Communication

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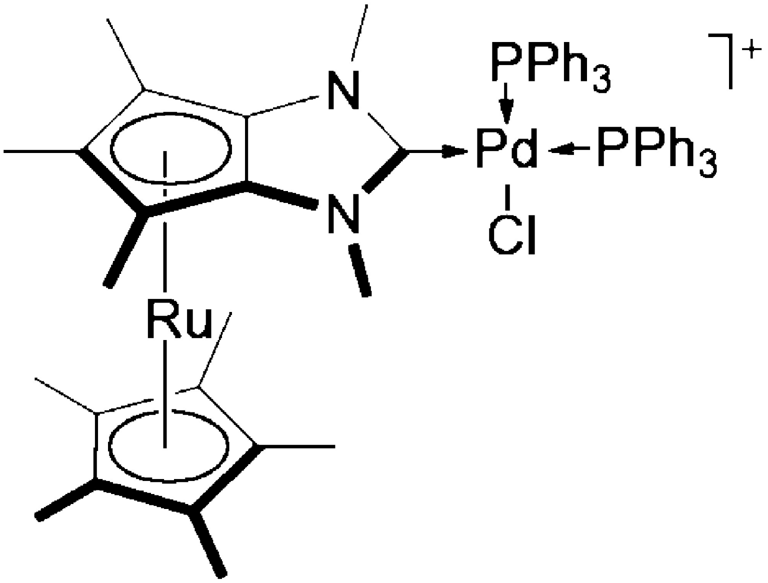

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# A Bimetallic Complex Containing a Cyclopentadienyl-Annulated Imidazol-2-ylidene

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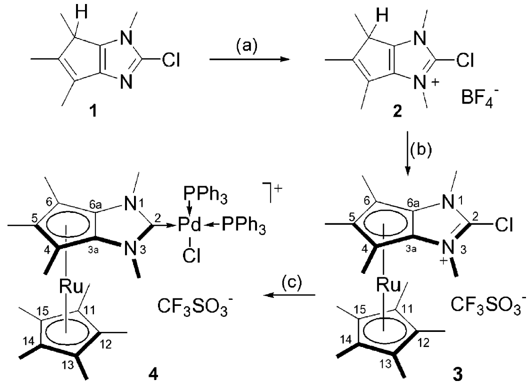
Variations of the basic imidazol-2-ylidene structure have proliferated since the discovery of the first isolable analogues, and these carbenes are finding expanding application in modern catalysis.[1] Pursuant to our ongoing interest in imidazol-2-ylidene chemistry, we recently reported the synthesis 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-2-ylidene enables the incorporation of multiple metals into a single molecule through a combination of tightly coupled $\sigma$- and $\pi$-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 cyclopentadienyl-annulated imidazol-2-ylidene moiety. A preliminary example of Suzuki coupling employing such a metallocene-fused imidazol-2-ylidene-derived catalyst is described.

***Scheme 1.*** Synthesis of Complex **4**[a]



[a] Conditions: (a) $(CH_3)_3O^+BF_4^-$; (b) $Cp^*Ru(CH_3CN)_3^+CF_3SO_3^-$, 4 Å molecular sieves; (c) $Pd(PPh_3)_4$.

Treatment of **1**[2b] with Meerwein's salt afforded imidazolium tetrafluoroborate **2** in 95% yield. Reaction of **2** with pentamethylcyclopentadienylrutheniumtris(acetonitrile) triflate[4] 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 KANVAS[5] 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]

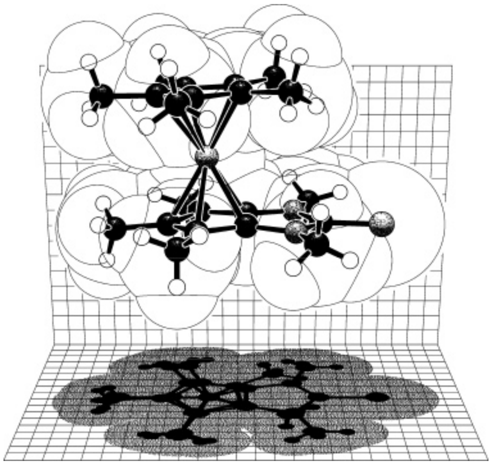


***Figure 1.*** KANVAS drawing of the complex **3**. Selected bond lengths (pm) and angles (deg): C2−N1(3) = 132.9(2), 133.2(2); N1(3)−C6a(3a) = 140.7(2), 141.0(2); C3a−C6a = 140.7(2); C3a(6a)−C4(6) = 142.9(2), 142.2(2); C4(6)−C5 = 145.3(2), 144.7(3); av(Ru−C3a−6a) = 219.04; C2−Cl = 168.48(19); av(Ru−$C^{Cp^*}$) = 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)−C6(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 $Pd(PPh_3)_4$ 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 $^{31}P$ signals at $\delta$ 30.35 (d, $^2J_{P-P} = 24.5$ Hz) and $\delta$ 19.90 (d, $^2J_{P-P} = 24.5$ 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, $\delta$ 182.39 ($^2J_{C-P(cis)} = 7$ Hz and $^2J_{C-P(trans)} = 157$ 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 $\sigma$-donor than the chlorine atom.

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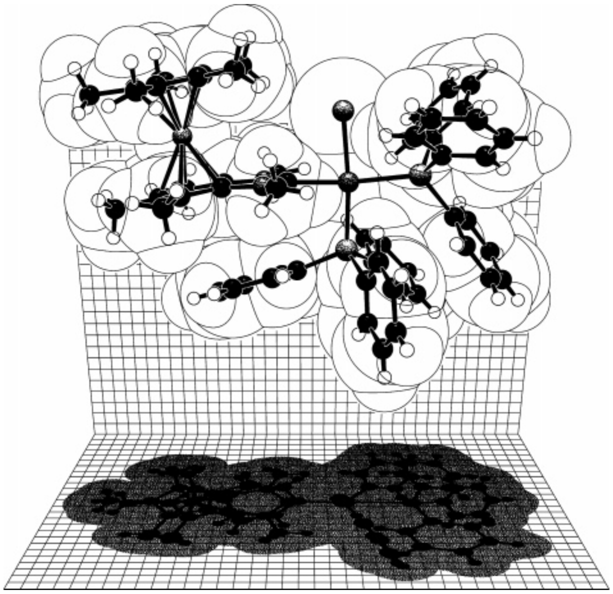
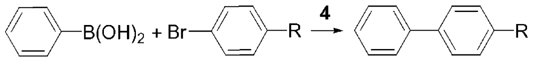


***Figure 2.*** KANVAS drawing of the complex **4**. Selected bond lengths (pm) and angles (deg): C2−N1(3) = 134.3(4), 134.9(5); N1(3)−C6a(3a) = 140.9(5), 141.1(4); Pd−P1(2) = 227.48(10), 238.24(10); C3a−C6a = 139.4(5); C3a(6a)−C4(6) = 142.5(5), 142.5(5); C4(6)−C5 = 146.0(6), 144.7(6); av(Ru−C3a−6a) = 216.5; C2−Pd = 202.9(3); av(Ru−C$^{\mathrm{Cp*}}$) = 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)−C6a(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 ($E_{\mathrm{pa}}$ = 1.09 V vs SCE) than complex **4** ($E_{\mathrm{pa}}$ = 0.96 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 ($E_{\mathrm{pc}}$ = 0.83 V). In general, ruthenocene derivatives show irreversible redox behavior, presumably due to the susceptibility of ruthenocenium ions toward nucleophilic attack[9] 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*-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 *para*-bromoanisole 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.

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



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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## References

(1) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc*. **1991**, *113*, 361−363. (b) Lee, S.; Hartwig, J. F. *J. Org. Chem*. **2001**, *66*, 3402−3415. (c) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem*. **1998**, *557*, 93−96. (d) Herrmann, W. A.; Kocher, C.; Goosen, L. J.; Artus, G. R. J. *Chem.*−*Eur. J*. **1996**, *2*, 1627−1636. (e) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun*. **2001**, *22*, 2340−2341. (f) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954−4955. (g) Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K. H.; Wurst, K. *J. Organomet. Chem.* **1998**, *552*, 54−61. (h) Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterböck, M.; Ongania, K. H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325−4336. (i) Seo, H.; Park, H. J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618−620. (j) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun*. **2002**, 32−33.

(2) (a) Arduengo, A. J., III; Bannenberg, T. P.; Tapu, D.; Marshall, W. J. *Chem. Lett.* **2005**, *34*, 1010−1011. (b) Arduengo, A. J., III; Bannenberg, T. P.; Tapu, D.; Marshall, W. J. *Tetrahedron Lett.* **2005**, *46*, 6847−6850.

(3) McGuinness, D. S.; Cavell, K. J.; Yates, B. F.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 8317−8328.

(4) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698−1719.

(5) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (The University of Alabama), to produce the back and shadowed planes. The planes bear a 50 pm grid, and the lighting source is at infinity so that shadow size is meaningful.

(6) (a) Langer, V.; Huml, K.; Reck, G. *Acta Crystallogr., Sect. B* **1982**, *38*, 298−300. (b) Luger, P.; Ruban, G. *Z. Kristallogr*. **1975**, *142*, 177−185. (c) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753−1754.

(7) Fürstner, A.; Seidel, G.; Kremzow, D.; Lehmann, C. W. *Organometallics* **2003**, *22*, 907−909.

(8) Cyclic voltammograms were measured in dichloromethane at 20 °C containing 0.1 mol dm$^{-3}$ *n*-Bu$_4$NBF$_4$ as a supporting electrolyte using a Pt electrode; scan rate was 200 mV s$^{-1}$.

(9) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4687−4690.

(10) Droege, M. W.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 1309−1315.

(11) Mueller-Westerhoff, U. T.; Rheingold, A. L.; Swiegers, G. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1352−1354.

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