198 mg, 1.8 mmol), and 1,3-dicyclohexylimidazolium tetrafluoroborate (459 mg, 1.5 mmol) were suspended in THF (40 mL), and the mixture was stirred at room temperature for 16 h. The solvent was removed, the products were separated by column chromatography (silica, Et_2O) in air, and the red-orange fraction was isolated. Evaporation gave the product as a red microcrystalline powder in 72% yield (628 mg). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.99 (s, 4H, NC*H*=C*H*N), 5.23

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(m, 4H, NC*H*), 2.30 (m, 8H, CH_2), 1.93 (m, 8H, CH_2), 1.82 (m, 4H, CH_2), 1.63 (m, 8H, CH_2), 1.43 (m, 8H, CH_2), 1.24 (m, 4H, CH_2). ^{13}C{^{1}H} NMR: δ 148.9 (s, N*C*N), 119.4 (s, N(*C*H)$_2$N), 60.7 (s, N*C*H), 33.4 (s, *C*H_2), 25.7 (s, *C*H_2), 25.6 (s, *C*H_2). Anal. Found (calcd) for $C_{30}H_{48}N_4Pd_2I_4$: C, 30.52 (30.40); H, 4.04 (4.08); N, 4.68 (4.73).

1,3,5-{Tris(3-*tert*-butylimidazolium)methyl}-2,4,6-triethylbenzene Tribromide. 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene (2.00 g, 4.58 mmol) was dissolved in 1,4-dioxane (100 mL) in air in a 250 mL round-bottomed flask. The solution was vigorously stirred and 1-*tert*-butylimidazole added (1.66 g, 14 mmol), resulting in the immediate formation of a cloudy suspension. This was stirred for a further 1 h and then heated at 50 °C for 30 min. After cooling, the solid was filtered off, washed with Et_2O (3 × 30 mL), and dried under vacuum to give a white solid. Yield: 2.80 g (76%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 10.88 (s, 3H, NC*H*N), 7.53 (s, 3H, NCH=C*H*N), 7.13 (s, 3H, NCH=C*H*N), 5.79 (s, 6H, $-CH_2$N), 2.66 (quart, 6H, J_{HH} = 7.4 Hz, $-CH_2CH_3$), 1.72 (s, 27H, NC(CH_3)$_3$), 1.09 (t, 9H, J_{HH} = 7.4 Hz, $-CH_2CH_3$). ^{13}C{^{1}H} NMR: δ 147.0 (s, *C*-CH_2N or *C*-CH_2CH_3), 135.9 (s, N*C*H=CHN), 126.9 (s, *C*-CH_2CH_3 or *C*-CH_2N), 121.8 (s, N*C*H=CHN), 120.1 (s, NCH=*C*HN), 60.9 (s, N*C*(CH$_3$)$_3$), 47.4 (s, C-*C*H$_2$N), 30.4 (s, NC(*C*H$_3$)$_3$), 26.7 (s, C-*C*H$_2$CH$_3$), 15.4 (s, C-CH$_2$*C*H$_3$).

1,3,5-{Tris(3-(2,6-diisopropylphenyl)imidazolium)methyl}-2,4,6-triethylbenzene Tribromide. The reaction was performed as for 1,3,5-{tris(3-*tert*-butylimidazolium)methyl}-2,4,6-triethylbenzene tribromide but using 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (3.00 g, 6.8 mmol) and 2,6-diisopropylphenylimidazole (4.65 g, 20.4 mmol). The initially formed suspension was stirred for 24 h at room temperature, then heated at 50 °C for 1 h. The dioxane was removed under vacuum, and the resulting solid filtered and washed with Et_2O (3 × 30 mL). Yield: 4.98 g (65%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 10.69 (s, 3 H, NC*H*N), 8.92 (s, 3 H, NC*H*=CHN), 7.45 (t, 3H, J_{HH} = 7.65 Hz, C$_6$^{i}Pr$_2$*H*$_3$), 7.22 (d, 6H, J_{HH} = 7.65 Hz, C$_6$^{i}Pr$_2$*H*$_3$), 7.07 (s, 3H, NCH=C*H*N), 6.10 (s, 6H, CH_2N), 2.78 (sept, 6H, J_{HH} = 7.65 Hz, C*H*(CH$_3$)$_2$), 2.20 (quart, 6H, J_{HH} = 6.90 Hz, $-CH_2CH_3$), 1.13, (d, 18H, J_{HH} = 7.65 Hz, CH(CH_3)$_2$), 1.07 (d, 18H, J_{HH} = 7.65 Hz, CH(CH_3)$_2$), 0.84 (t, 9H, J_{HH} = 7.53 Hz, $-CH_2CH_3$). ^{13}C{^{1}H} NMR: δ 148.9 (s, *C*-CH_2N), 145.1 (s, *C*$_6$^{i}Pr$_2$H$_3$), 137.9 (s, N*C*HN), 131.9 (s, *C*$_6$^{i}Pr$_2$H$_3$), 130.4 (s, *C*-CH_2CH_3), 128.6 (s, *C*$_6$^{i}Pr$_2$H$_3$) 125.3 (s, N*C*H=CHN), 124.7 (s, *C*$_6$^{i}Pr$_2$H$_3$), 124.4 (s, NCH=*C*HN), 48.7 (s, $-CH_2$N), 31.1 (s, N*C*H(CH$_3$)$_2$), 24.6 (s, NCH(*C*H$_3$)$_2$), 24.3 (s, $-CH_2CH_3$), 24.2 (s, CH(*C*H$_3$)$_2$), 15.9 (s, $-CH_2CH_3$).

***trans*-Pd(ICy)(PPh$_3$)I$_2$.** PPh_3 (273 mg, 1.04 mmol) was added to a THF solution (30 mL) of [Pd(ICy)I$_2$]$_2$ (628 mg, 0.52 mmol), and the mixture stirred rapidly at room temperature for 30 min. Removal of solvent gave an orange residue, which was washed with hexane (3 × 10 mL) and then redissolved in CH_2Cl_2. Slow addition of hexane precipitated out *cis*-Pd(ICy)(PPh_3)I$_2$,[29] leaving *trans*-Pd(ICy)(PPh_3)I$_2$ in solution. After removal of the solid by cannula filtration, the filtrate was reduced to dryness to leave *trans*-Pd(ICy)(PPh_3)I$_2$ as an orange solid, which was recrystallized from $CHCl_3$/hexane. Yield: 482 mg (54%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (m, 6H, PPh_3), 7.39 (m, 9H, PPh_3), 6.96 (d, 2H, J_{HP} = 1.52 Hz, NC*H*=C*H*N), 4.78 (m, 2H, NC*H*), 2.38 (m, 4H, CH_2), 1.88 (m, 4H, CH_2), 1.77 (m, 4H, CH_2), 1.42 (m, 4H, CH_2), 1.23 (m, 2H, CH_2), 1.06 (m, 2H, CH_2). ^{31}P{^{1}H} NMR: δ 17.9 (s). ^{13}C{^{1}H} NMR: δ 152.9 (d, J_{CP} = 191 Hz, N*C*N), 135.6 (d, J_{CP} = 11 Hz, PPh_3), 133.0 (d, J_{CP} = 44 Hz, PPh_3), 131.0 (d, J_{CP} = 3 Hz, PPh_3), 128.0 (d, J_{CP} = 11 Hz, PPh_3), 118.6 (d, J_{CP} = 6 Hz, NCH=*C*HN), 60.6 (s, N*C*H), 33.0 (s, *C*H$_2$), 26.0 (s, *C*H$_2$), 25.6 (s, *C*H$_2$). Anal. Found (calcd) for $C_{33}H_{39}N_2PPdI_2\cdot CHCl_3$: C, 41.68 (41.92); H, 4.07 (4.13); N, 2.96 (2.87).

(timteb^{tBu}){Pd(ICy)I$_2$}$_3$ (4a). *trans*-Pd(ICy)(PPh_3)I$_2$ (482 mg, 0.56 mmol) and 1,3,5-{tris(3-*tert*-butylimidazol-2-ylidene)-methyl}-2,4,6-triethylbenzene (timteb^{tBu}, 161 mg, 0.28 mmol) were suspended in THF (30 mL) in an ampule fitted with a J. Young PTFE valve, and the mixture was stirred at 70 °C for 4 h. After cooling to room temperature, the solvent was removed under vacuum and the residue washed with EtOH (1 × 10 mL) and hexane (3 × 10 mL) to afford the product as a pale yellow solid. Yield: 296 mg (68%). ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.00 (br s, 3H, NCH=C*H*N), 6.93 (s, 6H, NC*H*=C*H*N), 6.14 (br s, 3H, NCH=C*H*N), 5.94 (br m, 6H, CH_2N), 5.08 (m, 6H, NC*H*), 2.65 (br m, 6H, CH_2CH$_3$), 2.40 (m, 24H, CH_2), 1.98 (s, 27H, C(CH_3)$_3$), 1.90 (m, 6H, CH$_2$), 1.74 (m, 6H, CH$_2$), 1.70 (m, 12H, CH$_2$), 1.44 (m, 21H, CH$_2$ + CH$_2$CH_3). ^{13}C{^{1}H} NMR: δ 167.6 (s, N*C*N), 164.9 (s, N*C*N), 148.9 (s, *C*-CH_2N or *C*-CH_2CH_3), 130.3 (s, *C*-CH_2N or *C*-CH_2CH_3), 118.8 (s, N*C*H=CHN), 117.8 (s, N*C*H=*C*N), 60.3 (s, N-*C*H$_2$N), 60.1 (s, N-*C*H), 58.4 (s, N*C*(CH$_3$)$_3$), 33.4 (s, NC(*C*H$_3$)$_3$), 33.3 (s, *C*H$_2$), 26.3 (s, *C*H$_2$), 25.7 (s, *C*H$_2$), 25.6 (s, *C*H$_2$CH$_3$), 17.8 (s, CH$_2$*C*H$_3$). Anal. Found (calcd) for $C_{81}H_{126}N_{12}Pd_3I_6\cdot 3C_4H_8O$: C, 43.28 (43.54); H, 5.67 (5.66); N, 6.66 (6.55).

(timteb^{tBu}){Pd(PPh$_3$)I$_2$}$_3$ (5a). 1,3,5-{Tris(3-*tert*-butylimidazolium)methyl}-2,4,6-triethylbenzene tribromide (250 mg, 0.307 mmol), Pd(OAc)$_2$ (206 mg, 0.924 mmol), NaI (555 mg, 3.696 mmol), and KO^{t}Bu (104 mg, 0.924 mmol) were suspended in THF (50 mL), and the mixture was stirred at room temperature for 48 h. The solvent was removed and the products were separated by column chromatography (silica, THF) in air. The orange-yellow fraction that eluted was evaporated to give 120 mg of an orange solid. This was redissolved in THF (15 mL) and stirred with PPh_3 (70 mg, 0.267 mmol) for 30 min at room temperature. The solvent was removed and the residue washed with hexane (3 × 10 mL) to afford a pale yellow solid, which was recrystallized from CH_2Cl_2/hexane to give 160 mg (19%) of **5a**. ^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.75 (m, 18H, PPh_3), 7.38 (m, 27H, PPh_3), 7.00 (br s, 3H, NC*H*=CHN), 6.21 (br s, 3H, NCH=C*H*N), 5.52 (m, 6H, CH_2N), 2.61 (m, 6H, CH_2CH$_3$), 1.93 (s, 27H, C(CH_3)$_3$), 1.16 (m, 9H, CH$_2$CH_3). ^{31}P{^{1}H} NMR: δ 18.0 (s). ^{13}C{^{1}H} NMR: δ 155.0 (d, J_{CP} = 192 Hz, N*C*N), 147.2 (s, *C*-CH_2N or *C*-CH_2CH_3), 147.0 (s, *C*-CH_2N or *C*-CH_2CH_3), 135.1 (d, J_{CP} = 11 Hz, P*C*$_6$H$_5$), 132.9 (d, J_{CP} = 44.4 Hz, P*C*$_6$H$_5$), 130.2 (s, P*C*$_6$H$_5$), 128.0 (d, J_{CP} = 10 Hz, P*C*$_6$H$_5$), 119.9 (s, N*C*H=NCH), 119.4 (s, NCH=N*C*H) 58.8 (s, N*C*(CH$_3$)$_3$), 50.5 (s, N*C*H$_2$), 37.4 (s, C(*C*H$_3$)$_3$), 27.0 (s, *C*H$_2$CH$_3$), 16.0 (s, CH$_2$*C*H$_3$). Anal. Found (calcd) for $C_{90}H_{99}N_6P_3Pd_3I_6$: C, 44.63 (44.33); H, 3.88 (4.09); N, 3.80 (3.45).

(timteb^{dipp}){Pd(PPh$_3$)I$_2$}$_3$ (5b). 1,3,5-{Tris(3-(2,6-diisopropylphenyl)imidazolium)methyl}-2,4,6-triethylbenzene tribromide (334.8 mg, 0.298 mmol), Pd(OAc)$_2$ (200 mg, 0.893 mmol), NaI (535.7 mg, 3.571 mmol), and KO^{t}Bu (100.3 mg, 0.894 mmol) were suspended in THF (50 mL), and the mixture was stirred at room temperature for 48 h. The solvent was removed and the products were separated by column chromatography (silica, Et_2O) in air. The red fraction that eluted was evaporated to leave 192 mg of a red solid. This was redissolved in CH_2Cl_2 (15 mL) and stirred with PPh_3 (80 mg, 0.305 mmol) for 1 h at room temperature. Removal of the solvent gave an orange residue, which was washed with cold hexane (3 × 10 mL) and then recrystallized from CH_2Cl_2/hexane to afford 153 mg (19% yield) of **5b**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56−7.27 (m, 54H, C$_6$^{i}Pr$_2$H$_3$ + PPh_3), 6.99 (s, 3H, NC*H*=CHN), 6.49 (s, 3H, NCH=C*H*N), 5.88 (s, 6H, N-CH_2), 3.26 (br m, 6H, C*H*(CH$_3$)$_2$), 2.92 (br s, 6H, CH_2CH$_3$), 1.31 (d, J_{HH} = 5.6 Hz, 18H, CH(CH_3)$_2$), 1.14 (br s, 9H, CH$_2$CH_3), 1.02 (d, J_{HH} = 5.6 Hz, 18H, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR: δ 16.2 (s). ^{13}C{^{1}H} NMR: δ 163.2 (d, J_{CP} = 196 Hz), 149.2 (s, *C*-CH_2N or *C*-CH_2CH_3), 147.6

(29) Spectroscopic data for *cis*-Pd(ICy)(PPh_3)I$_2$. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73 (m, 6H, PC$_6$*H*$_5$), 7.37 (m, 9H, PC$_6$*H*$_5$), 6.93 (s, 2H, NC*H*=C*H*N), 5.09 (m, 2H, NC*H*), 2.40 (m, 4H, CH_2), 1.94 (m, 4H, CH_2), 1.79 (m, 2H, CH_2), 1.49 (m, 4H, CH_2), 1.25 (m, 2H, CH_2). ^{31}P{^{1}H} NMR: δ 24.9 (s). ^{13}C{^{1}H} NMR: δ 165.0 (s, N*C*N), 135.5 (d, J_{CP} = 11 Hz, P*C*$_6$H$_5$), 133.0 (d, J_{CP} = 43 Hz, P*C*$_6$H$_5$), 130.9 (s, P*C*$_6$H$_5$), 128.6 (d, J_{CP} = 11 Hz, P*C*$_6$H$_5$), 117.8 (s, N*C*H=*C*HN), 60.1 (s, N*C*H$_2$), 33.4 (s, *C*H$_2$), 25.8 (s, *C*H$_2$), 25.3 (s, *C*H$_2$).

Table 4. Crystal Data and Structure Refinement for 4a, 5a, and 6a

	4a	5a	6a
empirical formula	$C_{86.50}H_{129}Cl_{11}I_6N_{12}Pd_3$	$C_{93}H_{102}Cl_9I_6N_6P_3Pd_3$	$C_{75.50}H_{115}Cl_7Cu_6F_{12}N_{12}O_2P_2$
fw	2807.57	2796.37	2142.13
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	15.6880(2)	17.1220(3)	16.8277(5)
b/Å	19.6950(2)	18.2790(3)	16.9316(6)
c/Å	20.6950(3)	21.0660(5)	17.3903(5)
α/deg	64.251(1)	113.781(1)	75.988(3)
β/deg	87.499(1)	96.783(1)	89.409(2)
γ/deg	76.260(1)	108.888(1)	81.522(3)
U/Å^3	5581.55(12)	5467.95(18)	4753.2(3)
Z	2	2	2
D_c/g cm^{-3}	1.671	1.698	1.497
μ/mm^{-1}	2.445	2.489	1.620
F(000)	2750	2712	2198
cryst size/mm	0.30 × 0.30 × 0.25	0.20 × 0.20 × 0.02	0.43 × 0.21 × 0.04
θ min., max. for data collection	3.55, 27.48	3.77, 22.00	3.64, 26.37
index ranges	$-20 \le h \le 20$; $-25 \le k \le 25$; $-26 \le l \le 26$	$-18 \le h \le 18$; $-19 \le k \le 18$; $-22 \le l \le 22$	$-20 \le h \le 21$; $-21 \le k \le 21$; $-21 \le l \le 17$
reflns collected	89 235	70 271	33 920
indep reflns, R_{int}	25 391, 0.0515	13 290, 0.1294	19 379, 0.0295
reflns obsd ($>2\sigma$)	18 519	8376	11 896
data completeness	0.991	0.992	0.997
absorp corr	multiscan	multiscan	analytical (face indexation)
max., min transmn	0.659, 0.506	0.962, 0.886	0.748, 0.177
data/restraints/params	25 391/0/1082	13 290/184/1224	19 379/28/1062
goodness-of-fit on F^2	1.085	1.050	0.904
final R_1, wR_2 [$I > 2\sigma(I)$]	0.0639, 0.1633	0.0761, 0.1632	0.0405, 0.0910
final R_1, wR_2 (all data)	0.0937, 0.1822	0.1314, 0.1986	0.0731, 0.0958
largest diff. peak, hole/e Å^{-3}	2.281, −1.861	3.332, −1.877	0.713, −0.447

(s, *C*-CH(CH$_3$)$_2$), 135.4 (d, J_{CP} = 10 Hz, P*C*$_6$H$_5$), 134.8 (s, *C*-CH$_2$N or *C*-CH$_2$CH$_3$) 133.3 (d, J_{CP} = 45 Hz, P*C*$_6$H$_5$), 130.5 (d, J_{CP} = 5 Hz, P*C*$_6$H$_5$),130.1 (s, C$_6$^{i}Pr$_2$H$_3$), 127.2 (d, J_{CP} = 10 Hz, P*C*$_6$H$_5$), 124.8 (s, N*C*H=CHN), 124.3 (s, C$_6$^{i}Pr$_2$H$_3$), 119.2 (s, NCH=*C*HN), 50.7 (s, N*C*H$_2$), 29.1 (s, *C*H(CH$_3$)$_2$), 23.6 (s, CH$_2$*C*H$_3$), 26.9 (s, CH(*C*H$_3$)$_2$), 16.8 (s, CH$_2$*C*H$_3$). Anal. Found (calcd) for $C_{114}H_{123}N_6I_6P_3Pd_3$: C, 49.77 (49.65); H, 4.51 (4.43); N, 3.06 (3.15).

[(timteb^{tBu})Cu$_3$(μ_3-O)]PF$_6$ (6a). A suspension of 1,3,5-{tris(3-*tert*-butylimidazolium)methyl}-2,4,6-triethylbenzene tribromide (360 mg, 0.45 mmol), [Cu(NCMe)$_4$]PF$_6$ (500 mg, 1.34 mmol), and NaO^{t}Bu (129 mg, 1.34 mmol) in thf (20 mL) was stirred at room temperature for 2 h. The mixture was passed through a pad of Celite, and the filtrate reduced to dryness. Extraction with CH_2Cl_2 gave a yellow solution, which upon addition of Et_2O gave a colorless solution along with a brown oil. The solution was decanted off and reduced to dryness to afford a white solid. Yield: 210 mg (51%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K): δ 7.33 (s, 3H, NC*H*=CHN), 7.28 (s, 3H, NCH=C*H*N), 5.25 (s, 6H, NCH_2), 2.53 (quart, J_{HH} = 7.57 Hz, 6H, CH_2CH$_3$), 1.72 (s, 27H, NC(CH_3)$_3$), 1.17 (br t, 9H, CH$_2$CH_3). ^{13}C{^{1}H} NMR: δ 169.2 (s, N*C*N), 148.8 (s, *C*-CH$_2$N or *C*-CH$_2$CH$_3$), 131.4 (s, *C*-CH$_2$N or *C*-CH$_2$CH$_3$), 121.6 (s, N*C*H=CHN), 120.1 (s, NCH=*C*HN), 58.3 (s, N*C*-(CH$_3$)$_3$), 49.1 (s, N*C*H$_2$), 32.3 (s, NC(*C*H$_3$)$_3$), 24.7 (s, *C*H$_2$CH$_3$), 14.7 (s, CH$_2$*C*H$_3$). Anal. Found (calcd) for $C_{36}H_{54}N_6OCu_3PF_6$: C, 46.28 (46.87); H, 5.82 (5.90); N, 8.73 (9.11). MS (FAB+): m/z 777.2, [M]$^+$ calculated 777.0.

[(timteb^{dipp})Cu$_3$(μ_3-O)]BF$_4$ (6b). The reaction was performed as for **6a** but with 1,3,5-{tris(3-(2,6-diisopropylphenyl)-imidazolium)methyl}-2,4,6-triethylbenzene tribromide (563 mg, 0.53 mmol), [Cu(NCMe)$_4$]BF$_4$ (500 mg, 1.59 mmol), and NaO^{t}Bu (153 mg, 1.59 mmol) to afford 570 mg (91%) of **6b**. ^{1}H NMR (CD_2Cl_2, 400 MHz, 273 K): δ 7.59 (t, J_{HH} = 7.6 Hz, 3H, ^{i}Pr$_2$C$_6$*H*$_3$), 7.31 (s, 3H, NC*H*=CHN), 7.25 (d, J_{HH} = 7.6 Hz, 6H, ^{i}Pr$_2$C$_6$*H*$_3$), 6.94 (s, 3H, NCH=C*H*N), 5.49 (s, 6H, CH_2N), 2.79 (quart, J_{HH} = 6.8 Hz, 6H, CH_2CH$_3$), 2.36 (sept, J_{HH} = 7.6 Hz, 6H, C*H*(CH$_3$)$_2$), 1.17 (d, J_{HH} = 7.6 Hz, 18H, CH(CH_3)$_2$), 1.09 (d, J_{HH} = 7.6 Hz, 18H, CH(CH_3)$_2$), 0.92 (t, J_{HH} = 6.8 Hz, 9H, CH$_2$*C*H$_3$). ^{13}C{^{1}H} (273 K): δ 177.6 (s, NCN), 148.1 (s, *C*-CH$_2$N or *C*-CH$_2$CH$_3$), 145.7 (s, *C*(CH(CH$_3$)$_2$), 136.0 (s, N-C$_6$^{i}Pr$_2$H$_3$), 130.1 (s, *C*-CH$_2$N or *C*-CH$_2$CH$_3$), 129.8 (s, *p*-*C*H), 124.4 (s, N*C*H=CHN), 124.0 (s, N-C$_6$^{i}Pr$_2$H$_3$), 21.9 (s, NCH=*C*HN), 48.3 (s, *C*H$_2$N), 31.3 (s, *C*H(CH$_3$)$_2$, 28.4 (s, *C*H$_2$CH$_3$), 24.3 (s, CH(*C*H$_3$)$_2$), 15.5 (s, CH$_2$*C*H$_3$). Anal. Found (calcd) for $C_{60}H_{78}N_6OCu_3BF_4$: C, 60.74 (61.24); H, 6.48 (6.68); N, 6.72 (7.14). MS (FAB+): m/z 1089.4, [M]$^+$ calculated 1089.4.

General Catalytic Procedures. (i). Pd-Catalyzed Suzuki−Miyaura Coupling. Aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), cesium carbonate (1.0 mmol), palladium complex (1 mol %), and 1,4-dioxane (1.5 mL) were combined in a J. Young ampule modified to fit a Thermo Scientific Omnistation reactor and heated at 80 or 120 °C for 2 or 3 h. After cooling to room temperature, a 30 μL aliquot was withdrawn and diluted with 1 mL of 1,4-dioxane. A 5 μL amount of anisole was added as an internal standard and the mixture analyzed by GC.

(ii). Pd-Catalyzed Sonogashira Coupling. As for (i) but with aryl halide (0.5 mmol), phenylacetylene (0.7 mmol), cesium carbonate (1.0 mmol), copper iodide (0.01 mmol), palladium complex (1 mol %), and 1,4-dioxane (1.5 mL).

(iii). Cu-Catalyzed Sonogashira Coupling. Similar to (i) but with aryl halide (0.5 mmol), phenylacetylene (0.6 mmol), cesium carbonate (0.6 mmol), copper catalyst (1 mol %), and DMSO (1.5 mL). The mixture was heated and stirred at 120 °C for 24 h, after which it was cooled to room temperature, diluted with 10 mL of CH_2Cl_2, and filtered. The filtrate was washed with water (3 × 10 mL) and dried over $MgSO_4$. The solvent was removed under vacuum to yield the crude product, which was analyzed by NMR to determine the conversion. The products were identified by comparison to the literature.

(iv). Cu-Catalyzed Ullmann-Type Arylation Reactions. Similar to (i) but with aryl halide (1.0 mmol), imidazole or phenol (1.5 mmol), cesium carbonate (2.0 mmol), copper catalyst (1 mol %), and DMSO (1.5 mL). The mixture was heated and stirred at 100 °C for 24 h, after which it was cooled to room temperature, diluted with 10 mL of CH_2Cl_2, and filtered. The filtrate was washed with 5% w/w aqueous $KHCO_3$ solution (2 × 10 mL) and water (2 × 10 mL) and finally dried over $MgSO_4$. The solvent was removed under vacuum to yield the crude product, which was analyzed by NMR to determine the conversion. The products were identified by comparison to the literature.

X-ray Crystallography. Single crystals of compounds for **4a**, **5a**, and **6a** were studied at 150 K using Mo(Kα) radiation. Data collection for **6a** was effected on an Oxford Diffraction Gemini diffractometer, while **4a** and **5a** were analyzed on a Nonius Kappa CCD machine. Details of the data collections, solutions, and refinements are given in Table 4. The structures were solved using SHELXS-97[30] and refined using full-matrix least-squares in SHELXL-97.[30] Refinements were not entirely straightforward, and specific points that merit note are as follows.

In **4a**, the asymmetric unit was seen to contain 4.5 molecules of dichloromethane per one molecule of the complex. Residual electron density is located in the region of the iodides and, as such, is not chemically significant. The asymmetric unit in **5a** consists of one molecule of the gargantuan complex and four regions of solvent (chloroform). The solvent based on C93 is present at full occupancy, while that based on C93 and C94 is each present 60% of the time. The chloroform moiety based on C91 equates to 80% of a full molecule, disordered between two proximate sites in a 60:80 ratio. While the refinement of the model in **5a** provides unambiguous proof of the molecular structure, the caliber of the data is not as high as the authors would wish, and we do not wish to make detailed claims based on the associated metric data. The key issue was that, despite stringent and copious efforts, this compound crystallized as plates of mediocre quality. The smallest dimension of the crystals meant that there was little diffraction at higher Bragg angles; this is also reflected in the R_{int} value and the weighting scheme. Thus, in order to secure a credible refinement, data were truncated at a $2\theta_{max}$ value of 44°. Refinement was also hampered by some disorder and solvent fragments with partial occupancy. Within the complex, N1, N2, and C20−25 exhibited disorder over two sites in a 50:50 ratio. C−Cl and Cl···Cl distance restraints and some ADP restraints were applied to the fractional atoms in disordered solvent regions in order to assist convergence. The residual density maxima are at nonchemically significant distances from I3 and I6, respectively. Efforts to model the two iodides as being split over two sites proved unfruitful and, hence, were abandoned. There is also an artifact of electron density proximate to C57, which resulted in several restraints being incorporated on behalf of the aromatic ring to which this carbon belongs. Finally, there was no evidence for twinning in **5a**.

Two cations, two anions, and 3.5 molecules of dichloromethane constitute the motif in the structure of **6a**. Four of the fluorines in the anion based on P2 were found to be disordered in a 50:50 ratio. P−F and F···F distances were restrained in this disordered region. Cl3 was also disordered over two sites (65:35 ratio in this instance). Hydrogens in this solvent moiety were included at calculated positions relative to the major Cl3 fraction. Unfortunately, 1.5 molecules of the solvent were so badly disordered that modeling was not possible. Hence, PLATON SQUEEZE was employed, and the results were consistent with three additional CH_2Cl_2 entities in the unit cell (1.5 in the asymmetric unit). The formula presented herein has been amended to reflect the presence of this extra solvent.

Crystallographic data for compounds **4a**, **5a**, and **6a**, along with $[Pd(ICy)I_2]_2$ (ESI only), have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 785334−785337. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: CIF files giving X-ray crystallographic data for **4a**, **5a**, and **6a**. X-ray structure of $[Pd(ICy)I_2]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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