

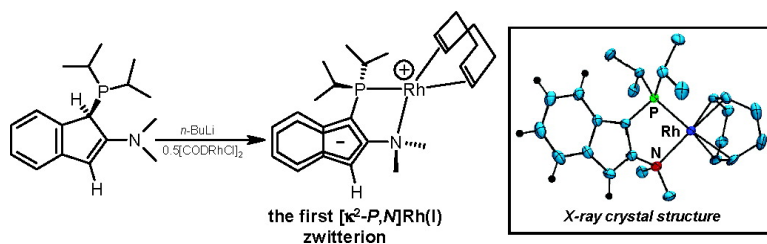
Communication

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 Featuring a P,N-Substituted “Naked” Indenide Ligand**

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J. Am. Chem. Soc., **2003**, 125 (19), 5618-5619 • DOI: 10.1021/ja034543v • Publication Date (Web): 18 April 2003

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A Catalytically Active, Charge-Neutral Rh(I) Zwitterion Featuring a P,N-Substituted “Naked” Indenide Ligand

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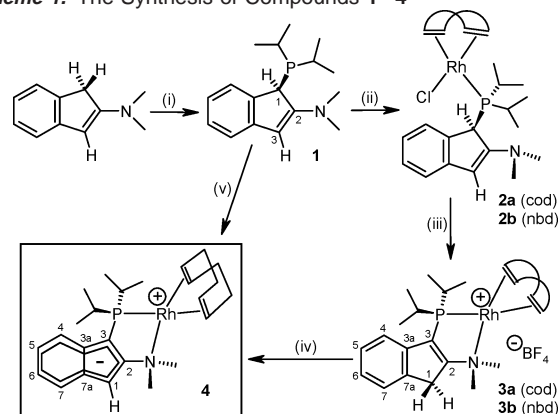
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Cationic complexes of Rh(I) figure prominently in the field of homogeneous catalysis, as they are capable of mediating substrate transformations that are often difficult to achieve by use of neutral catalysts.¹ In particular, cationic Rh(I) complexes supported by hemilabile phosphine-amine (P,N) bidentate ligands have attracted considerable attention.^{2,3} These species often exhibit reactivity properties that are superior to the corresponding diphosphine and diamine complexes.^{2–4} Unfortunately, the polar nature of Rh(I) salts can necessitate the use of high-dielectric reaction media, possibly leading to attenuated catalytic activity resulting from unfavorable competition between substrate molecules and the counteranion or solvent for the metal active site. The use of charge-neutral zwitterionic complexes represents a means of circumventing such problems.⁵ Zwitterionic Rh(I) complexes have been shown to catalyze a wide range of reactions under mild conditions and with high selectivity.⁶ To date, the construction of Rh(I) zwitterions has relied almost exclusively on borato-type ligands,⁷ and, surprisingly, while both “N,N” and “P,P” bidentate zwitterions of Rh(I) have been explored, the corresponding “P,N” zwitterions are unknown.

In the pursuit of new and synthetically useful metal-mediated reaction chemistry, we sought to prepare alternative classes of platinum-group zwitterions that do not rely on borate ligation. In this context, we envisaged that the incorporation of an extended Hückel aromatic carbanion within the periphery of an ancillary ligand might provide an efficient means of inducing formal charge separation. Although main group functionalized indenyl compounds have been widely used as carbocyclic π -ligands, the sequestering of an anionic charge in the form of a 10- π indenide unit built into the backbone of a bidentate ligand has thus far been overlooked.⁸ Herein we report that this unusual new ligation strategy provides access to the first charge-neutral $[\kappa^2\text{-P,N}]\text{Rh(I)}$ zwitterion, **4**, a complex that functions as a catalyst for the dehydrogenative coupling of C–H and Si–H fragments.

The new indene-supported P,N ligand, **1**, can be prepared in 93% yield via low-temperature lithiation of 2-dimethylaminoindene, followed by the addition of $i\text{Pr}_2\text{P}(\text{Cl})$ (Scheme 1). The formulation of **1** as the allylic (C1) rather than the vinylic (C3) isomer is consistent with data obtained from NMR spectroscopic studies.^{9a} Treatment of **1** with 0.5 equiv of either $[\text{CODRhCl}]_2$ (COD = 1,5-cyclooctadiene) or $[\text{NBDRhCl}]_2$ (NBD = 2,5-norbornadiene) produces the corresponding mononuclear phosphine complexes, **2a** and **2b**, respectively. These and the other Rh(I) species depicted in Scheme 1 are formed quantitatively (based on ³¹P NMR data obtained from the crude reaction mixtures), and in all cases the desired complexes can be isolated as analytically pure solids in high yield. An X-ray crystallographic study of **2a** confirms that the coordinated indenyl ligand (**1**) is bound exclusively through the phosphorus donor.^{9b}

Scheme 1. The Synthesis of Compounds **1–4**^a



^a Reagents: (i) *n*-BuLi, Cl^iPr_2 ; (ii) 0.5 $[\text{L}_2\text{RhCl}]_2$, $\text{L}_2 = \text{COD}$, **2a**; or NBD, **2b**; (iii) AgBF_4 ; (iv) using **3a**, NaTMS_2 ; (v) *n*-BuLi, 0.5 $[\text{CODRhCl}]_2$.

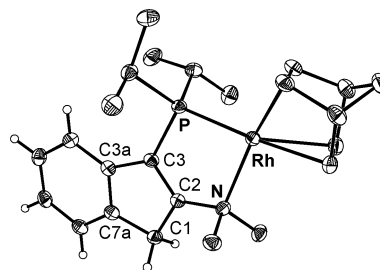


Figure 1. The crystallographically determined structure of **3b**, shown with 40% displacement ellipsoids. Selected hydrogen atoms, as well as the THF solvate and BF_4^- counterion, have been omitted for clarity. Selected interatomic distances (Å): Rh–P 2.2798(7); Rh–N 2.179(2); P–C3 1.806(3); N–C2 1.455(3); C1–C2 1.509(4); C2–C3 1.346(4); C3–C3a 1.477(4); C3a–C7a 1.404(4); C1–C7a 1.499(4).

Chloride abstraction (AgBF_4) from rhodium in either **2a** or **2b** generates the cationic chelate complexes, **3a** and **3b**, respectively, in which the indenyl framework has undergone a structural rearrangement that places the $i\text{Pr}_2\text{P}$ fragment at the C3 position. The crystallographically determined structure of **3b** is shown in Figure 1^{9c} and is comparable to other $[(\kappa^2\text{-P,N})\text{Rh}(\text{olefin})]^+\text{X}^-$ salts reported in the literature.¹⁰

In contrast, the alkane-soluble zwitterionic Rh(I) species, **4**, is without precedent. This novel complex can be cleanly generated either by deprotonation of **3a** or via lithiation of **1** followed by treatment with 0.5 equiv of $[\text{CODRhCl}]_2$. The preference of the $[\text{CODRh}^+]$ fragment in **4** to coordinate at the P,N site rather than binding in an η^5 -fashion to the indenyl ring is highly unusual, especially in light of the numerous $(\eta^5\text{-indenyl})\text{Rh}(\text{olefin})_2$ complexes that are known.¹¹ The crystallographically determined structure of **4** is shown in Figure 2.^{9d} Particularly striking are the differences between the interatomic distances within the C₅ ring

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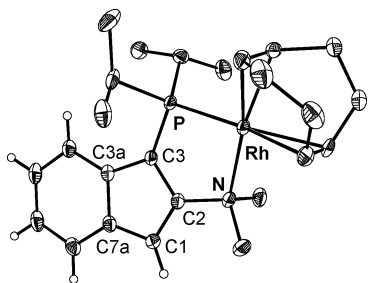
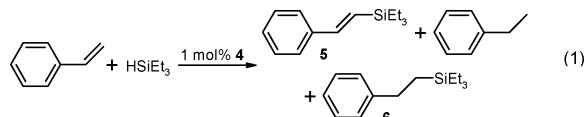


Figure 2. The crystallographically determined structure of **4**, shown with 40% displacement ellipsoids. Nonindenide hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Rh–P 2.3173(6); Rh–N 2.242(2); P–C3 1.758(2); N–C2 1.479(3); C1–C2 1.386(3); C2–C3 1.419(3); C3–C3a 1.446(3); C3a–C7a 1.442(4); C1–C7a 1.430(4).

of **3b** (e.g., C1–C2 = 1.509(4) Å; C2–C3 = 1.346(4) Å) and those found in **4** (e.g., C1–C2 = 1.386(3) Å; C2–C3 = 1.419(3) Å). Whereas the cation exhibits bond length alternation consistent with an indene framework, the indenide unit in **4** possesses a highly delocalized structure and is appropriately described as a “naked” indenide anion.¹²

Given our interest in the development of catalysts for E–H bond activation (E = main group element), we selected the dehydrogenative silylation (DS) of styrene as an initial means of benchmarking the catalytic performance of **4** (eq 1). The reaction of 3 equiv of styrene (functioning both as a substrate and as an H₂ acceptor) with 1 equiv of Et₃SiH in the presence of 1 mol % **4** at 80 °C for 2.5 h in toluene results in the consumption of the silane, along with the production of **5**, **6** (~83:17), and ethylbenzene.^{9a,e} Notably, the selectivity of **4** for DS over hydrosilylation (HS) in this reaction (i.e., the preferred formation of **5** over **6**) approaches that of the most effective Rh(I) catalyst systems for DS.¹³



A head-to-head comparison of the cation, **3a**, and its charge-neutral analogue, **4**, was also conducted in THF at 50 °C.^{9f} After 22 h using 1 mol % **4**, Et₃SiH is consumed, and the silanes **5** and **6** are formed (~82:18). In contrast, when 1 mol % **3a** is employed under these conditions, complete consumption of Et₃SiH is not observed, and the selectivity for DS over HS is greatly diminished (**5**:**6** ≈ 59:41). These preliminary data suggest that the zwitterion, **4**, may provide reactivity advantages over related Rh(I) cations under appropriate conditions. A more thorough survey of the stoichiometric and catalytic reactivity of **4** and its derivatives is currently underway and will be the subject of future reports.

In conclusion, a modular and high-yielding strategy for the construction of new classes of cationic and zwitterionic Rh(I) complexes has been introduced. This methodology provides access to the first [κ^2 -P,N]Rh(I) zwitterion, **4**, a unique complex that mediates the cross-coupling of C–H and Si–H fragments. We anticipate that the confluence of hemilabile and zwitterionic

characteristics brought about by this new ligand set will engender reactivity in a variety of late transition metal fragments.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and Dalhousie University for financial support, Mr. Juergen Mueller (Dalhousie) for the preparation of custom Schlenk glassware, and Dr. James Pincock (Dalhousie) and Dr. Robert Singer (St. Mary’s University) for assistance in the acquisition of GC data.

Supporting Information Available: Experimental details and characterization data for **1–4** including tabulated crystallographic data for **2a**, **3b**, and **4** (PDF), as well as X-ray crystallographic information files (CIF) for **2a**, **3b**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (a) Full experimental details, including spectroscopic characterization data for all of the compounds reported herein, are provided in the Supporting Information. (b) Crystal data for **2a**·CH₂Cl₂: space group = P2₁/n; a = 15.773(1) Å; b = 8.2243(6) Å; c = 20.994(2) Å; β = 91.688(1)°; V = 2722.2(3) Å³; data/restraints/parameters = 5548/0/289; GOF = 1.019; R₁ = 0.0328; wR₂ = 0.0874. Largest difference peak and hole = 1.362 and –0.861 e Å^{–3}. (c) Crystal data for **3b**·C₄H₈O: space group = P-1; a = 9.4626(5) Å; b = 12.2347(6) Å; c = 12.9609(6) Å; α = 77.6417(9)°; β = 73.6000(9)°; γ = 82.7989(9)°; V = 1402.7(1) Å³; data/restraints/parameters = 5714/0/334; GOF = 1.047; R₁ = 0.0355; wR₂ = 0.0871. Largest difference peak and hole = 0.813 and –0.451 e Å^{–3}. (d) Crystal data for **4**: space group = P2₁/n; a = 9.7054(6) Å; b = 16.985(1) Å; c = 14.5743(9) Å; β = 109.392(1)°; V = 2266.2(2) Å³; data/restraints/parameters = 4611/0/253; GOF = 1.083; R₁ = 0.0329; wR₂ = 0.0861. Largest difference peak and hole = 1.335 and –0.694 e Å^{–3}. (e) GC-MS/GC-FID. (f) THF used to ensure complete dissolution of **3a**.
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