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Facile Preparation of Homo- and Hetero-dimetallic Complexes with a 4-Phosphino Substituted NHC Ligand. Toward the Design of Multifunctional Catalysts

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Abstract

A series of bimetallic complexes supported by a 4-phosphino substituted NHC ligand have been synthesized. The use of the stable ligand reduces the number of synthetic steps and allows for a wide range of metal combinations.

Keywords

Carbenes; Phosphines; Copper; Gold; Palladium

Introduction

The replacement of multistep, waste generating, and expensive chemical synthesis has become an important challenge in the fields of catalysis and environmental chemistry.^[1] The development of “one-pot” multifunctional processes has promoted the search for ligands capable of combining several metal centers in a cooperative manner, with the goal of optimizing current procedures or provide outcomes not accessible otherwise.^[2] N-heterocyclic carbenes (NHC's) have emerged as an important family of ligands widely employed in the synthesis of homogeneous catalysts.^[3] Due to their strong donor capabilities and designable topology, they provide a myriad of metal complexes, which in most cases feature a greater thermal stability in comparison to other monodentate ligands.^[4] So far, most of the existing homogeneous catalysts, bearing NHC ligands, feature monometallic or homobimetallic discrete units.^[5] The rare exceptions (Figure 1) include heterobimetallic complexes of 1,2,4-triazolyl-3,5-diylidenes (**A** and **B**)^[6] and 1,3-imadozyl-2,4-diylidenes **C**,^[7] as well as N- and C-metalated-NHCs (**D** and **E**).^[8] The syntheses of complexes **A** and **B** involve a stepwise deprotonation of a dicationic salt in which the azole ligand first acts as a monocarbene while still possesses a CH bond that can be used to generate a second carbene center. Complexes **C** are obtained by the reduction and selective C4 backbone deprotonation (potassium naphthalenide) of an amino-tethered NHC-lanthanide precursor, whereas complexes **D** and **E** result from the base promoted metal C-bound to N-bound tautomerization, followed by a subsequent metal complexation. All of these synthetic procedures lead to the desired complexes with moderate yields, they require several reaction steps and purification treatments, and meta-free carbene precursors are not available.^[9]

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With the aim of tuning the electronic properties of NHC's, we have recently developed a convenient method for the preparation of 4-substituted imidazol-2-ylidenes by deprotonation of a 2-substituted imidazolium salt (Scheme 1).^[10] The reaction scope is quite general and permits the installation of various electron-withdrawing and electron-donating groups on the NHC backbone. By taking advantage of this methodology, we envisioned the possibility of attaching a substituent capable of providing an extra coordination site at the imidazol-2-ylidene, thus generating a bidentate platform that could be useful for the preparation of multifunctional complexes.

We describe herein the coordination capabilities of a 4-diphenylphosphine substituted NHC (**2**), which allows for the facile preparation of homo- and heterobimetallic complexes containing Cu(I), Au(I) and Pd(II) centers. Interestingly, the rare combination of a carbene and a phosphine in a single ligand could open the gate for the design of catalysts in which a single platform provides two completely different electronic environments around metals.

Results and Discussion

Stoichiometric addition of NHC **2** to CuCl in THF readily produces the monometallic complex **3** as an air sensitive white solid in 87% yield (Scheme 2). Interestingly, complex **3** could also be prepared in 91% yield by the “one-pot” *in situ* deprotonation of the imidazolium precursor **1** in presence of CuCl at -78°C . The latter result implies that the migration of the diphenylphosphine group to the imidazolium 4-position is faster than metal coordination to the carbene, avoiding the formation of a possible abnormal NHC complex **4**.^[11-13] The ^{13}C NMR spectrum of **3** displays a signal at 182.5 ppm, in the range observed for other NHC-Cu(I) complexes,^[14] and the ^{31}P NMR chemical shift (-40.2 ppm) is similar to that observed for the free carbene precursor **1** (-39.3 ppm) revealing that the diphenyl phosphine group remained uncoordinated.

In order to test the availability of the diphenylphosphine group for metal coordination, we performed the reaction of complex **3** with one equivalent of CuCl in THF. After simple washing of the crude material with hexane or pentane, the homobimetallic complex **5** was isolated in 86% yield (Scheme 3). The ^{13}C NMR spectra of **5** displays the carbene signal at 184.8 ppm, close to that of the precursor **3**, while the ^{31}P NMR spectrum featured a broad peak with a larger downfield shift (-28.9 ppm), suggesting the coordination of the Cu(I) center to the diphenylphosphine group. The exact structure of **5** was unambiguously assigned by a single crystal X-ray analysis.^[15] (Figure 2). Complex **5** crystallizes in the triclinic *P*-1 space group, and the molecular structure comprises a dimeric unit with the Cl(2) and Cl(3) atoms bridging the two copper centers that are coordinated to the diphenylphosphine groups [Cu(2) and Cu(3)]. The central [Cu-Cl]₂ linkage forms a pseudo-rectangle with Cu-Cl bond distances and Cu-Cl-Cu angles similar to analogously bridged phosphine complexes.^[16] The Cu-P bond distances vary from 2.149(3) to 2.168(3) Å, also within the typical values for Cu(I)-phosphine complexes. The dimer lies on the crystallographic inversion center with a Cu-Cu bond of 2.881 Å, a possible evidence for a weak metalophilic closed shell (d^{10} - d^{10}) interaction.^[17] The carbene coordinated copper centers Cu(1) and Cu(4), feature a slightly distorted linear geometry with C-Cu-Cl angles and C-Cu bond distances in the range to those observed for NHC-Cu(I) compounds.^[14]

Peris and co-workers have recently reported the synthesis of a series of mixed Ir^{III}/Rh^{III} and Pd^{II}/Ir^{III} complexes that are able to catalyze two different organic transformations in a single pot reaction.^[6,18] Motivated by these results, we decided to investigate the suitability of complex **3** as a precursor for heterobimetallic complexes. Since NHC-Cu complexes have been shown to act as carbene transfer reagents (transmetallation)^[19] we were aware that a mixture of isomers could be obtained when reacting **3** with Au^I and Pd^{II} complexes.

Fortunately, the treatment of **3** with equimolar amounts of (Me₂S)AuCl or [(allyl)PdCl]₂ in THF produced cleanly the heterobimetallic complexes **6** and **7** in 95 and 77% yields, respectively (Scheme 3). The ¹³C NMR spectra for complex **6** displayed the carbene peak at 186.1 ppm while, in the case of complex **7**, limited solubility avoided the acquisition of a reliable spectrum. The ³¹P NMR spectra of **6** and **7** showed single peaks at +4.69 and +4.73 ppm, respectively, which confirmed the metal coordination to the diphenylphosphine center. Single crystals of complexes **6** and **7** were grown from a mixture of CHCl₃/hexane (1:3) and the ORTEP drawings, selected bond distances and angles are depicted in Figure 3. Both complexes feature monomeric structures with usual C-Cu and Cu-Cl bond distances for NHC complexes. The P-Au and P-Pd bond distances [2.2142(6) and 2.3041(6) Å, respectively] are also comparable to those usually observed for phosphine complexes.^[20,21] The P-Au-Cl and C-Cu-Cl angles are close to the expected 180° for linear geometries while, in the case of complex **7**, the geometry around the palladium center could be regarded as a distorted trigonal planar.

Gratified by the successful synthesis of heterodinuclear complexes **6** and **7** using the NHC-Cu(I) precursor **3**, we then decided to study the scope of our synthetic strategy for the preparation of heterodimetallic complexes. As a proof of concept, we synthesized the monometallic Au(I) and Pd(II) complexes **8** and **10**, and after subsequent treatment with one equivalent of CuCl and (Me₂S)AuCl, the heterobimetallic complexes **9** and **11** were isolated in 83 and 79% yields, respectively (Scheme 4).

Remarkably, bimetallic complexes **5-7**, **9** and **11** remain unchanged after several days under air exposure and they are thermally stable up to 100 °C for several hours. These features make them interesting catalyst candidates for a wide range of organic transformations.

Conclusion

In summary we have reported a convenient methodology for the preparation of homo- and hetero-bimetallic complexes employing a single 4-diphenylphosphino substituted NHC ligand. Particularly appealing is the possibility of using the present strategy for the synthesis of almost any combination of metal centers, thus allowing for an extended library of complexes. The catalytic performance of these multifunctional units is a subject of current investigations in our laboratory.

Experimental Section

General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard methods and distilled under argon. ¹H, ³¹P, and ¹³C NMR spectra were recorded on Bruker 300 spectrometer at 25 °C. Melting points were measured with a Büchi melting point apparatus system. 2-phosphinoimidazolium chloride **1** and 4-phosphino-imidazol-2-ylidene **2** were prepared following the literature procedure^[10] and all other starting materials were purchased from commercial sources.

Typical Procedures for the preparation of C-metallated complex of **2**, illustrated by the synthesis of [IDipp{Ph₂P}]CuCl **3**

Method A: Copper(I) chloride (0.0693 g, 0.701 mmol) and [IDipp{Ph₂P}] **2** (0.400 g, 0.698 mmol) were combined in a Schlenk flask and dissolved with THF (20 mL). The resulting suspension was stirred overnight at room temperature. The final white suspension was dried under vacuum and the residue was washed with hexane (15 mL) and extracted with dichloromethane (DCM, 12 mL). After filtration and solvent removal, complex **3** was obtained as a white solid in 87% yield (0.408 g, 0.607 mmol). Method B: Copper(I) chloride

(0.098 g, 0.990 mmol), potassium hexamethyldisilazide (0.196 g, 0.985 mmol), and [IDipp{Ph₂P}}][Cl] **1** (0.600 g, 0.985 mmol) were combined in a Schlenk flask and dissolved with THF (20 mL) at -78°C. The resulting mixture was stirred for 16 h. The final white suspension was dried under vacuum, and the residue was washed with hexane (25 mL) and extracted with DCM (18 mL). After filtration and solvent removal, complex **3** was obtained as a white solid in 91% yield (0.602 g, 0.896 mmol). Mp: 264-266 °C. ¹H NMR (CDCl₃, 300 MHz): δ 0.87 (d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂), 1.14 (d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂), 1.24 (d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂), 1.27 (d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂), 2.30 (sept, *J* = 6.9 Hz, 2 H, CH(CH₃)₂), 2.56 (sept, *J* = 6.9 Hz, 2 H, CH(CH₃)₂), 6.68 (s, 1 H, CH_{imid}), 7.18-7.24 (m, 8 H, CH_{ar}), 7.27-7.34 (m, 5 H, CH_{ar}), 7.40 (d, *J* = 7.8 Hz, 2 H, CH_{ar}), 7.44 (t, *J* = 7.8 Hz, 1 H, CH_{ar}). ¹³C NMR (CDCl₃, 75 MHz): δ 21.6, 24.1, 24.4, 26.0 (CH(CH₃)₂), 28.9, 29.1 (CH(CH₃)₂), 123.3 (CH_{ar}), 124.1 (CH_{ar}), 124.2 (CH_{ar}), 129.0 (d, *J*_{CP} = 8.6 Hz, CH_{ar}), 129.8 (CH_{ar}), 130.6 (CH_{ar}), 130.8 (CH_{imid}), 132.9 (CH_{ar}), 133.1 (C_{ar}), 133.8 (d, *J*_{CP} = 9.9 Hz, C_{ar}), 134.3 (C_{ar}), 135.1 (d, *J*_{CP} = 9.5 Hz, C_{imid}), 145.0 (C_{ar}), 145.9 (C_{ar}), 182.5 (C_{carbene}). ³¹P NMR (CDCl₃, 121 MHz): δ -40.2.

Typical Procedure for the preparation of heterodimetallic complexes of **2** illustrated by the synthesis of [IDipp{Ph₂P(AuCl)}]CuCl **6**

Chloro(dimethylsulfide)gold(I) (0.132 g, 0.448 mmol) and [IDipp{Ph₂P}}]CuCl **3** (0.301 g, 0.448 mmol) were combined in a Schlenk flask and dissolved with THF (15 mL). The resulting clear solution was stirred overnight at room temperature. After performing a similar work up as that for complex **3**, complex **6** was obtained as a white solid in 95% yield (0.382 g, 0.423 mmol). Mp: 294-296 °C. ¹H NMR (CDCl₃, 300 MHz): δ 0.98 (d, *J* = 6.7 Hz, 6 H, CH(CH₃)₂), 1.19 (d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂), 1.28 (d, *J* = 6.9 Hz, 6 H, CH(CH₃)₂), 1.33 (d, *J* = 6.7 Hz, 6 H, CH(CH₃)₂), 2.21 (sept, *J* = 6.7 Hz, 2 H, CH(CH₃)₂), 2.54 (sept, *J* = 6.9 Hz, 2 H, CH(CH₃)₂), 7.04 (s, 1 H, CH_{imid}), 7.27 (d, *J* = 7.8 Hz, 2 H, CH_{ar}), 7.30 (d, *J* = 7.8 Hz, 2 H, CH_{ar}), 7.35 (d, *J* = 7.8 Hz, 2 H, CH_{ar}), 7.45-7.53 (m, 8 H, CH_{ar}), 7.61 (t, *J* = 7.8 Hz, 1 H, CH_{ar}), 7.67 (t, *J* = 7.8 Hz, 1 H, CH_{ar}). ¹³C NMR (CDCl₃, 75 MHz): δ 22.8, 24.2, 24.4, 26.4 (CH(CH₃)₂), 29.2, 29.6 (CH(CH₃)₂), 123.2 (CH_{ar}), 124.4 (CH_{ar}), 124.6 (CH_{ar}), 125.4 (CH_{ar}), 129.9 (d, *J*_{CP} = 16.3 Hz, CH_{ar}), 130.9 (CH_{ar}), 131.4 (CH_{imid}), 133.1 (CH_{ar}), 133.3 (C_{ar}), 133.5 (C_{ar}), 134.9 (d, *J*_{CP} = 9.3 Hz, C_{ar}), 135.3 (d, *J*_{CP} = 9.8 Hz, C_{imid}), 145.2 (C_{ar}), 145.7 (C_{ar}), 186.1 (C_{carbene}). ³¹P NMR (CDCl₃, 121 MHz): δ 4.69.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Reported heterobimetallic complexes based on NHC ligands.

Scheme 1.

General synthesis of 4-substituted imidazol-2-ylidenes.

Scheme 2.
Synthesis of complex **3** using precursors **1** and **2**.

Figure 2.

ORTEP diagram of complex **5** (thermal ellipsoids at 50% probability, hydrogen atoms have been omitted for clarity). Selected bond distances [Å] and angles [°]: N1-C2 1.321(14), N3-C2 1.348(13), N3-C4 1.355(14), C4-P1 1.840(12), C2-Cu1 1.876(12), Cu1-Cl1 2.101(3), P1-Cu2 2.168(3), Cu2-Cl2 2.309(3), Cu2-Cl3 2.255(3), Cu3-Cl2 2.293(3), Cu3-Cl3 2.274(4), P2-Cu3 2.149(3), P2-C9 1.797(10), N6-C7 1.364(13), C7-N8 1.334(12), N8-C9 1.395(13), C7-Cu4 1.872(11), Cu4-Cl4 2.094(4), N1-C2-N3 104.0(10), C4-P1-Cu2 118.9(4), Cu2-Cl2-Cu3 79.02(12), Cu3-P2-C9 116.8(4), N6-C7-N8 103.9(9).

Scheme 3.

Synthesis of homo- and hetero-bimetallic complexes 5-7.

Figure 3. ORTEP diagrams of complexes **6** (left) and **7** (right) (thermal ellipsoids at 50% probability, hydrogen atoms have been omitted for clarity). Selected bond distances [Å] and angles [°]; **6**: N1-C2 1.359(3), N3-C2 1.355(2), N3-C4 1.395(3), C4-P1 1.795(2), C2-Cu1 1.896(2), Cu1-Cl1 2.0957(7), P1-Au1 2.2142(6), Au1-Cl2 2.2754(7), N1-C2-N3 104.11(17), C4-P1-Au1 115.69(6); **7**: N1-C2 1.361(3), N3-C2 1.359(3), C4-P1 1.811(2), C2-Cu1 1.878(2), Cu1-Cl1 2.1017(7), P1-Pd1 2.3041(6), Pd1-Cl1 2.3652(7), N1-C2-N3 104.1(2), C4-P1-Pd1 117.32(8).

Scheme 4.
Synthesis of heterobimetallic complexes **9** and **11**.