Reactivity of a coordinatively unsaturated Cp*Ru(κ²-P,O) complex†

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Whereas a new coordinatively unsaturated Cp*Ru(κ²-P,O) complex (1a) forms adducts with two-electron donors (including σ-H₂ and μ-N₂ ligands), double Si–H bond activation is observed upon treatment with Ph_2SiH_2 or $PhSiH_3$, leading to the clean formation of products corresponding to the net insertion of a Ph_2Si: or Ph(H)Si: fragment into the Ru–O bond of 1a.

Studies documenting the reactivity properties of coordinatively unsaturated $(\eta^5\text{-}C_5R_5)RuL_n$ ($\eta^5\text{-}C_5H_5$ = Cp; $\eta^5\text{-}C_5Me_5$ = Cp*) species are of considerable significance, since complexes of this type represent key reactive intermediates in a range of prominent metal-catalyzed transformations.[1] Moreover, novel stoichiometric reactivity identified in the course of such investigations expands our understanding of the substrate transformations that can occur within the coordination sphere of unsaturated $(\eta^5\text{-}C_5R_5)RuL_n$ species, thereby providing the basis for the development of new and/or mechanistically distinct metal-catalyzed reactivity.[2] While considerable insight has been gained through the investigation of both neutral Cp*RuL(X) complexes and [Cp*RuL₂]⁺X⁻ salts,[1c,d] the examination of alternative classes of complexes supported by new ancillary ligands continues to advance our appreciation of how even subtle alterations to the ligand steric and/or electronic properties can influence the reactivity behavior of coordinatively unsaturated Cp*RuLₙ species.

Reports documenting the reactivity of well-defined, coordinatively unsaturated Cp*RuLₙ complexes supported by monoanionic, heterobidentate ligands are rare.[1,3] In this context, we have reported previously on our efforts to prepare the formally zwitterionic species, Cp*Ru(κ²-3-PⁱPr₂-2-NMe₂-indenide); this complex alleviates coordinative unsaturation by rearranging to an 18-electron κ²-P,C hydridocarbene complex via intramolecular, double geminal C–H bond activation involving a ligand NMe group.[4] In expanding upon this research, we sought to develop structurally related Ru complexes that might be capable of mediating intermolecular double geminal E–H bond activation processes (E = main group element). In consideration of the hard (N) and soft (P) donor ligands featured in the aforementioned zwitterion,[4] and given the beneficial reactivity properties imparted

by anionic κ²-P,O ligands on alternative classes of metal complexes,[5] we identified coordinatively unsaturated Cp*Ru(κ²-P,O) complexes supported by phosphinoenolate chelating ligands as appealing targets of inquiry. Although heterobidentate species of this type were unknown prior to this work, Caulton and co-workers have demonstrated that π-donation from oxygen in related Cp*RuPR₃(OR′) complexes can serve to stabilize such unsaturated species, and to promote metal-mediated substrate transformations.[6] Herein we provide a preliminary account of the reactivity of the new coordinatively unsaturated Cp*Ru(κ²-P,O) complex 1a (Scheme 1), with comparisons made to the structurally related monodentate species Cp*Ru(PⁱPr₂Ph)(OCH₂CF₃) 1b.[6] In addition to forming adducts with a number of two-electron donors (including σ-H₂ and μ-N₂ ligands), complex 1a mediates double Si–H bond activation reactions involving Ph_2SiH_2 or $PhSiH_3$, affording products derived from the net insertion of Ph_2Si: or Ph(H)Si: fragments into the Ru–O bond of 1a.

Treatment of 1-diisopropylphosphino-2-indanone with 0.25 [Cp*RuCl]₄ afforded (κ²-P,O-1-diisopropylphosphino-2-indanone)Cp*RuCl in 96% isolated yield, which in turn was spectroscopically and crystallographically characterized (Fig. 1);‡ the structural features noted in this complex compare well with those found in a related (κ²-P,O)Cp*RuCl compound.[7] In the pursuit of 1a, a deep red solution of (κ²-P,O-1-diisopropylphosphino-2-indanone)Cp*RuCl in benzene was treated with NaN(SiMe₃)₂; ³¹P NMR analysis of the resulting dark green solution revealed the quantitative conversion to a single phosphorus-containing product (1a₂·(μ-N₂); δ ³¹P = 50.1 ppm, $\Delta\nu_{1/2}$ = 213 Hz, C₆D₆, 300 K), which was isolated in 78% yield (Scheme 1).[8a] The assignment of this product as the new dinuclear
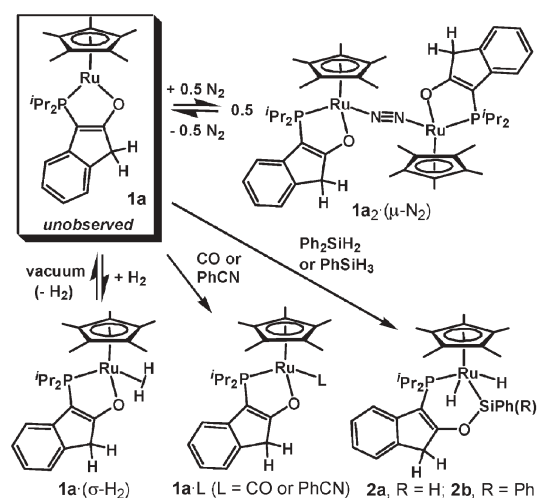
Scheme 1   Reactivity of 1a with small molecule substrates.

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Fig. 1 ORTEP diagrams for (κ^2-*P,O*-1-P^{i}Pr$_2$-2-indanone)Cp*RuCl·0.5C$_6$H$_6$ (left), **1a$_2$**·(μ-N$_2$) (middle), and **2b** (right), shown with 50% ellipsoids. The benzene solvate and selected H-atoms have been omitted for clarity. Bond lengths (Å) for (κ^2-*P,O*)Cp*RuCl: Ru–P 2.3421(6); Ru–O 2.220(2); Ru–Cl 2.4508(6); ^{i}Pr$_2$P–C 1.873(2); C–O 1.228(3); C1–C2 1.505(3); C2–C3 1.508(3). Bond lengths (Å) and angles (°) for **1a$_2$**·(μ-N$_2$): Ru–N 1.996(7), 1.994(7); Ru–O 2.147(6), 2.151(6); Ru–P 2.360(2), 2.370(3); C–O 1.31(1), 1.29(1); C2–C3 1.39(1), 1.38(1); ^{i}Pr$_2$P–C 1.763(8), 1.797(9); N–N 1.131(8); Ru–N–N 165.5(7), 163.5(6). Bond lengths (Å) for **2b**: Ru–P 2.3081(5); Ru–Si 2.3102(6); Si–O 1.705(2); C–O 1.333(3); C2–C3 1.360(3); ^{i}Pr$_2$P–C 1.820(2).

phosphinoenolate complex **1a$_2$**·(μ-N$_2$) was ultimately achieved by use of single-crystal X-ray diffraction techniques (Fig. 1).‡ Notably, **1a$_2$**·(μ-N$_2$) represents a rare example of a (η^5-C$_5$R$_5$)RuL$_n$ complex featuring a bridging dinitrogen ligand.[1c,9] The Ru–N and N–N distances as well as the modestly non-linear Ru–N–N fragments found in **1a$_2$**·(μ-N$_2$) compare well with those of [(CpRuP$_2$)$_2$(μ-N$_2$)]$^{2+}$ dications reported by Valerga and co-workers.[10] While no N–N stretch is observed in the IR spectrum of **1a$_2$**·(μ-N$_2$), the Raman spectrum of this complex features a band at 2042 cm^{-1} attributable to the μ-N$_2$ unit.[10] By comparison, the isolable monodentate complex **1b** apparently does not exhibit a propensity to coordinate dinitrogen.[6a] In contrast to the rather short Ru–O distance observed in the coordinatively unsaturated species Cp*Ru(PCy$_3$)(OCH$_2$CF$_3$) (1.992(10) Å),[6a] the elongated Ru–O distances in **1a$_2$**·(μ-N$_2$) suggest that π-donation from oxygen is negligible in this dinuclear complex, in keeping with the adduct Cp*Ru(PCy$_3$)(OCH$_2$CF$_3$)(CO) (Ru–O 2.090(3) Å).[6a] The ability of **1a$_2$**·(μ-N$_2$) to serve as a reactive source of **1a** was demonstrated upon exposure to an atmosphere of CO, or two equiv. of PhCN; in both cases, the corresponding **1a**·L adduct (L = CO, 93%; L = PhCN, 91%) was obtained. The observation of nearly identical C–O stretching frequencies in the IR spectra of **1a**·CO (1903 cm^{-1}) and Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$)(CO) (1906 cm^{-1})[6d] indicates that the P,O ligand sets in these related complexes have comparable electron-donating abilities.

Interest in the reactivity of coordinatively unsaturated (η^5-C$_5$R$_5$)RuL$_n$ complexes with H$_2$ and silanes can be attributed to the potential involvement of such reaction steps in homogeneous catalytic reaction cycles.[1,2,11] Notably, the course of such reactions has been found to be dependent on the nature of the ancillary ligand(s). For example, whereas Cp*RuP^{i}Pr$_3$(Cl)[12] and [Cp*Ru(κ^2-*N*Me$_2$CH$_2$CH$_2$*N*Me$_2$)]$^+$X^{-}[13] are unreactive toward H$_2$, related [Cp*RuP$_2$]$^+$X^{-} complexes react to give [Cp*RuP$_2$-(H)$_2$]$^+$X^{-}; in some cases, non-classical [Cp*RuP$_2$(σ-H$_2$)]$^+$X^{-} species exist in equilibrium with the dihydride product, or are detected spectroscopically at low temperatures as reactive intermediates.[1c,11] Given the differing reactivity exhibited by these related complexes featuring either N- or P-based ligands, we became interested in examining the behavior of the 'hard–soft' chelate complex **1a** with H$_2$ and silane substrates. Exposure of a

degassed toluene-d_8 solution of **1a$_2$**·(μ-N$_2$) to an atmosphere of H$_2$ at 24 °C resulted in the quantitative formation of a single phosphorus-containing product (**1a**·(σ-H$_2$); δ ^{31}P = 65.2 ppm, $\Delta v_{1/2}$ = 180 Hz, toluene-d_8, 300 K).[8a] Our assignment of this product as a non-classical dihydrogen adduct, rather than a dihydride complex, was made initially based on the observation of a broad ^{1}H NMR resonance centered at −5.7 ppm; variable-temperature NMR data obtained for this complex, including the rather short $T_{1(min)}$ relaxation value (17 ms, 218 K, 250 MHz) associated with the dihydrogen ligand, confirmed this structural assignment.[11] Conversely, Caulton and co-workers[6c] have noted that treatment of **1b** with <2 equiv. H$_2$ under similar conditions afforded Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$)(H)$_2$, while the addition of excess H$_2$ produced HOCH$_2$CF$_3$ and the trihydride Cp*Ru-(P^{i}Pr$_2$Ph)(H)$_3$. Despite this divergent reactivity, it is interesting to note that both **1a**·(σ-H$_2$) and Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$)(H)$_2$ liberate H$_2$ upon exposure to vacuum. The facile loss of H$_2$ from **1a**·(σ-H$_2$) has thus far prevented the isolation of this complex.

In monitoring the progress of the reaction of **1a$_2$**·(μ-N$_2$) with 2 equiv. PhSiH$_3$ in C$_6$D$_6$ by use of NMR methods, the consumption of the starting materials was noted after 15 min, along with the formation of three phosphorus-containing products, one of which being **2a**. Subsequent analysis of the reaction mixture (^{31}P NMR) after a total of 3 h revealed the quantitative formation of **2a**, which in turn was isolated in 95% yield. Under similar conditions employing 2 equiv. Ph$_2$SiH$_2$, **2b** was formed quantitatively after only 15 mins, thereby allowing for the isolation of this complex in 95% yield.[8b] The assignment of **2a** and **2b** as products derived from double geminal Si–H bond activation and net insertion of a Ph(H)Si: or Ph$_2$Si: fragment into the Ru–O bond of **1a** is in keeping with the ^{1}H, ^{13}C and ^{29}Si NMR spectra obtained, including the observation of two Ru–*H* signals (−11.14 and −11.92 ppm) and an Si–*H* resonance in the ^{1}H NMR spectrum of the C_1-symmetric **2a**, as well as a single ^{1}H NMR resonance (−11.02 ppm) attributable to the equivalent Ru–*H* ligands in the C_S-symmetric **2b**. The crystallographically determined structure of **2b** (Fig. 1)‡ exhibits Ru–Si and Si–O distances that are in keeping with those found in related complexes featuring bidentate Ru(κ^2-*Si*Ph$_2$OC$_5$H$_4$*N*) and Ru(κ^2-*Si*Ph$_2$OC(Me)=*O*) ligands.[14] Notably, the long Ru–*H*⋯*Si* contacts observed in the

structure of **2b** (*ca.* 2.12 Å and 2.14 Å), along with the relatively low measured $^2J_{SiH}$ values (**2a**: 9.4 Hz; **2b**: 9.8 Hz),[15] support the view of **2a** and **2b** as being classical dihydride complexes. In the absence of conclusive experimental data we are unable to comment definitively on the mechanism of this transformation. However, we favor a process involving initial intermolecular Si–H oxidative addition to **1a**, Si–O reductive elimination, and finally intramolecular Si–H oxidative addition involving the tethered silyl ether fragment.[8c] The absence of observable chemical exchange (^{1}H EXSY) involving the Ru–*H* and Si–*H* groups of **2a** suggests that if the intramolecular Si–H oxidative addition to Ru in such a mechanistic scenario is reversible, this Si–H addition–elimination process occurs at a rate that is slow relative to the dynamic exchange NMR timescale. In keeping with our proposed mechanism for the formation of **2a,b**, Caulton and co-workers[6c] observed that treatment of **1b** with Ph$_2$SiH$_2$ generated a 1 : 1 mixture of Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(SiXPh$_2$) (X = H or OCH$_2$CF$_3$) as the Ru-containing products. In rationalizing the formation of these two products, Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$)(H)(SiHPh$_2$) was invoked as the first-formed oxidative addition product; upon elimination of Ph$_2$Si(H)(OCH$_2$CF$_3$), the resultant coordinatively unsaturated reactive intermediate Cp*Ru(P^{i}Pr$_2$Ph)(H) could undergo an intermolecular Si–H oxidative addition with either Ph$_2$Si(H)(OCH$_2$CF$_3$) or additional Ph$_2$SiH$_2$ to afford the two observed Ru products. By comparison, tethering of the silyl ether fragment to the phosphine donor that occurs during the reaction of **1a** with Ph$_2$SiH$_2$ in our proposed mechanism sets up an intramolecular Si–H addition, leading to the clean formation of **2b**. The observed stoichiometric reaction steps may be of relevance to the Ru-mediated alcoholysis of silanes.[16]

In summary, a preliminary account of the reactivity of the new coordinatively unsaturated Cp*Ru(κ^2-*P,O*) complex **1a** has been provided. Notably, the reactivity profile of **1a** has been found to differ from that of the monodentate complex Cp*Ru(P^{i}Pr$_2$Ph)-(OCH$_2$CF$_3$) (**1b**),[6] as well as some other established classes of coordinatively unsaturated Cp*RuL$_n$ species. Encouraged by these observations, and given the paucity of coordinatively unsaturated Cp*RuL$_n$ complexes supported by monoanionic, heterobidentate ligands, we are exploring further the stoichiometric reactivity of **1a** and related derivatives and will report on these studies in due course.

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