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Synthesis, Structure, and Coordination Chemistry of Phosphine-Functionalized Imidazole/Imidazolium Salts and Cleavage of a C−P Bond in an NHC−Phosphenium Salt using a Pd(0) Precursor

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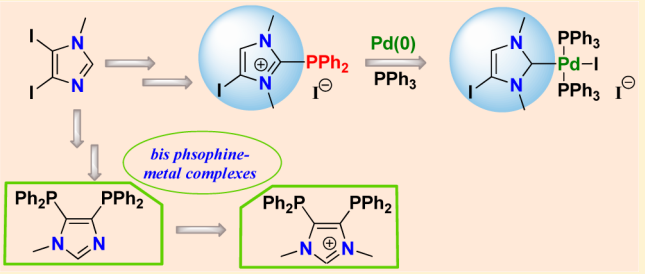
Supporting Information

ABSTRACT: A simple method involving metal−halogen exchange reaction(s) to prepare various phosphine-functionalized imidazole/imidazolium salts and their coordination chemistry with different metal precursors has been described. Interestingly, the reaction of 1,3-dimethyl-2-(diphenylphosphino)-4-iodoimidazolium iodide (**6**) with $Pd_2(dba)_3$ in the presence of triphenylphosphine affords a Pd(II)−NHC complex which involves the cleavage of a C−P bond presumably occurring via oxidative addition of Pd(0) to a C−I bond to afford an in situ generated Pd(II) species, which subsequently reacts with another 1 equiv of **6** through the phosphine center to form an adduct followed by a dephosphinylation reaction.



INTRODUCTION

Phosphines and N-heterocyclic carbenes (NHCs) have played a pivotal role in the development of organometallic chemistry, and stitching these two classes of neutral, two-electron σ-donor ligands together would further foster their application as ligands for transition metals which may prove valuable in catalysis. In view of this, several approaches to append a phosphine group to the NHC skeleton have been made[1,2] and metalation via both functionalities was successfully achieved.[2] A detailed account of this subject has appeared recently.[3] Phosphines attached to the imidazolium (NCN) carbon center are better described as NHC−phosphenium adducts and act as poor donors toward transition metals. The dative and labile nature of the C−P bond is echoed in their reactivity toward weak nucleophiles such as chloride ion, which results in heterolytic cleavage of the C−P bond in such systems to give chlorodiphenylphosphine and free NHC which, although not isolated, has been successfully trapped by Chauvin and co-workers.[4] A similar reactivity pattern was observed in the coordination sphere of metal complexes (Pd, Rh, Cu, etc.) to afford metal−NHC complexes.[4,5] Also, cleavage of a C−P bond in NHC−phosphenium salts with an electron-rich metal center such as Pt(0) was reported by Baker and co-workers involving a nonoxidative addition pathway.[6]

Metal−halogen exchange reactions[7] with diiodoimidazole are particularly handy to achieve functionalization at the backbone position(s) of imidazole and imidazolium salts with mild reagents and conditions. We have recently reported backbone-functionalized imidazolium salts which act as precursors for synthesizing the metal complexes of both normal and mesoionic carbenes.[8] In this contribution, we report metal−halogen exchange reaction(s) with 1-methyl-4,5-diiodoimidazole (**1**) and 1,3-dimethyl-4,5-diiodoimidazolium iodide (**5**) using chlorodiphenylphosphine as the source of the electrophile to afford a phosphine-functionalized imidazole/imidazolium salt at the backbone position for the former case and at the 2-position for the latter. The coordination chemistry of the aforementioned phosphines (**3**, **4**, and **6**) with various metal precursors and, in addition, a rare example of C−P bond cleavage in an NHC−phosphenium salt using a Pd(0) precursor to afford a palladium(II)−carbene complex are discussed.

RESULTS AND DISCUSSION

Synthesis and General Characterization of Functionalized Imidazole/Imidazolium Salts and Their Metal Complexes. The phosphine-functionalized imidazole(s) **2** and **3** were synthesized starting from **1** using sequential metal−halogen exchange reactions. The synthesis of **2** was previously described,[8b] and compound **3** was synthesized by subjecting **2** to another metal−halogen exchange reaction followed by addition of chlorodiphenylphosphine. Compound **3**, isolated as a colorless solid, is stable to air and moisture and show two doublets at −36.2 and −29.3 ppm in its ^{31}P NMR spectrum. Compound **3** on methylation with trimethyloxonium tetrafluoroborate in dichloromethane gave the corresponding imidazolium salt **4** in moderate yield (Scheme 1). The imidazolium salt **4**, with triflate as counteranion, was previously reported by Ruiz and Mesa with a different procedure involving the intermediacy of free carbenes.[2c] On the other hand, metal−

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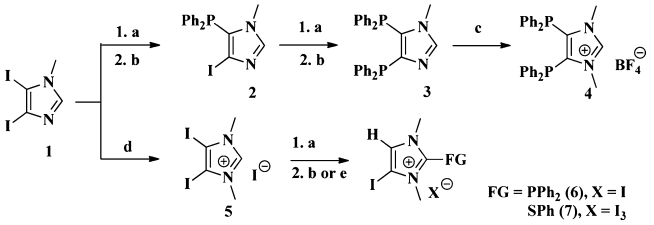
Scheme 1. Synthesis of Phosphine-Functionalized Imidazole/Imidazolium Salts[a]

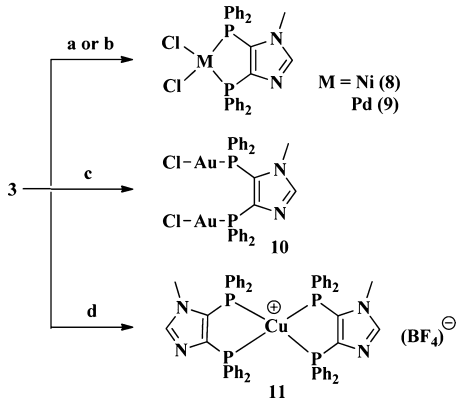


[a]Reagents and conditions: (a) ^{i}PrMgCl, LiCl, THF; (b) PPh_2Cl; (c) $(CH_3)_3O(BF_4)$, DCM; (d) CH_3I, CH_3CN, reflux; (e) $PhSSO_2Ph$ in THF.

halogen exchange reaction with **5**, followed by quenching with electrophile, resulted in the formation of 2-substituted imidazolium salts **6** and **7**, which could be purified by crystallization with methanol. The reaction is envisaged to occur via migration of initially formed carbanion at a backbone center to a more stable NCN carbon center. The products were thoroughly characterized, and their identities were unambiguously established by single-crystal X-ray crystallography (Figures S1 and S2 in the Supporting Information). The C−P bond distance (1.857(8) Å) in **6** is within the range of those observed for similarly known compounds,[9,5c] and crystals of **7** contain a triiodide counteranion plausibly obtained by aerial oxidation of iodide ion during crystallization.

The coordination chemistry of **3** was explored with different metal precursors preferring different coordination geometries, and all of the complexes were structurally characterized (Scheme 2 and Figure 1). Complexes **8** and **9** (Figure S3 in

Scheme 2. Various Binding Modes of 3 with Metals[a]



[a]Reagents and conditions: (a) $NiCl_2·6H_2O$, EtOH + DCM; (b) $PdCl_2$, CH_3CN + DCM; (c) AuCl, DCM; (d) $[Cu(CH_3CN)_4]BF_4$, DCM.

the Supporting Information) are isostructural, with the central metal atom in a square-planar disposition and the five-membered metallacycle almost coplanar to the imidazole ring with the dihedral angles of 5.337(10) and 5.351(9)°, respectively. The bite angles in **8** and **9** were found to be 90.4 and 88.9°, respectively (Table 1), and the values are comparable to those of diphenylphosphinopropane (dppp).[10] The molecular structure of digold complex **10** shows almost two linear P−Au−Cl bonds which are skewed to show intramolecular aurophilic interactions with a Au···Au distances of 3.060(3) and 3.032(1) Å in two crystallographically independent Au−phosphine complexes in the asymmetric unit.

Reaction of **3** with tetrakis(acetonitrile)copper(I) tetrafluoroborate in a 2/1 ratio in dichloromethane afforded the homoleptic complex **11**, in which copper adopts a highly distorted tetrahedral geometry due to the smaller bite angle of **3**. The ^{31}P NMR of **11** shows two broad signals at −15.4 and −19.9 ppm, indicating the nonequivalence of two phosphorus centers. Additionally, the molecular ion peak at m/z 963.2128 $(M - BF_4^-)^+$ in the ESI-MS spectrum indicates the stability of **11** in the solution state.

The coordinating properties of **4** are only marginally different in comparison to **3**, and noteworthy and confounding is the nonreactivity of **4** toward nickel chloride or palladium chloride under experimental conditions similar to those used for the synthesis of **8** or **9**. The ligand **4** is the phosphine analogue of the "Y"-shaped tris(imidazolium) salt reported by Peris and co-workers which afforded homo- and heterodimetallic complexes with different coordination environments.[11] Reaction of **4** with cuprous chloride in a 1/1 metal to ligand ratio afforded two products, **12** and **13**, in which **13** is the major product; both the complexes were thoroughly characterized (Scheme 3). Complex **12** shows a broad signal centered at −27.4 ppm in its ^{31}P NMR spectrum, and all 12 methyl protons appear as a singlet in its ^{1}H NMR spectrum. The molecular structure of **12** consists of a four-membered chloro-bridged dicopper structure with a Cu···Cu bond distance of 2.916(1) Å, and the dihedral angle between the two $CuCl_2$ planes in Cu_2Cl_2 is 25.54(5)° (Figure 2 and Table 2). The bite angle (P−Cu−P) indicates severe distortion from a regular tetrahedral geometry, and the values are comparable to those of DHP (deer-head phosphine, *o*-phenylenebis(diisopropylphosphine), with a bite angle of 92.44(3)°)[12] and **12** crystallizes with one $CuCl_2$ unit and a BF_4 anion. However, the other product **13** was a homoleptic complex similar to **11** with bite angles of 93.26(5)° (P(1)−Cu−P(2)) and 93.38(5)° (P(3)−Cu−P(4)) and was characterized by a single broad peak at −15.2 ppm in its ^{31}P NMR spectrum.

Interestingly, reaction of **4** with tetrakis(acetonitrile)copper(I) tetrafluoroborate in a 1/1 ratio in dichloromethane afforded complex **14**, in which copper is bound to only one bis-phosphine ligand and the other two coordinating sites are occupied by acetonitrile molecules. The coordinated acetonitrile molecules are labile and can be substituted by nitrogen-containing linkers to afford discrete systems or coordination polymers. When complex **14** was treated with 2 equiv of linear linker 4,4′-bipyridine (4,4′-bpy), a discrete Cu_4 tetramer (**15**) was obtained, which was structurally characterized (Figure 3 and Table 3). The asymmetric unit of complex **15** consists of a dinuclear copper complex with two types of Cu centers separated by a distance of 11.088(2) Å, and the tetramer is related by inversion symmetry. The four coordination sites are fulfilled by a bis-phosphine unit and two nitrogen atoms from two different 4,4′-bpy units in Cu(2) (crystallographic numbering), while Cu(1) is bound to two nitrogen donor ligands, namely 4,4′-bpy and acetonitrile molecule, in addition to the bis-phosphine ligand **4**.

C−P Bond Cleavage. Baker and co-workers observed the cleavage of a C−P bond when a NHC−phosphenium adduct was treated with $Pt(PPh_3)_3$ to afford a three-coordinate platinum phosphenium complex via a nonoxidative addition pathway,[6] plausibly with the intermediacy of a NHC−diaminophosphenium−platinum complex.[4b]

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Organometallics XXXX, XXX, XXX−XXX

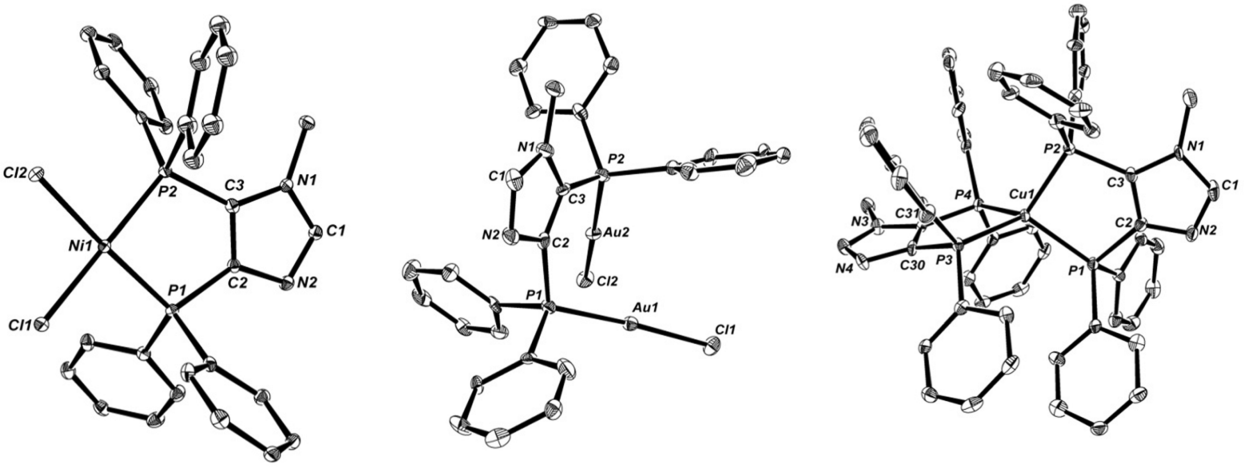
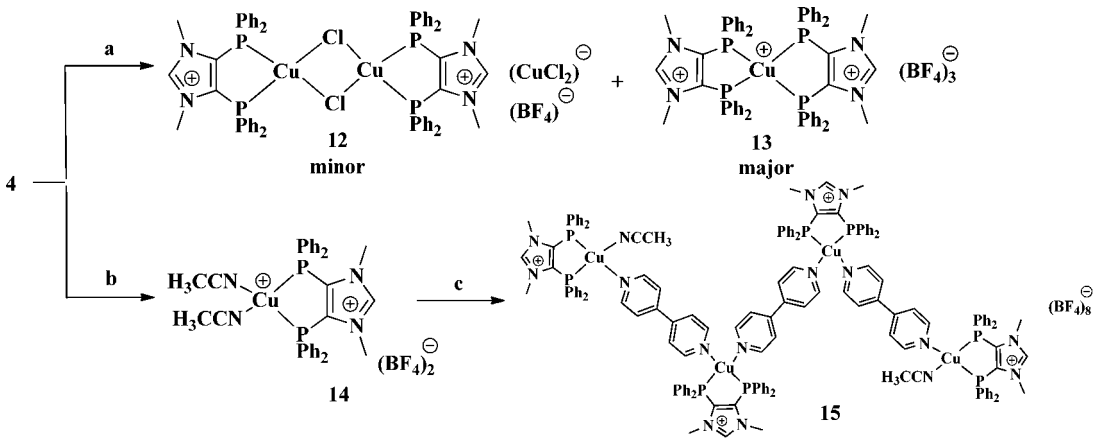


Figure 1. ORTEP diagrams showing 30% probability thermal ellipsoids and selected atom labels for complexes **8** (left), **10** (middle), and **11** (right). Hydrogen atoms, counteranions, and solvent(s) of crystallization have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complexes 8−11

8		9		10		11	
N1−C1	1.335(5)	N1−C1	1.364(4)	N1−C1	1.347(13)	N1−C1	1.367(11)
N2−C1	1.328(5)	N2−C1	1.329(4)	N2−C1	1.314(14)	N2−C1	1.306(12)
C2−C3	1.347(5)	C2−C3	1.375(5)	C2−C3	1.364(15)	C2−C3	1.382(11)
N(1)−C(1)−N(2)	113.7(3)	N(1)−C(1)−N(2)	113.0(3)	N(1)−C(1)−N(2)	114.5(10)	N(1)−C(1)−N(2)	112.3(7)
P(1)−Ni−P(2)	90.38(4)	P(1)−Pd−P(2)	88.89(3)	P(1)−Au(1)−Cl(1)	175.45(11)	P(1)−Cu(1)−P(2)	93.29(8)
				P(2)−Au(2)−Cl(2)	172.28(11)	P(3)−Cu(1)−P(4)	93.20(7)

Scheme 3. Coordination Chemistry of Phosphine-Functionalized Imidazolium Salt 4[a]



[a]Reagents and conditions: (a) CuCl, THF; (b) $[Cu(CH_3CN)_4]BF_4$, DCM; (c) 4,4′−bipyridine, CH_3CN.

On the other hand when the NHC−phosphenium iodide **6** was treated with tris(dibenzylideneacetone)dipalladium(0) in the presence of 2 equiv of triphenylphosphine, the palladium−NHC complex **16** was isolated (Scheme 4). In the solid-state structure of **16** (Figure 4), palladium adopts a square-planar geometry with a Pd−$C_{carbene}$ bond length of 1.996(13) Å, which is in the range of those reported in the literature.[13] The two triphenylphosphine groups coordinated to palladium are trans to each other, consistent with the single sharp peak observed in their ^{31}P NMR spectrum.

The donor ability of this NHC ((I)IMe) on the basis of δ(P) was calculated (TEP 2051 cm^{-1} (CD_2Cl_2) and 2052 cm^{-1} (DMSO-d_6)) using the TEP equation proposed by Iglesias and Albrecht,[14] and it is comparable to those of IMe ([Ir(IMe)-$(CO)_2Cl$]; TEP 2051 cm^{-1}).[15]

The reaction was envisaged to occur via an initial oxidative addition[16] of Pd(0) to the C−I bond to afford a Pd^{II}−MIC species (**A**) (MIC = mesoionic carbene) as an intermediate, which subsequently reacts with another 1 equiv of **6** to form an adduct (**B**). The proposed intermediates could not be isolated, although an ion peak corresponding to **A** (m/z 1037.1063) was observed in the crude reaction mixture through ESI-MS recorded in positive mode (Supporting Information). In the presence of water, the Pd−MIC bond in adduct **B** cleaves to afford the imidazolium salt **17**, and the concomitant nucleophilic attack of hydroxide ion on any one of the possible

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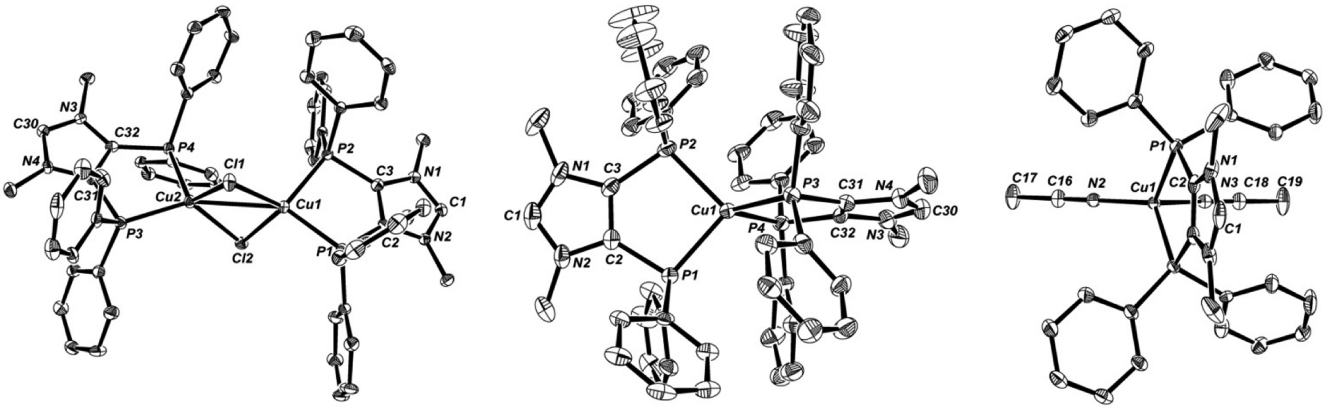


Figure 2. ORTEP diagrams showing 30% probability thermal ellipsoids and selected atom labels for complexes **12** (left), **13** (middle), and **14** (right). Hydrogen atoms, counteranions, and solvent(s) of crystallization have been omitted for clarity.

Table 2. Selected Bond Lengths and Angles in Complexes 12 and 13

12				13			
bond length (Å)		bond angle (deg)		bond length (Å)		bond angle (deg)	
C(2)−C(3)	1.374(6)	P(1)−Cu(1)−P(2)	92.99(5)	C2−C3	1.360(6)	N(1)−C(1)−N(2)	109.8(5)
Cu(1)−P(1)	2.2705(14)	P(3)−Cu(1)−P(4)	93.51(5)	C31−C32	1.344(7)	N(3)−C(30)−N(4)	110.4(5)
Cu(1)−P(2)	2.2691(14)	Cu(1)−Cl(1)−Cu(2)	77.31(5)	Cu−P(1)	2.2740(14)	P(1)−Cu−P(2)	93.26(5)
Cu(1)−Cl(1)	2.3217(14)	Cu(1)−Cl(2)−Cu(2)	76.94(4)	Cu−P(2)	2.2773(13)	P(3)−Cu−P(4)	93.38(5)
Cu(1)−Cl(2)	2.3414(14)	Cl(1)−Cu(1)−Cl(2)	100.98(5)	Cu−P(3)	2.2721(14)	P(1)−Cu−P(3)	124.72(5)
Cu···Cu	2.9164(10)	Cl(2)−Cu(2)−Cl(1)	100.09(5)	Cu−P(4)	2.2690(15)	P(2)−Cu−P(4)	123.05(5)

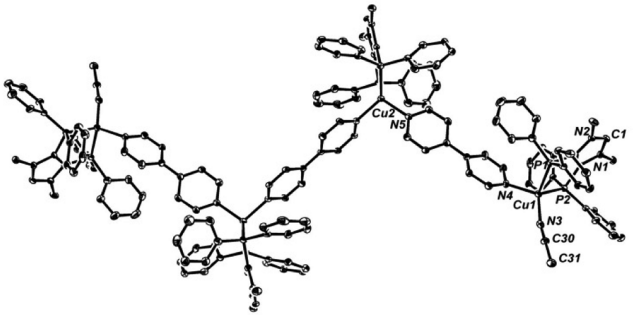
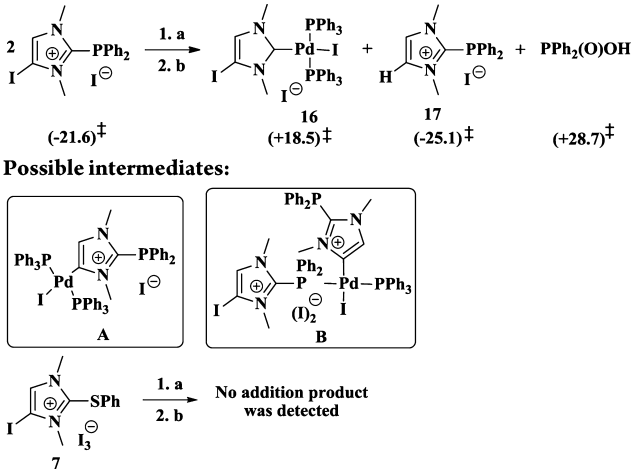


Figure 3. ORTEP diagram showing 30% probability thermal ellipsoids and selected atom labels for complex **15**. Hydrogen atoms, counteranion, and solvent(s) of crystallization have been omitted for clarity.

centers ($P/C_{carbene}/Pd$)[4a] in **B** led to the cleavage of a C−P bond to afford the Pd−NHC complex **16**.

The formation of **17** was supported by ESI-MS (m/z 281.1201), and a signal at −25.1 ppm in the ^{31}P NMR spectrum compares well with that of **6** and similarly known

Scheme 4. Formation of Pd−NHC Complex 16[a]



[a]Reagents and conditions: (a) $Pd_2(dba)_3$, PPh_3, DCM; (b) H_2O. Legend: (‡) values in parentheses correspond to ^{31}P NMR δ values in ppm recorded in CD_2Cl_2.

Table 3. Selected Bond Lengths and Angles in Complexes 14 and 15

14				15			
bond length (Å)		bond angle (deg)		bond length (Å)		bond angle (deg)	
N(1)−C(1)	1.322(4)	N(1)−C1−N(1)#	110.5(4)	C2−C3	1.361(6)	N(1)−C(1)−N(2)	110.6(4)
C2−C2#	1.361(7)	P(1)−Cu−P(1)#	94.11(5)	Cu(1)−P(1)	2.2981(13)	P(1)−Cu(1)−P(2)	93.87(4)
Cu−P(1)	2.2738(9)	N(2)−Cu−N(3)	112.78(15)	Cu(1)−P(2)	2.2663(13)	N(3)−Cu(1)−N(4)	115.09(15)
Cu−N(2)	1.957(4)	N(3)−Cu−P(1)	103.40(7)	Cu(1)−N(3)	1.984(4)	N(4)−Cu(1)−P(1)	100.88(11)
Cu−N(3)	2.006(4)	C(2)−P(1)−Cu(1)	99.94(11)	Cu(1)−N(4)	2.055(3)	N(3)−Cu(1)−P(2)	115.04(11)

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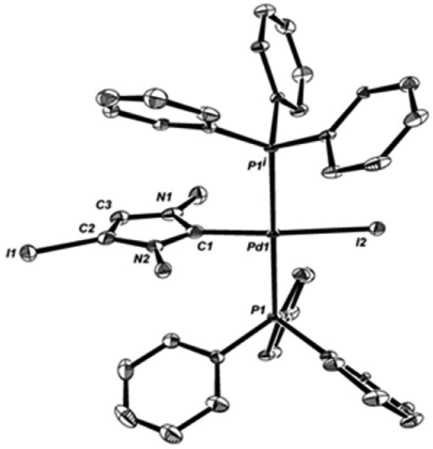

Figure 4. ORTEP diagram showing 30% probability thermal ellipsoids and selected atom labels for complex **16**. Hydrogen atoms, counteranion (I^-), and solvent of crystallization (dichloromethane) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−C1 = 1.369(15), N2−C1 = 1.321(16), C2−C3 = 1.33(2), Pd−C1 = 1.996(13), Pd−I2 = 2.6345(11), Pd−P1 = 2.3433(17); N1−C1−N2 = 105.8(11), C1−Pd−I2 = 170.8(4).

compounds.[9,17] In addition, diphenylphosphinic acid, which could be identified from the crude product mixture using mass spectrometry (m/z 219.0594 $(M + H)^+$ (Figure S5 in the Supporting Information) and ^{31}P NMR (δ 28.7 ppm (CD_2Cl_2), δ 28.1 ppm (DMSO-d_6)), and palladium black were also observed. When a similar reaction was attempted with imidazolium salt **7**, no addition product was detected, indicating the crucial role of the iodide counteranion. The scope of this method to generate a metal−NHC complex with other low-valent metals and detailed mechanistic aspects of the reaction are currently being studied in our laboratory.

CONCLUSIONS

In summary, we have described the synthesis of various phosphine-functionalized imidazole/imidazolium salts using metal−halogen exchange reactions and their coordination chemistry with different metal precursors. Reaction of **4** with various copper(I) precursors afforded different mono- and dinuclear copper complexes (**12**−**14**), and reaction of **14** in the presence of a linker such as 4,4′-bpy gave the interesting tetranuclear complex **15**. In addition the first example of C−P bond cleavage in an NHC−phosphenium salt (**6**) using a Pd(0) precursor to afford a Pd−NHC complex (**16**) is reported.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an inert atmosphere of nitrogen using a standard Schlenk line technique, and solvents were dried according to the standard literature procedures and freshly distilled prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on JEOL (400 and 500 MHz) spectrometers in $CDCl_3$/CD_2Cl_2/DMSO-d_6/CD_3CN as a solvent. The chemical shifts were referenced with respect to TMS and 85% H_3PO_4 for ^1H and ^{31}P NMR, respectively. The ESI mass spectra were recorded on a Waters QTOF instrument. IR spectra were recorded in KBr pellets using an FTIR spectrophotometer operating from 400 to 4000 cm^{-1}. The melting points reported are uncorrected. Phenyl benzenethiosulfonate[18a] and tetrakis(acetonitrile)copper(I) tetrafluoroborate[18b] were prepared according to the literature procedures, and the former was subjected to azeotropic distillation twice in dry toluene and was stored in a glovebox. All other reagents were used as received; isopropylmagnesium chloride was freshly prepared before use.

Synthesis of 3. To a stirred suspension of **2** (3.24 g, 8.26 mmol) and lithium chloride (0.39 g, 9.1 mmol) in dry THF (25 mL) was added a solution of freshly prepared isopropylmagnesium chloride (9.1 mmol) in THF (7 mL) at −20 °C, and after the cold bath was removed, the reaction mixture was stirred for 1.5 h followed by addition of chlorodiphenylphosphine (1.48 mL, 8.26 mmol) at −20 °C. The reaction mixture was further stirred for 3 h, and then all the volatiles were removed under vacuum. The residue was dissolved in DCM, a half-saturated aqueous ammonium chloride solution (40 mL) was added to this solution, the mixture was stirred for a few minutes, and then the layers were separated. The aqueous layer was extracted with DCM (4 × 30 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated to dryness to give an off-white solid. The compound was purified by performing column chromatography (silica gel, 100−200 mesh, eluted using a solvent mixture of 30% ethyl acetate in hexane). Yield: 1.9 g (51%). Mp: 126−130 °C. Anal. Calcd for $C_{28}H_{24}N_2P_2$: C, 74.66; H, 5.37; N, 6.22. Found: C, 74.38; H, 5.50; N, 6.11. ^1H NMR ($CDCl_3$, 500 MHz; δ, ppm): 3.19 (s, 3H, N-CH_3), 7.26−7.43 (m, 20H, C_6H_5), 7.74 (s, 1H, NC*H*N). ^{13}C NMR ($CDCl_3$, 100 MHz; δ, ppm): 34.1, 128.2, 128.3, 128.5, 128.7, 132.0, 132.2, 133.6, 133.8, 134.6, 138.1, 144.7. ^{31}P NMR ($CDCl_3$, 202.49 MHz; δ, ppm): −36.2 (d), −29.3 (d). IR (KBr, cm^{-1}): 3047 (w, br), 1582 (w), 1479 (m), 1431 (m), 1347 (w), 1318 (w), 1268 (w), 1235 (w), 1194 (m), 1092 (w), 998 (w), 965 (w), 910 (w), 860 (w), 751 (s), 739 (vs), 696 (vs), 543 (m), 525 (w), 510 (w), 495 (m), 458 (m), 438 (w). ESI-MS: 451.1493 $(M + H^+)^+$.

Synthesis of 4. To a stirred solution of **3** (0.98 g, 2.18 mmol) in dry DCM was added trimethyloxonium tetrafluoroborate (0.32 g, 2.18 mmol) at room temperature, and the mixture was stirred for 16 h. After that, all the volatiles were removed under vacuum to afford a white flaky solid, which was purified by column chromatography (silica gel 100−200 mesh, eluted using a solvent mixture of 5% methanol in DCM) to afford the title compound as a white solid. Yield: 0.78 g (65%). Mp: 132−138 °C. Anal. Calcd for $C_{29}H_{27}BF_4N_2P_2$: C, 63.07; H, 4.93; N, 5.07. Found: C, 62.80; H, 4.74; N, 5.17. ^1H NMR ($CDCl_3$, 400 MHz; δ, ppm): 3.39 (s, 6H, N-CH_3), 7.28−7.35 (m, 20 H, PPh_2), 9.19 (s, 1H, NC*H*N). ^{13}C NMR ($CDCl_3$, 100 MHz; δ, ppm): 36.7, 129.4, 129.8, 131.0, 132.1, 132.2, 132.3, 145.1. ^{31}P NMR ($CDCl_3$, 162 MHz; δ, ppm): −29.8. IR (KBr, cm^{-1}): 3439 (w, br), 3160 (w), 3053 (w), 2923 (w), 1571 (w), 1481 (w), 1435 (s), 1284 (w), 1203 (w), 1059 (vs), 849 (w), 795 (w), 743 (vs), 696 (vs), 616 (w), 560 (w), 517 (w), 499 (w), 477 (w), 447 (w). ESI-MS: m/z 465.1646 $(M - BF_4^-)^+$.

Synthesis of 5. To a stirred solution of **1** (0.67 g, 2 mmol) in dry acetonitrile (20 mL) was added methyl iodide (0.25 mL, 4 mmol) dropwise at 0 °C. The solution was refluxed for 14 h, during which a colorless precipitate was obtained. The reaction mixture was again cooled to 0−5 °C for complete precipitation. The precipitate obtained after filtration was washed with diethyl ether and dried under vacuum. Yield: 0.90 g (95%). Mp: 230−232 °C dec. Anal. Calcd for $C_5H_7I_3N_2$: C, 12.62; H, 1.48; N, 5.89. Found: C, 12.80, H, 1.50; N, 5.92. ^1H NMR (DMSO-d_6 500 MHz; δ, ppm): 3.78 (s, 6H, CH_3), 9.38 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-d_6 125 MHz; δ, ppm): 39.4, 95.1, 141.2. IR (KBr, cm^{-1}): 3104 (w), 3017 (m), 2934 (w), 1641 (w), 1549 (s), 1501 (w), 1426 (m), 1202 (s), 1099 (s), 769 (w), 608 (w), 463 (w) cm^{-1}. ESI-MS: 348.8691 $(M - I^-)^+$.

Synthesis of 6. To a stirred suspension of **5** (4.71 g, 9.9 mmol) and lithium chloride (0.46 g, 10.9 mmol) in dry THF (50 mL) was added a solution of isopropylmagnesium chloride (10.9 mmol) in THF (9 mL) at −20 °C. The cold bath was removed, and the reaction mixture was stirred further for 1 h 15 min, followed by addition of chlorodiphenylphosphine (1.8 mL, 9.9 mmol) at −20 °C, and stirred for another 4 h, after which all volatiles were removed under vacuum. The residue was dissolved in DCM, and an aqueous half-saturated ammonium chloride solution (40 mL) was added. The resulting mixture was filtered through a frit containing a pad of Celite, and the organic layer was dried over magnesium sulfate and filtered. The

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Organometallics XXXX, XXX, XXX−XXX

filtrate was concentrated to give a light brown oil, which was triturated with diethyl ether to give a powdery yellow solid. The solid on washing with cold methanol (three to four times) gave a white solid, which was crystallized in methanol. Yield: 2.8 g (53% excluding crystallization losses). Mp: 150−155 °C dec. Anal. Calcd for $C_{17}H_{17}I_2N_2P$: C, 38.23; H, 3.21; N, 5.24. Found: C, 38.27; H, 3.10; N, 5.28. ^{1}H NMR (DMSO-d_6, 500 MHz; δ, ppm): 3.55 (s, 3H, N-CH_3), 3.58 (s, 3H, N-CH_3), 7.41−7.53 (m, 10H, PPh_2), 8.20 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6, 125 MHz; δ, ppm): 36.5, 37.8, 128.1, 129.9, 130.1, 131.6, 131.7, 132.5, 139.9. ^{31}P NMR (DMSO-d_6, 202.49 MHz; δ, ppm): −23.6. IR (KBr, cm^{-1}): 3049 (m), 1636 (w), 1546 (w), 1468 (m), 1434 (s), 1310 (w), 1198 (m), 1090 (m), 918 (w), 819 (m), 744 (vs), 700 (s), 688 (vs), 668 (m), 627 (w), 536 (m), 506 (s), 455 (w), 433 (m). ESI-MS: 407.0175 $(M - I^-)^+$.

Synthesis of 7. The same procedure as for **6** was used. **5** (5.23 g, 11.0 mmol), LiCl (0.51 g, 12.1 mmol), isopropylmagnesium chloride (12.1 mmol), and phenyl benzenethiosulfonate (11.0 mmol, 2.75 g) in 15 mL of THF were used. The product was crystallized in methanol as brown crystals. Yield: 2.13 g (27%). Mp: 104−110 °C. Anal. Calcd for $C_{11}H_{12}I_4N_2S$: C, 18.56; H, 1.70; N, 3.93. Found: C, 18.61; H, 1.59; N, 3.96. ^{1}H NMR (DMSO-d_6, 500 MHz; δ, ppm): 3.80 (s, 6H, N-CH_3), 7.40 (br, 5H, SPh), 8.22 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6, 125 MHz; δ, ppm): 37.2, 38.7, 126.1, 129.3, 129.7, 130.6, 130.9, 132.6, 140.0. IR (KBr, cm^{-1}): 3145 (m), 1576 (w), 1543 (w), 1476 (s), 1439 (m), 1427 (m), 1181 (w), 998 (w), 790 (w), 745 (vs), 695 (m), 686 (m), 617 (w), 521 (w), 473 (w). ESI-MS: m/z 330.9766 $(M - I_3^-)^+$.

Synthesis of Complex 8. To an ethanolic solution (10 mL) of nickel chloride hexahydrate (0.053 g, 0.22 mmol) was added a dichloromethane (20 mL) solution of **3** (0.10 g, 0.22 mmol). Immediately an intensely red solution was formed, which was stirred further for 1 h. The solution was filtered, and the filtrate was kept for crystallization under slow evaporation to afford red crystals of **8** suitable for single-crystal X-ray diffraction. Yield: 0.084 g (65%). Mp: >250 °C. Anal. Calcd for $C_{28}H_{24}Cl_2N_2NiP_2$: C, 57.98; H, 4.17; N, 4.83. Found: C, 57.60; H, 4.20; N, 4.81. ^{1}H NMR (CD_2Cl_2, 400 MHz; δ, ppm): 3.19 (s, 3H, N-CH_3), 7.43−8.01 [m, 21H, 2(PPh_2), NCHN]. ^{13}C NMR (CD_2Cl_2, 100 MHz; δ, ppm): 29.7, 128.6, 128.7, 129.3, 131.6, 132.2, 133.5, 133.6, 134.2. ^{31}P NMR (CD_2Cl_2, 162 MHz; δ, ppm): 9.1 (d), 13.9 (d). IR (KBr, cm^{-1}): 3401 (m, br), 1623 (w), 1482 (m), 1434 (s), 1339 (w), 1256 (w), 1216 (m), 1187 (m), 1136 (m), 1096 (s), 1028 (w), 998 (w), 855 (w), 760 (m), 746 (s), 710 (vs), 691 (vs), 620 (w), 583 (vs), 531 (vs), 507 (s), 487 (s). ESI-MS: m/z 575.0400 $(M - Cl^- + CH_3OH)^+$.

Synthesis of Complex 9. To a suspension of palladium chloride (0.021 g, 0.12 mmol) in acetonitrile (10 mL) was added a dichlormethane solution (15 mL) of **3** (0.054 g, 0.12 mmol). The resulting orange solution was stirred for 1 h and was filtered to give a clear solution, which was kept for crystallization. Slow evaporation led to the formation of yellow crystals suitable for single-crystal X-ray diffraction. Yield: (0.060 g, 80%). Mp: >250 °C. Anal. Calcd for $C_{28}H_{24}Cl_2N_2P_2Pd$: C, 53.57; H, 3.85; N, 4.46. Found: C, 53.87; H, 3.70; N, 4.55. ^{1}H NMR (DMSO-d_6, 400 MHz; δ, ppm): 3.25(s, 3H, N-CH_3), 7.49−7.84 (m, 20 H, PPh_2), 8.46 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-d_6, 100 MHz; δ, ppm): 34.5, 126.6, 129.4, 129.5, 130.0, 130.1, 132.6, 133.3, 133.9, 134.0, 134.2. ^{31}P NMR (DMSO-d_6, 162 MHz; δ, ppm): 18.1 (d), 22.4 (d). IR (KBr, cm^{-1}): 3441 (w, br), 1481 (m), 1434 (vs), 1338 (w), 1257 (w), 1217 (m), 1187 (w), 1144 (w), 1097 (vs), 997 (w), 983 (w), 857 (w), 761 (w), 746 (s), 711 (vs), 690 (vs), 621 (w), 587 (vs), 532 (vs), 507 (s), 465 (w). ESI-MS: m/z 632.0416 $(M - Cl^- + CH_3CN)^+$.

Synthesis of Complex 10. To a stirred solution of **3** (0.15 g, 0.33 mmol) in DCM was added AuCl (0.155 g, 0.66 mmol) as a solid, and the reaction mixture was stirred for 3 h and filtered to give a clear colorless solution. The filtrate was concentrated to dryness under vacuum to afford the title compound as a colorless solid. Yield: 0.29 g (94%). Mp: 165−170 °C. Anal. Calcd for $C_{28}H_{24}Au_2Cl_2N_2P_2$: C, 36.74; H, 2.64; N, 3.06. Found: C, 36.68; H, 2.59; N, 2.99. ^{1}H NMR (CD_3CN, 500 MHz; δ, ppm): 2.96 (s, 3H, N-CH_3), 7.47−7.64 (m, 20H, PPh_2), 7.86 (s, 1H, NCHN). ^{13}C NMR (CD_3CN, 100 MHz; δ, ppm): 35.4, 129.0, 129.1, 129.8, 130.0, 132.1, 132.6, 133.2, 133.3, 134.5, 134.7. ^{31}P NMR (CD_3CN, 162 MHz; δ, ppm): 4.4 (d), 14.5 (d). IR (KBr, cm^{-1}): 3433 (br, w), 3094 (w), 3056 (w), 1586 (w), 1494 (w), 1481 (w), 1436 (s), 1357 (w), 1309 (w), 1252 (w), 1207 (w), 1184 (w), 1127 (w), 1101 (m), 1027 (w), 997 (w), 875 (w), 750 (s), 717 (s), 690 (vs), 634 (w), 619 (w), 578 (vs), 554 (m), 522 (w), 502 (s), 492 (s), 412 (w). ESI-MS: sample does not give a satisfactory ESI-MS analysis.

Synthesis of Complex 11. To a dichloromethane solution of **3** (0.14 g, 0.32 mmol) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.050 g, 0.16 mmol) as a solid, and the reaction mixture was stirred for 3 h followed by filtration with a medium-porosity frit to give a clear solution. The filtrate was concentrated to dryness under vacuum to afford the title compound as a colorless solid. Yield: 0.15 g (93%). Mp: >250 °C. Anal. Calcd for $C_{56}H_{48}BCuF_4N_4P_4$: C, 63.98; H, 4.60; N, 5.33. Found: C, 64.28; H, 4.57; N, 5.53. ^{1}H NMR ($CDCl_3$, 500 MHz; δ, ppm): 3.05 (s, 6H, N-CH_3), 6.98−7.30 (m, 42H, PPh_2, NCHN). ^{13}C NMR ($CDCl_3$, 100 MHz; δ, ppm): 34.2, 128.8, 129.6, 129.8, 130.1, 130.5, 130.6, 130.8, 131.1, 132.2, 132.9, 149.5. ^{31}P NMR ($CDCl_3$, 202.49 MHz; δ, ppm): −15.4 (br), −19.9 (br). IR (KBr, cm^{-1}): 3445 (w, br), 3054 (w), 1586 (w), 1482 (s), 1435 (s), 1330 (w), 1250 (w), 1210 (w), 1185 (w), 1055 (vs), 998 (m), 741 (s), 711 (m), 692 (vs), 558 (s), 528 (s), 511 (m), 498 (m), 479 (m). ESI-MS: m/z 963.2128 $(M - BF_4^-)^+$.

Synthesis of Complexes 12 and 13. To a stirred solution of **4** (0.102 g, 0.185 mmol) in THF (30 mL) was added CuCl (0.018 g, 0.185 mmol) as a solid, and the mixture was stirred overnight (12 h), during which a colorless solid precipitated out. The residue and the filtrate were separated, the residue was washed once with THF, and the washings were combined with the filtrate. Slow diffusion of diethyl ether into an acetonitrile solution of the residue gave crystals of **12** in low yield. The filtrate obtained as above was kept for crystallization by slow evaporation, and colorless crystals of **13** were obtained in THF after 3 days. Data for complex **12** are as follows. Yield: 6.3 mg (5%). Mp: >250 °C. Anal. Calcd for $C_{58}H_{54}BCl_4Cu_3F_4N_4P_4$: C, 51.59; H, 4.03; N, 4.15. Found: C, 51.82, H, 4.09; N, 4.16. ^{1}H NMR (CD_3CN, 500 MHz; δ, ppm): 3.23 (s, 12H, N-CH_3), 7.44−7.53 (m, 40H, PPh_2), 8.71 (s, 2H, NCHN). ^{13}C NMR (CD_3CN, 125 MHz; δ, ppm): 36.5, 127.3, 129.5, 131.0, 132.6, 146.7. ^{31}P NMR (CD_3CN, 202.49 MHz; δ, ppm): −27.4. IR (KBr, cm^{-1}): 3451 (br, w), 3162 (w), 3054 (w), 2250 (w), 1562 (m), 1515 (w), 1483 (m), 1435 (s), 1373 (w), 1208 (w), 1099 (m), 1084 (s), 1059 (s), 916 (w), 855 (w), 791 (w), 748 (vs), 695 (vs), 612 (w), 539 (m), 517 (m), 500 (m), 475 (m). ESI-MS: 1215.1224 $[M - (CuCl_2)^-]^+$. Data for complex **13** are as follows. Yield: 0.10 g (86%). Mp: >250 °C. Anal. Calcd for $C_{58}H_{54}B_3CuF_{12}N_4P_4$: C, 55.51; H, 4.34; N, 4.46. Found: C, 55.82; H, 4.11; N, 4.20. ^{1}H NMR (CD_3CN, 400 MHz; δ, ppm): 3.11 (s, 12H, N-CH_3), 7.18−7.41(m, 40H, PPh_2), 8.99 (s, br, 2H, NCHN). ^{13}C NMR (CD_3CN, 100 MHz; δ, ppm): 36.4, 129.8, 131.1, 131.2, 131.3, 131.4, 131.6. ^{31}P NMR (CD_3CN, 162 MHz; δ, ppm): −15.2 (br). IR (KBr, cm^{-1}): 3557 (w), 3613 (w), 3400 (m, br), 3145 (w), 3074 (w), 2959 (w), 2861 (w), 1634 (w), 1562 (m), 1482 (m), 1438 (s), 1285 (w), 1213 (m), 1055 (vs, br), 997 (s), 793 (w), 745 (s), 696 (s), 613 (w), 559 (w), 544 (m), 513 (m), 499 (m), 478 (m), 460 (m). ESI-MS: m/z 331.0806 $[(M - 3BF_4^-)^{3+}/3]$.

Synthesis of Complex 14. The imidazolium salt **4** (0.20 g, 0.37 mmol) and $[Cu(CH_3CN)_4]BF_4$ (0.12 g, 0.37 mmol) were combined in a Schlenk flask, and dichloromethane (20 mL) was added. The reaction mixture was stirred for 3 h and then filtered under nitrogen using a frit. The filtrate, obtained as a clear solution, was concentrated to dryness to give the title compound as a colorless solid. The compound was crystallized by layering an acetonitrile solution of **14** with diethyl ether at 0 °C. Yield: 0.27 g (94%). Mp: 202−207 °C dec. Anal. Calcd for $C_{33}H_{33}B_2CuF_8N_4P_2$: C, 50.51; H, 4.24; N, 7.14. Found: C, 50.52; H, 4.22; N, 7.24. ^{1}H NMR (CD_2Cl_2, 400 MHz; δ, ppm): 2.12 [s, 6H, 2(CH_3CN)], 3.37 (s, 6H, N-CH_3), 7.48−7.54 (m, 20H, PPh_2), 8.86 (s, 1H, NCHN). ^{13}C NMR (CD_2Cl_2, 100 MHz; δ, ppm): 2.2, 36.8, 125.7, 130.1, 131.5, 131.9, 132.0, 132.1, 148.0. ^{31}P NMR (DMSO-d_6, 202.49 MHz; δ, ppm): −26.9. IR (KBr, cm^{-1}): 3443 (w, br), 3174 (w), 2964 (w), 2275 (w), 1631 (w), 1568 (w), 1483 (w), 1438 (w), 1262 (s), 1217 (w), 1094 (vs), 1031 (vs), 863

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Organometallics XXXX, XXX, XXX−XXX

(w), 801 (vs), 745 (w), 695 (m), 613 (w), 559 (w), 500 (w), 481 (w). ESI-MS: m/z 656.1272 $[M - (BF_4)^- - CH_3CN]^+$.

Synthesis of Complex 15. To an acetonitrile solution of complex **14** (0.040 g, 0.05 mmol) was added 4,4′-bpy (0.016 g, 0.10 mmol) as a solid, the mixture was stirred for 5 h, and a clear colorless solution was obtained. The reaction mixture was concentrated to one-third of its volume and filtered, and the filtrate was layered with diethyl ether and kept at 0 °C. Pale yellow crystals were obtained after 1 week, which were collected, washed with diethyl ether, and dried under vacuum. Yield: 0.036 g (84%). Mp: 140−145 °C. Anal. Calcd for $C_{151}H_{141}B_8Cu_4F_{32}N_{16}P_8$: C, 53.72; H, 4.21; N, 6.64. Found: C, 53.98; H, 4.30; N, 7.02. IR (KBr, cm^{-1}): 3439 (w, br), 3057 (w), 1605 (m), 1564 (w), 1532 (w), 1484 (w), 1437 (m), 1411 (w), 1285 (w), 1218 (w), 1057 (vs), 914 (w), 809 (m), 747 (m), 697(m), 620 (w), 542 (w), 478 (w).

Synthesis of 16. $Pd_2(dba)_3$ (0.091 g, 0.10 mmol) and PPh_3 (0.105 g, 0.40 mmol) were combined in a Schlenk flask, and dichloromethane (20 mL) was added. The resulting red mixture was stirred for 10 min under nitrogen, after which it was transferred to a solution of **6** (0.107 g, 0.20 mmol) in dichloromethane through a cannula; the reaction mixture was heated to reflux under nitrogen for 4 h. After it was cooled, the resulting mixture was filtered through a pad of Celite, the filtrate was washed with water (4 × 30 mL), and the organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated to dryness and washed with pentane to afford the title compound as a yellow solid. Slow evaporation of a dichloromethane solution of **16** afforded single crystals suitable for X-ray diffraction. Yield: 0.105 g (47% with respect to $Pd_2(dba)_3$). Mp: 90−95 °C dec. Anal. Calcd for $C_{41}H_{37}I_3N_2P_2Pd$: C, 44.49; H, 3.37; N, 2.53. Found: C, 44.79; H, 3.43; N, 2.51. ^{1}H NMR (DMSO-d_6, 500 MHz; δ, ppm): 3.03 (s, 3H, N-CH_3), 3.35 (s, 3H, N-CH_3), 6.92 (s, 1H, C_5H), 7.42−7.55 (m, 30H, PPh_3). ^{13}C NMR (DMSO-d_6, 100 MHz; δ, ppm): 37.7, 38.1, 126.1, 128.9, 129.0, 129.1, 129.2, 129.4, 129.5, 131.6, 131.9, 132.0, 132.6, 133.7, 134.5, carbene carbon signal could not be detected. ^{31}P NMR (DMSO-d_6, 162 MHz; δ, ppm): 18.3. IR (KBr, cm^{-1}): 3434 (w, br), 3051 (w), 1649 (w), 1617 (w), 1585 (w), 1572 (w), 1479 (m), 1434 (vs), 1389 (w), 1337 (w), 1310 (w), 1265 (w), 1182 (m), 1095 (s), 1026 (w), 998 (w), 743 (m), 693 (vs), 616 (w), 542 (w), 521 (s), 511 (s), 494 (m), 458 (w), 425 (w). ESI-MS: m/z 978.9639 $(M - I^-)^+$.

X-ray Structure Solution and Refinement.[19] The crystal data were collected on a Bruker Apex Smart diffractometer. Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All of the structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2. All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. One of the disordered counteranions BF_4^- present in the crystal structure of **13** and disordered solvent molecules in **11**, **13**, and **15** were treated by squeeze refinement using PLATON.[20]

■ ASSOCIATED CONTENT

Supporting Information

Figures, a table, and CIF files giving crystal structure diagrams of **6**, **7**, and **9**, isotopic distributions of **16**, NMR spectra, and crystallographic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00336.

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Notes

The authors declare no competing financial interest.

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