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A Bimetallic Complex Containing a Cyclopentadienyl-Annulated Imidazol-2-ylidene

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Variations of the basic imidazol-2-ylidene structure have proliferated since the discovery of the first isolable analogues, and these carbenes are finding expanding application in modern catalysis.¹ Pursuant to our ongoing interest in imidazol-2-ylidene chemistry, we recently reported the synthesis of the first directly cyclopentadienyl-fused imidazolium salts and imidazol-2-thiones.² A new class of metallocene-fused imidazol-2-ylidene complexes is available from these precursors. The architecture of a Cp-fused imidazol-2vlidene enables the incorporation of multiple metals into a single molecule through a combination of tightly coupled σ - and π -type bonding schemes and provides a mechanism for varying the imidazol-2-ylidene electronics. Deprotonation of an imidazolium moiety followed by metalation is a standard method for synthesis of carbene-metal complexes. Oxidative insertion reactions are less frequently employed to achieve metalation, but this methodology appears to be well-suited to 2-haloimidazolium-cyclopentadienide precursors.³ Herein, using this approach, we report a new bimetallic carbene complex architecture that incorporates a cyclopentadienylannulated imidazol-2-ylidene moiety. A preliminary example of Suzuki coupling employing such a metallocene-fused imidazol-2ylidene-derived catalyst is described.

Scheme 1. Synthesis of Complex 4^a



 a Conditions: (a) (CH₃)₃O⁺BF₄⁻⁻; (b) Cp*Ru(CH₃CN)₃⁺CF₃SO₃⁻⁻, 4 Å molecular sieves; (c) Pd(PPh₃)₄.

Treatment of 1^{2b} with Meerwein's salt afforded imidazolium tetrafluoroborate 2 in 95% yield. Reaction of 2 with pentamethylcyclopentadienylrutheniumtris(acetonitrile) triflate⁴ in the presence of 4 Å molecular sieves leads to ruthenocene 3. The imidazolium salt 3 was crystallized from THF to afford crystals for X-ray diffraction studies. Selected bond distances and angles for 3 are included in the Figure 1 caption. A KANVAS⁵ depiction of the structure of 3 is shown in Figure 1. The crystal structure displays a C2–Cl bond of 168.5(2) pm and a N1–C2–C3 angle of 113.3(2)° that is larger than that in typical imidazolium ions.⁶



Figure 1. KANVAS drawing of the complex **3**. Selected bond lengths (pm) and angles (deg): C2-N1(3) = 132.9(2), 133.2(2); N1(3)-C6a(3a) = 140.7(2), 141.0(2); C3a-C6a = 140.7(2); C3a(6a)-C4(6) = 142.9(2), 142.2(2); C4(6)-C5 = 145.3(2), 144.7(3); av(Ru-C3a-6a) = 219.04; C2-C1 = 168.48(19); $av(Ru-C^{Cp*}) = 217.12$; C2-N1(3)-C6a(3a) = 106.42(15), 106.51(15); C4-C5-C6 = 110.93(15); N1-C2-N3 = 113.33(16); N1(3)-C6a(3a)-C3a(6a) = 107.09(15), 106.60(15); C3a(6a)-C6a(3a)-C6d(4) = 110.24(15), 110.07(15); C3a(6a)-C4(6)-C5 = 104.15(15), 104.56(15).

The reaction of imidazolium salt **3** with an equimolar amount of Pd(PPh₃)₄ in refluxing methylene chloride proceeded to complete conversion to the mixed palladium—ruthenium complex **4**. Complex **4** was isolated as a yellow solid, melting at 236–238 °C. NMR spectroscopy indicated a *cis* geometry at the palladium center. Two sets of ³¹P signals at δ 30.35 (d, ²*J*_{P-P} = 24.5 Hz) and δ 19.90 (d, ²*J*_{P-P} = 24.5 Hz) were observed, indicating the presence of two phosphorus atoms at nondegenerate sites (i.e., *cis* isomer). The C2 center (former carbene) in **4** resonates as a doublet of doublets, δ 182.39 (²*J*_{C-P(cis)} = 7 Hz and ²*J*_{C-P(trans)} = 157 Hz).

X-ray quality crystals of 4 were grown by slow evaporation of a saturated dichloromethane solution. The solid-state structure of 4 is depicted by the KANVAS drawing in Figure 2. The cis geometry of the palladium center is confirmed. Conversion of the cis isomer to a trans isomer does not take place. The stability of the cis isomer is contrary to results with previously reported palladium complexes whose cis isomers are the kinetic products which easily isomerize to more stable trans isomers.⁷ This stability of the cis isomer of 4 is likely due to steric congestion which would arise in the trans isomer. The ring internal angle at C2 is 108.7-(3)°. The palladium and phosphorus distance is slightly longer for the atom opposite to the imidazol-2-ylidene moiety ($r_{(Pd-P2)}$ = 238.2(1) pm) than for that *trans* to the chlorine atom $(r_{(Pd-P1)} =$ 227.5(1) pm). These latter distances are consistent with a greater *trans*-effect exerted by the carbene center, a stronger σ -donor than the chlorine atom.

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Figure 2. KANVAS drawing of the complex 4. Selected bond lengths (pm) and angles (deg): C2-N1(3) = 134.3(4), 134.9(5); N1(3)-C6a(3a)= 140.9(5), 141.1(4); Pd-P1(2) = 227.48(10), 238.24(10); C3a-C6a =139.4(5); C3a(6a)-C4(6) = 142.5(5), 142.5(5); C4(6)-C5 = 146.0(6),144.7(6); av(Ru-C3a-6a) = 216.5; C2-Pd = 202.9(3); $av(Ru-C^{Cp^*}) =$ 219.34; C2-N1(3)-C6a(3a) = 109.1(3), 109.4(3); C4-C5-C6 = 110.7(3); N1-C2-N3 = 108.7(3); C2-Pd1-P2 = 173.76(10); C2-Pd1-P1 =88.95(10); N1(3)-C6a(3a)-C3a(6a) = 106.8(3), 105.9(3); C3a(6a)-C3a(6a) = 106.8(3), 105.9(3); C3a(6a)-C3a(6a)-C3a(6a) = 106.8(3), 105.9(3); C3a(6a)-C3a(6a)-C3a(6a) = 106.8(3), 105.9(3); C3a(6a)-C3a(6C6a(3a)-C6(4) = 110.2(3), 110.8(3); C3a(6a)-C4(6)-C5 = 103.8(3),104.5(3).

A comparative cyclic voltammetry study was conducted for 3 and $4.^8$ As expected, the ruthenocene 3 is more difficult to oxidize $(E_{pa} = 1.09 \text{ V vs SCE})$ than complex 4 $(E_{pa} = 0.96 \text{ V})$, due to the inductive effect of the chlorine in the 2-position. Interestingly, while 3 shows an irreversible oxidation wave, 4 shows a reduction wave $(E_{\rm pc} = 0.83 \text{ V})$. In general, ruthenocene derivatives show irreversible redox behavior, presumably due to the susceptibility of ruthenocenium ions toward nucleophilic attack9 or dimerization.^{10,11} Steric hindrance may suppress these side reactions for 4.

Demonstration that the palladium-ruthenium complex 4 is an active catalyst for aqueous Suzuki coupling reactions was provided by preliminary experiments (Scheme 2). Cross-coupling of para-

Scheme 2. Suzuki Cross-Coupling Reactions Catalyzed by 4 $(H_2O:CH_3CN = 9:1, Na_2CO_3, 80 \circ C, 2 h)$



bromobenzoic acid with phenylboronic acid in the presence of 2.4 mol % of 4 in a water: acetonitrile (9:1) mixture afforded the expected product in 94% yield. para-Bromophenol and parabromoanisole yielded the respective coupling products with phenylboronic acid in 83.3 and 82.4%, respectively. Fusion of the ruthenocene moiety to the imidazole ring does not impair the catalytic activity of the metal bound to the carbene center and may offer some advantages for aqueous-based systems.

In conclusion, we have synthesized and characterized the first bimetallic ruthenium-palladium complex containing a cyclopentadienyl-annulated imidazol-2-ylidene ligand and demonstrated its capability to function as catalyst in the Suzuki reaction in aqueous media. We are currently investigating this novel ligand class and its application to a variety of catalytic processes.

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Supporting Information Available: Description of the preparation, NMR spectra, and elemental analyses of 2, 3, and 4, cross-coupling procedures; cyclic voltammograms and a complete description of the X-ray crystallographic determination on 3 and 4, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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