ORGANOMETALLICS-

Synthesis of Imidazole-Based Functionalized Mesoionic Carbene Complexes of Palladium: Comparison of Donor Properties and Catalytic Activity toward Suzuki–Miyaura Coupling

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S Supporting Information

ABSTRACT: Three different backbone-monofunctionalized imidazolium salts have been synthesized using the metal-halogen exchange procedure, and their corresponding mesoionic carbene complexes with palladium were prepared via oxidative addition without protection of the C2 position. The donor properties were evaluated with ³¹P NMR spectroscopy of the respective palladium complexes. The catalytic activity of these complexes toward Suzuki–Miyaura coupling of aryl bromides was also explored. Also, in one case, a comparison of donor properties was made with those of a "normal" carbene with similar steric bulk.

T he first report of isolation of imidazol-2-ylidenes in the free state by Arduengo, and an ensuing arsenal of metal complexes associated with it, has immensely contributed to the field of organometallic chemistry.^{1,2} The scope of binding of imidazole-based carbenes to metal was extended beyond the conventional neutral divalent carbon (C2) to mesoionic carbenes (MICs) (C4 or C5). Since the report of imidazole-based MIC-metal complexes by Crabtree³ and co-workers and successful isolation of MICs in the free state by Bertrand's group,⁴ the family of MICs has received great attention and has begun to find applications as antitumor agents,⁵ in photovoltaic cells,⁶ and as ligands in transition-metal-catalyzed reactions⁷ mainly on account of their enhanced donation capacity in comparison to the "normal" carbenes, which has been established by both experimental and theoretical methods.^{8,9}

Metalation of MICs via oxidative addition to C–X bond remains a preferred route, as blocking at C2 and C5 in the case of the imidazolium ring is not necessary and is independent of C2–H acidity.^{7b} Using this strategy, Albrecht's group reported a number of N-functionalized imidazolium salts with chelating donors and their corresponding MIC–Pd complexes (Chart 1).¹⁰ In recent years, heteroatom-containing functional groups at the backbone position of imidazol-2-ylidene and their metal







complexes have gained attention, as they can enable new catalyst design with broader electronic tunability and enhanced catalytic activity.¹¹ Although synthetic methods for backbone-functionalized imidazol-2-ylidene-metal complexes are readily available, relatively little is known about imidazole-based functionalized MICs, and in particular MICs with heter-oatom-containing functional groups are elusive.¹²

Recently, we have reported metal complexes of bisthiofunctionalized imidazol-2-ylidene ((SPh)2IMe), and the functionalization was achieved via a sequential metal-halogen exchange procedure.¹³ The scope of this method has been augmented to synthesize the precursors for both normal and mesoionic carbenes. Herein, we report backbone-monofunctionalized imidazolium salt(s) as precursors for preparing metal complexes of functionalized "normal" carbene by deprotonation of C2-H achieved through a silver oxide route and mesoionic carbenes via oxidative addition, and subsequently the electronic properties of newly synthesized carbenes were determined on the basis of TEP calculated using the IR stretching frequencies of carbonyls in the complex $[Ir(SPhIMe)(CO)_2Cl]$ (12; (SPh)IMe = 1,3-dimethyl-5-(phenylthio)imidazol-2-ylidene) and ³¹P NMR for MICs in their respective Pd-MIC complexes 13-15. In addition, the catalytic activity of 13-15 toward Suzuki-Miyaura coupling was described. Attempts were made to prepare the heterobimetallic complex utilizing both the functional group tethered to the imidazolium ring and oxidative addition to the C-I bond using Pd(0) precursors.

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RESULTS AND DISCUSSION

The substituted imidazoles 2-4 were synthesized in high yield from 1 using the metal-halogen exchange procedure and were used to prepare imidazolium salts 6-9. Compound 6 was prepared by carrying out another metal-halogen exchange reaction of 4 using ethylmagnesium bromide and quenching with water to yield 1-methyl-5-(phenylthio)imidazole (5) followed by quaternization with methyl iodide, whereas 7-9could be prepared by directly quaternizing 2-4 with trimethyloxonium tetrafluoroborate in dichloromethane (Scheme 1). The salts 7-9 that were synthesized were soluble, and the fact that they can be chromatographed in silica indicate their stability toward air and moisture.





^aReagents and conditions: (a) ⁱPrMgCl, LiCl, THF, electrophile Me_3SiCl (2), PPh₂Cl (3), PhSSO₂Ph (4); (b) EtMgBr, H₂O, THF; (c) CH₃I, CH₃CN, reflux; (d) (CH₃)₃O(BF₄), DCM.

Metalation of **6** at C2 was achieved successfully using the silver oxide route.¹⁴ The silver carbene complex **10** on transmetalation to iridium using chloro(1,5-cyclooctadiene)-iridium dimer gave the [Ir(SPhIMe)(COD)Cl] complex **11**, which was crystallographically characterized. Purging of CO to a DCM solution of **11** gave [Ir(SPhIMe)(CO)₂Cl] (**12**) in high yield (Scheme 2). Complexes **10–12** were all characterized by

Scheme 2. Synthesis of Metal Complexes $10-15^a$



 $FG = Si(Me)_3$ (13), PPh_2 (14), SPh (15).

"Reagents and conditions: (a) Ag_2O , DCM; (b) $[Ir(COD)(Cl)]_2$, DCM; (c) CO (1 atm), DCM; (d) $Pd(PPh_3)_4$, toluene.

spectroscopic, spectrometric, and analytical methods. The composition of **10** in Scheme 2 is based on the NMR and microanalytical data, although a composition with the monomeric structure [Ag(SPhIMe)I] is also possible. The molecular structure of **11** shows that iridium adopts a square-planar geometry with Ir– $C_{carbene}$ and Ir–Cl bond lengths within the range of those observed for similarly known complexes (Figure 1).¹⁵ The mean Ir– C_{COD} (Cg1) distance (1.9782(5) Å)



Figure 1. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for complex **11**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–C1 = 1.351(12), N2–C1 = 1.395(12), Ir1–C1 = 1.997(11), C2–C3 = 1.323(14), Ir1–Cl1 = 2.373(2); N1–C1–N2 = 101.7(8), C1–Ir1–Cl1 = 88.0 (3).

trans to chlorine is shorter than the mean $Ir-C_{COD}(Cg2)$ distance (2.0641(6) Å) trans to the NHC, due to higher trans influence exhibited by the NHC¹⁶ (Figure S1, Supporting Information). In addition, the TEP of **12** determined using Nolan's linear correlation¹⁷ was found to be 2053 cm⁻¹, exhibiting a weak electron-withdrawing effect as was observed earlier for [(SPh)₂IMe].¹³

Facile oxidative addition of Pd(PPh₃)₄ to the C-I bond of the imidazolium salts 7-9 led to the formation of Pd-MIC complexes 13-15, which were isolated in high yields. Complexes 13-15 were all characterized by spectroscopic and analytical methods in addition to single-crystal X-ray diffraction methods. In the proton NMR, C2-H of all Pd-MIC complexes underwent an upfield shift of 1 ppm with respect to the parent imidazolium salts. The ESI-mass spectra recorded in the positive mode shows $[M - (BF_4)^-]^+$ as a prominent peak, and the distribution matches the simulated pattern well (Supporting Information). The molecular structure shows that complexes 13-15 adopt a square-planar geometry around palladium and the two triphenylphosphine ligands are mutually trans to each other, which is consistent with the sharp singlet peak observed in their respective ³¹P NMR spectra. The Pd-C_{carbene} bond in complex 15 is shorter and the Pd-I bond is relatively longer in comparison to those of complexes 13 and 14, indicating the higher trans influence¹⁸ exhibited by the SPhsubstituted MIC (Table 1).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg):

metric parameters	13	14	15
I1-Pd1	2.6475(5)	2.6489(5)	2.6555(5)
Pd1-C2 _{carbene}	2.025(5)	2.018(4)	2.003(4)
N1-C1	1.316(7)	1.324(6)	1.326(5)
N2-C1	1.336(6)	1.335(6)	1.340(5)
C2-C3	1.378(8)	1.366(6)	1.375(6)
Pd1-P1	2.3522(13)	2.3396(12)	2.3401(12)
Pd1-P2	2.3441(13)	2.3580(12)	2.3423(12)
N1-C1-N2	109.5(5)	109.7(4)	109.0(4)
C2-Pd1-I1	175.46(15)	171.40(12)	178.56(12)

Iglesias and Albrecht demonstrated the utility of ³¹P NMR values for determining the donor capacity of the mesoionic carbenes in their respective $[(NHC)Pd(PPh_3)_2]X^-$ complexes.¹⁹ Accordingly, the thioether substitution in **15** caused a shift of δ_P value to a lower field in comparison to their analogous complexes **13** and **14**, suggesting the SPh-substituted MIC (*a*(SPhIMe)) to be the stronger donor (Table 2), which is

 Table 2. Determination of TEP of Backbone-Functionalized

 Carbenes^{17,19}

complex	$\delta_{ m p}~({ m ppm})$	$ u_{\rm CO}({\rm av})~({\rm cm}^{-1})$	TEP (cm ⁻¹)
12		2027	2053 ^a
13	18.60		2050 ^b
14	18.66		2050 ^b
15	20.51		2043 ^b
a TEP = (0.847	$\nu \times \nu_{\rm CO}({\rm av})) + 3$	36 cm^{-1} . ^b TEP = 212	$4.01 \times \delta_{\rm P}$

also supported by a shorter Pd–C_{carbene} bond observed in the X-ray structure of **15** (Figure 2 and Figure S3). On the basis of these correlations we can arrange the donor ability of substituted MICs in the order $a(\text{SPhIMe}) > a(\text{PPh}_2\text{IMe}) \approx a(\text{SiMe}_3\text{IMe})$.



Figure 2. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for complex **15.** The hydrogen atoms, counteranion (BF_4^-) , and solvent of crystallization (toluene) have been omitted for clarity.

Thus, the TEP determined for "normal" carbene and MICs using different probes indicates that the thioether functional group containing mesoionic carbene behaves as a stronger donor in comparison to the analogous "normal" carbene. The results encouraged us to evaluate the catalytic properties of palladium–MIC complexes 13–15, which were screened for Suzuki–Miyaura coupling reactions.^{19,20} Preliminary results without optimization of conditions indicated that moderate to excellent yields could be obtained in the case of aryl bromides. Notably, the substrate containing the electron-donating group -OMe performed slightly better than bromobenzene in all three cases. The catalytic activity observed for the complexes in general could not be correlated to the donor ability of the MICs, and complex 14 afforded the highest yield in all three cases (Table 3). It should also be noted that the formation of a carbene-free palladium aggregate under the reaction conditions cannot be ruled out, as the yields are similar within experimental error.

Attempts To Synthesize a Heterobimetallic Complex. Treatment of compound 8 with gold(I) chloride afforded the gold phosphine complex 16, which was thoroughly analyzed and crystallographically characterized (Scheme 3 and Figure 3). C2–H of 8 in ¹H NMR does not shift significantly upon

Table 3. Suzuki–Miyaura Cross-Coupling Reaction of Aryl Bromides



 $R = NO_2, H, OCH_3$

entry	catalyst	substrate	product	yield ^ø (%)
1	13	1-bromo-4-nitrobenzene	4-nitrobiphenyl	93
2	14			93
3	15			86
4	13	bromobenzene	biphenyl	40
5	14			53
6	15			44
7	13	1-bromo-4- methoxybenzene	4- methoxybiphenyl	56
8	14			58
9	15			57

^aGeneral conditions: ArBr (1.0 mmol), PhB(OH)₂ (1.2 mmol), catalyst (1 mol %), K₂CO₃ (1.5 mmol), DMF (5 mL). ^bIsolated yield.

Scheme 3. Synthesis of Complex 16





Figure 3. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for complex **16**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C2– C3 = 1.361(9)/1.350(9), C3–P1 = 1.799 (6)/1.799(6), P1–Au1 = 2.225(2)/2.2279(18), Au1–Cl1 = 2.284(2)/2.2889(19); N1–C1–N2 = 108.9(5)/109.6(6). The corresponding values for the second crystallographically independent molecule are given in italics.

coordination with AuCl as it does on coordination with palladium in complex 14, although a marked shift in ³¹P NMR is observed (δ_P –23.7 ppm for 8 to 20.5 ppm for 16). Crystals of 16 were formed in low yield, with the chloride counteranion being plausibly obtained from AuCl. The metric parameters of 16 also do not differ considerably in comparison to the parent imidazolium salt (Figure S2, Supporting Information). Treatment of 16 with either Pd(PPh₃)₄ or Pd₂(dba)₃ did not give the oxidative addition product and resulted in Pd black formation in the former case; in addition, no coordination of

diphenylphosphine to AuCl was observed if 14 was used as the starting material.

In summary, we have synthesized an array of mesoionic carbene complexes of palladium (13-15) functionalized at C5 and the effects of various functional groups on the electronic properties of MICs were probed. A comparison of the TEPs of a thioether functionalized "normal" carbene and an MIC with the same steric factors using different probes shows that MICs are stronger donors than the Arduengo class of carbenes. The preliminary catalytic studies of complexes 13-15 toward Suzuki–Miyaura coupling suggest that the functional group can marginally affect the catalytic activity, although further studies are clearly desirable. Attempts to prepare bimetallic complexes utilizing both the functional group and C–I bond via oxidative addition have not been successful so far, although metalation could be separately achieved.

EXPERIMENTAL SECTION

General Procedures. All of the 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. The reported melting points are uncorrected. Isopropylmagnesium chloride was freshly prepared before use.

 \dot{S} ynthesis of Chloro(η^4 -1,5-cyclooctadiene)[1,3-dimethyl-5-(phenylthio)imidazol-2-ylidene]iridium(I) (11). To a solution of 10 (0.118 g, 0.134 mmol) in dry DCM was added $[Ir(COD)(Cl)]_2$ (0.09 g, 0.134 mmol), and the reaction mixture was stirred for 1 h, followed by filtration using a frit containing a pad of Celite. The filtrate was concentrated under vacuum, and the residue was washed once with pentane and again dried under vacuum to afford the title compound as a yellow solid. Yield: 0.127 g (88%). Anal. Calcd for C₁₉H₂₄ClIrN₂S: C, 42.25; H, 4.48; N, 5.19. Found: C, 42.10; H, 4.40; N, 5.26. ¹H NMR (CDCl₃, 500 MHz; δ, ppm): 1.61 (m, 2H, CH_{2 COD}), 1.75 (m, 2H, CH_{2 COD}), 2.20 (m, 4H, CH_{2 COD}), 2.88 (m,1H, CH_{COD}), 2.96 (m, 1H, CH_{COD}), 3.83 (s, 3H, N-CH₃), 4.01 (s, 3H, N-CH₃), 4.62 (d, 2H, CH_{COD}), 7.04-7.27 (m, 6H, C4-H, S(C₆H₅)). ¹³C NMR (CDCl₃, 125 MHz; δ, ppm): 29.5, 29.6, 33.5, 33.7, 35.0, 38.0, 51.6, 51.7, 85.2, 85.5, 121.3, 126.6, 126.7, 128.8, 129.6, 134.9, 184.7. IR (KBr, cm⁻¹): 2928 (vs), 2876 (vs), 2830 (s), 1983 (w), 1639 (w), 1580 (m), 1477 (s), 1440 (vs), 1390 (m), 1372 (s), 1326 (m), 1262 (m), 1176 (m), 1116 (m), 1096 (m), 1023 (m), 968 (w), 865 (w), 805 (m), 740 (s), 690 (m), 634 (w), 498 (w), 470 (w) cm⁻¹. ESI-MS: m/z 546.1577 (M - Cl⁻ + CH₃CN)⁺.

General Procedure Followed for Preparing Palladium–MIC Complexes 13–15. To a suspension of imidazolium salt in dry toluene was added $Pd(PPh_3)_4$ as a solid, and the mixture was stirred for 16 h, during which time a yellow compound precipitated. All volatiles were removed under vacuum, and the residue was washed many times with hexane and once with pentane and diethyl ether and dried under vacuum to afford the respective complex as a yellow solid (see the Supporting Information for specifics of the preparation of 13 and 14).

Complex **15.** Compound **9** (0.209 g, 0.5 mmol), $[Pd(PPh_3)_4]$ (0.578 g, 0.5 mmol), and dry toluene (100 mL) were used. The complex was crystallized by slow evaporation of **15** in a toluene–DCM solvent mixture. Yield: 0.477 g (91%). Mp: 256–260 °C dec. Anal. Calcd for C₄₇H₄₂BF₄IN₂P₂PdS: C, 53.81; H, 4.04; N, 2.67. Found: C, 53.68; H, 3.93; N, 2.68. ¹H NMR (CD₂Cl₂, 500 MHz; δ , ppm): 3.23 (s, 3H, N–CH₃), 3.29(s, 3H, N–CH₃), 6.80–7.06 (m, 5H, S(C₆H₅)) 7.34–7.50 (m, 30H, 2 P(C₆H₅)₃), 8.28 (s, 1H, NCHN). ¹³C NMR (CD₂Cl₂, 100 MHz; δ , ppm): 34.5, 38.1, 127.6, 128.4, 128.5, 129.0, 129.5, 131.2, 134.6, 140.2; carbene carbon signal was not observed. ³¹P NMR (CD₂Cl₂, 162 MHz; δ , ppm): 20.51. IR (KBr, cm⁻¹): 3147 (w), 3055 (w), 1564 (w), 1480 (w), 1435 (w), 1094 (w), 1020 (w), 745 (w), 692 (w), 520 (w), 511 (w) cm⁻¹. ESI-MS: *m/z* 961.0618 (M – BF₄⁻)⁺.

Synthesis of 16. To a solution of 8 (0.148 g, 0.3 mmol) in DCM was added AuCl (0.070 g, 0.3 mmol) as a solid, and the mixture was stirred for 10 min, during which time AuCl completely dissolved to give a clear solution, which was stirred for a further 2 h; after this time all volatiles were removed under vacuum and the residue was washed with diethyl ether and dried to afford the title compound as a colorless solid. Crystals were obtained by vapor diffusion of hexane into a DCM solution of 16. Yield (with BF_4^- counteranion): 0.197 g (91%). Mp: 145-150 °C dec. Anal. Calcd for C₁₇H₁₇AuBClF₄IN₂P: C, 28.11; H, 2.36; N, 3.86. Found: C, 28.40; H, 2.53; N, 3.92. ¹H NMR (CDCl₃, 500 MHz; δ, ppm): 3.49 (s, 3H, N-CH₃), 3.88 (s, 3H, N-CH₃), 7.59–7.75 (m, 10H, $P(C_6H_5)_2$), 9.26 (s, 1H, NCHN). ¹³C NMR (CDCl₃, 125 MHz; δ , ppm): 38.2, 39.1, 92.4, 123.4, 123.9, 129.8, 130.4, 130.6, 132.7, 133.8, 134.4, 134.5, 145.4. ³¹P NMR (CDCl₃, 162 MHz; δ, ppm): 20.5. IR (KBr, cm⁻¹):3159 (w), 3090 (w), 1571 (w), 1511 (w), 1482 (w), 1438 (m), 1341 (w), 1286 (w), 1206 (w), 1100 (s), 1058 (s), 997 (m), 788 (w), 750 (w), 715 (w), 693 (w), 618 (w), 566 (w), 516 (w), 475 (w) cm⁻¹. ESI-MS: m/z 638.9520 [M - $(BF_4^{-})]^+$.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving details of the experimental procedures, X-ray structures of 8, 13, and 14, crystallographic data for compounds 8, 11, and 13–16, and NMR spectra and theoretical and experimental distribution plots of complexes 13-15. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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