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Remarkably Facile and Reversible Ru−C(sp^3) Bond Cleavage to Give a Reactive 16-Electron Cp*Ru(κ^2-*P*,*C*arbene) Zwitterion

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Coordinatively and electronically unsaturated metal complexes represent key reactive intermediates in a diversity of stoichiometric and catalytic reactions, including transformations involving the activation of otherwise robust bonds in both organic and inorganic substrates. Although there is considerable interest in preparing isolable complexes of this type, the synthesis of reactive, low-coordinate species can pose a significant challenge: the use of sterically demanding ancillary ligands designed to stabilize such unsaturated species can inhibit access of substrates to the reactive metal center, while the generation of low-coordinate complexes in the absence of bulky stabilizing ligands commonly results in the irreversible degradation of the target complex. An alternative approach involves the use of an ancillary ligand whose strategic design affords stability to the resting state of the complex, while also providing access to the desired unsaturated metal species by way of a reversible ligand binding/reorganization process.[1] Indeed, cyclometalation,[1a,b] β-hydride elimination,[1b,c] hemilabile chelation,[1d] ligand-promoted dimer-to-monomer rearrangements,[1e] and other reversible processes have been exploited successfully as a means of unveiling unsaturated species in situ. In the pursuit of new classes of highly reactive complexes that are capable of mediating difficult bond activation reactions, the rational development of novel ancillary ligands whose dynamic coordination behavior renders the associated metal fragments *operationally unsaturated*[2] represents an important goal. Particularly appealing are functional ancillary ligands of this type that are capable of re-establishing coordinative unsaturation at a reactive metal center following an initial bond activation step and/or that enable substrate bond activation processes.[3] Herein we report the synthesis and characterization of the 18-electron Cp*Ru(κ^3-*P*,*C*,*C′*) species **3**—a complex that provides access to the 16-electron Cp*Ru(κ^2-*P*,*C*) zwitterion **4** by way of an unprecedented Ru−C(sp^3) bond cleavage process that is both facile and reversible. Notably, the anionic phosphine−carbene ancillary ligand in **4** facilitates the Ru-mediated double geminal Si−H bond activation of Ph_2SiH_2.

In the quest to establish new metal-mediated E−H bond activation chemistry (E is a main group element), and inspired by reports documenting the utility of unsaturated $Cp^*RuL_n^+$ complexes in a range of challenging stoichiometric and catalytic E−H bond activation processes,[4,5] we have initiated a research program targeting cationic and formally zwitterionic complexes of this type derived from 1-P^iPr_2-2-NMe_2-indene and related ancillary ligands.[6] In this context, we have reported previously the isomerization of a 16-electron zwitterionic Cp*Ru(κ^2-*P*,*N*) complex to the 18-electron hydridocarbene **1** (Figure 1) by way of double geminal C−H bond activation.[6a,b] We have observed subsequently that complex **1** is transformed cleanly into the chlorocarbene **2** upon exposure to CH_2Cl_2. In viewing this chlorocarbene as a potential precursor to new 16-electron $Cp^*RuL_n^+$ species via dehydrohalogenation, **2** was treated with $NaN(SiMe_3)_2$ and the progress of the reaction was monitored by use of ^{31}P NMR methods. Over the course of 45 min, complete conversion to a new phosphorus-containing product **3** was observed. While elemental analysis data for **3** were found to be consistent with the anticipated net removal of HCl from **2**, NMR spectroscopic and X-ray crystallographic data for **3** confirmed the identity of this complex as the C_1-symmetric, 18-electron Cp*Ru(κ^3-*P*,*C*,*C′*) species depicted in Figure 1.[7] Surprisingly, however, data from 1D and 2D EXSY ^1H NMR experiments provided definitive spectroscopic evidence for the operation of an unprecedented and reversible Ru−C(sp^3) bond cleavage process involving **3**. In the case of ^1H EXSY experiments, irradiation of either of the diastereotopic $P(CHMe_2)_2$ signals in **3** resulted in significant positively phased enhancement of the other methine resonance, indicating that these two sites undergo chemical exchange. Simi-

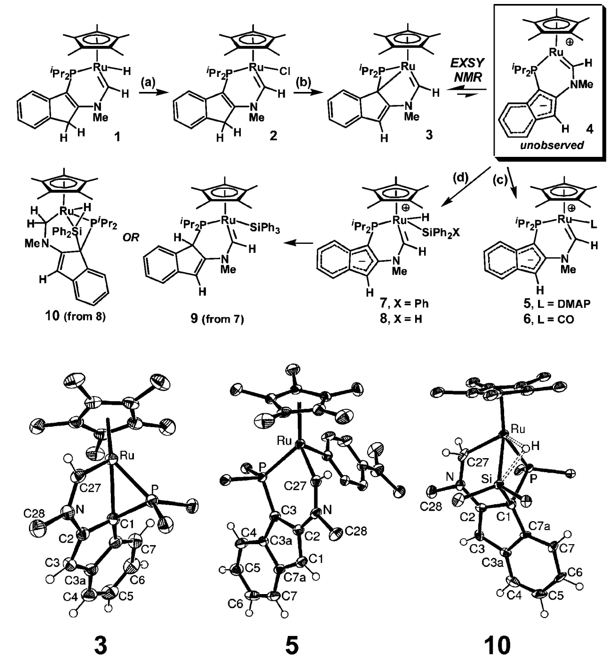

Figure 1. Reagents: (a) CH_2Cl_2; (b) $NaN(SiMe_3)_2$; (c) DMAP (DMAP = 4-dimethylaminopyridine, for **5**) or CO (for **6**); (d) Ph_3SiH (for **7**) or Ph_2SiH_2 (for **8**). ORTEP diagrams shown with 50% ellipsoids; selected C and H atoms have been omitted for clarity. Bond lengths (Å) for **3**: Ru−P 2.2158(5); Ru−C1 2.250(2); Ru−C27 1.941(2); P−C1 1.805(2); N−C2 1.397(2); N−C27 1.346(2). Bond lengths (Å) for **5**: Ru−P 2.3011(9); Ru−C27 1.949(3); Ru···C3 (shortest Ru−indenide distance) 3.403; P−C3 1.779(3); N−C2 1.425(4); N−C27 1.329(4). Bond lengths (Å) for **10**: Ru−P 2.295(2); Ru−Si 2.391(2); Ru−H 1.48(9); Ru−C27 2.169(8); P−C1 1.889(7); Si−C1 1.958(8); Si−H 1.90(8); N−C2 1.37(1); N−C27 1.47(1).

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larly, the ^{1}H−^{1}H EXSY spectrum of **3** exhibits positively phased off-diagonal exchange cross-peaks that connect the two diastereotopic P(C*H*Me$_2$)$_2$ environments, as well as pairs of P(CH*Me*$_2$)$_2$ resonances. These observations can be rationalized in terms of the reversible breaking and reforming of the Ru−C1 linkage in **3**, thereby providing access to the unsaturated C_s-symmetric intermediate **4**. Given that the Ru−C1 distance in **3** (2.250(2) Å) is not unusually long,[8] it is likely that the remarkable ease with which the Ru−C1 bond undergoes formal heterolytic cleavage in the reversible transformation of **3** into **4** can be attributed in part to the relief of ring strain in **3**, as well as to the energetic favorability of generating a 10π-electron indenide unit within the zwitterion **4** upon ring opening. Indirect support for the reversible generation of **4** from **3** was obtained through the isolation of **4**•L complexes (L = 4-dimethylaminopyridine (DMAP), **5**; L = CO, **6**) upon treatment of **3** with DMAP or CO; the delocalized bonding that is observed within the indenide unit of **5** (Figure 1) is consistent with a 10π-electron framework, in keeping with related zwitterionic complexes featuring donor-substituted indenide ligands.[6a,9] Interestingly, the facile Ru−C(sp^3) bond cleavage observed in the course of transforming the 18-electron Cp*Ru(κ^3-*P*,*C*,*C′*) complex **3** into **6** upon addition of CO contrasts the chemistry exhibited by Cp*Ru(κ^3-H*C*(PPh$_2$*N*Ph)$_2$), whereby a Cp*Ru(CO)(κ^2-*N*,*C*,N) adduct arising from net substitution of an ancillary ligand N-donor arm is produced.[8b]

Having established that **3** behaves as a masked source of the 16-electron Cp*Ru(κ^2-*P*,*C*) zwitterion **4** in reacting with L donors, we turned our attention to examining the reactivity of **3** with E−H-containing substrates. Exposure of **3** to H_2 (∼1 atm) in C_6D_6 afforded **1** in the absence of observable (^{31}P NMR) intermediates.[10a] In contrast, the first-formed product (**7**, Figure 1) that was observed spectroscopically upon combination of Ph_3SiH and **3** can be rationalized as arising from Si−H addition to the reactive intermediate **4**;[10b] after extended reaction times (weeks), **7** rearranged to the isolable, thermodynamic product **9**. An analogous intermediate **8** was identified as the kinetic product upon treatment of **3** with Ph_2SiH_2.[10b,c] However, in contrast to the net transfer of H^+ from Ru to the carbocyclic backbone that was observed in the slow transformation of **7** into **9**, compound **8** rearranged cleanly to the crystallographically characterized **10** (Figure 1) over the course of 24 h; experimentation directed toward elucidating the mechanistic pathway linking **8** and **10** is ongoing.[10d] Although we are hesitant to comment definitively regarding the location of the hydride in **10**, the final refined metrical parameters point to an unsymmetrical Ru−H···Si bridging interaction in this complex.[11] Notably, related Ru-mediated double geminal Si−H bond activation processes have been implicated in a novel alkene hydrosilylation mechanism reported recently by Glaser and Tilley.[5]

In summary, the 18-electron η^1-indenyl complex **3** provides access to the reactive 16-electron "η^0-indenide" zwitterion **4** by way of a remarkably facile and reversible Ru−C(sp^3) bond cleavage process, as evinced by data obtained from dynamic NMR investigations and reactivity studies. We propose that this unusual rearrangement is promoted by the incipient formation of a Hückel aromatic anion within the ligand backbone of **4** upon heterolytic cleavage of the Ru−C$_{\text{indenyl}}$ bond in **3**, and we anticipate that this unusual ancillary ligand design strategy will provide a general method of unveiling a diversity of reactive low-coordinate metal species in situ by way of carbanion hemilability. We are examining the utility of **4** and related unsaturated metal complexes in mediating a range of demanding stoichiometric and catalytic substrate transformations and will report the results of such studies in due course.

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Supporting Information Available: Experimental details and characterization data, including EXSY spectra for **3** and X-ray crystallographic information files (CIF) for **3**, **5**, and **10**. The material is available free of charge via the Internet at http://pubs.acs.org.

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