

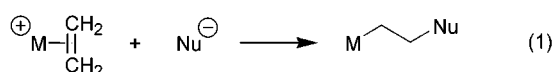
Hydrofunctionalization of Alkenes Promoted by Diruthenium Complexes
 $[\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_3(\eta^2\text{-CH}_2=\text{CH-R})(\mu\text{-H})\}]^+$
Featuring a Kinetically Inert Proton on a Metal–Metal Bond

Maxim V. Ovchinnikov, Eric LeBlanc, Ilia A. Guzei,[†] and Robert J. Angelici*

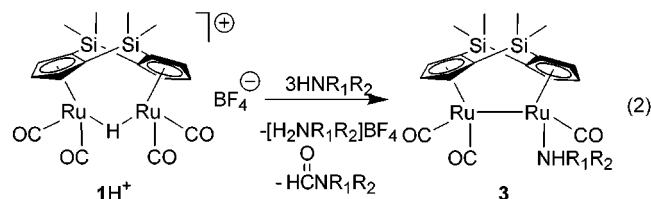
Department of Chemistry
 Iowa State University, Ames, Iowa 50011

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Metal-assisted nucleophilic attack on unsaturated ligands is a reaction of great synthetic importance and represents one of the most common and well-studied reactions in organometallic chemistry.¹ For example, amines and alkoxides attack a carbon of coordinated alkenes in transition metal complexes if the metal is sufficiently electropositive to promote such an attack (eq 1).²



One of the simplest approaches to making the metal in a complex more positive is to add a proton (H^+) to the metal center.³ However, either most protonated metal complexes containing unsaturated ligands do not react with nucleophiles because the metal is not sufficiently electropositive, or the nucleophiles simply deprotonate the metal to give the unreactive neutral metal complex. We recently reported⁴ the synthesis of the cationic dinuclear complex $[\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})\}]^+$ ($\mathbf{1H}^+$) whose carbon monoxide ligands are activated to attack by amine nucleophiles (eq 2) because of the positive charge on the complex



and the slow rate of deprotonation of the bridging hydride by the amines. In this communication we report the synthesis of protonated alkene complexes $[\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_3(\eta^2\text{-CH}_2=\text{CH-R})(\mu\text{-H})\}]^+$ ($\mathbf{2a-bH}^+$) and the activation of the alkene ligand in these complexes to attack by amines and other nucleophiles to give the alkylated nucleophiles. This type of reaction with amine nucleophiles is a key step in the catalytic intermolecular hydroamination of alkenes, a process of great current interest and importance.⁵

* To whom correspondence should be addressed. E-mail: angelici@iastate.edu.

[†] Iowa State University, Molecular Structure Laboratory.

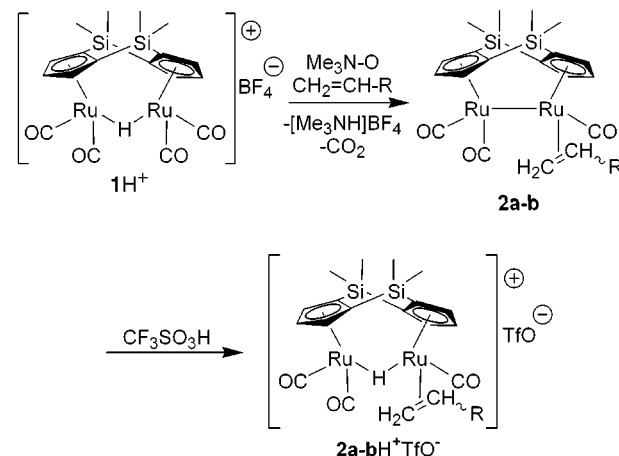
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Scheme 1. Synthesis of Complexes $\mathbf{2a-bH}^+\text{TfO}^-$ (R = H (a), CH₃ (b))



The reaction of $[\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_4(\mu\text{-H})\}]^+$ ($\mathbf{1H}^+$) with $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in the presence of the desired alkene forms complexes $[\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_3(\eta^2\text{-CH}_2=\text{CH-R})\}]^+$ ($\mathbf{2a-b}$; R = H, Me) in 72 and 65% isolated yields, respectively, as air- and moisture-sensitive yellow solids (Scheme 1; see Supporting Information for experimental details). Addition of 1 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ or $\text{CF}_3\text{SO}_3\text{D}$ to solutions of complexes $\mathbf{2a-b}$ in CH_2Cl_2 at room temperature gives the hydride-bridged dinuclear Ru complexes $\mathbf{2a-bH}^+$ in quantitative yields. Complex $\mathbf{2bH}^+\text{BF}_4^-$ exists as a mixture (2.3:1 ratio) of two isomers with Ru coordinated to different faces of the propylene ligand. The CO stretching frequencies of $\mathbf{2a-bH}^+$ are approximately 40 cm^{-1} higher than those of $\mathbf{2}$ and fall within the range where amine attack on coordinated alkenes is expected to occur.² An X-ray diffraction study of $\mathbf{2aH}^+\text{BF}_4^-$ (Figure 1)⁶ reveals an eclipsed orientation of the terminal CO and ethylene ligands on the two Ru atoms. The Ru–Ru distance in $\mathbf{2aH}^+\text{BF}_4^-$ (3.1306(6) Å) is similar to that in complex $\mathbf{1H}^+\text{BF}_4^-$ (3.1210(5) Å).⁷ Complexes $\mathbf{2a-bH}^+$ are slow to undergo deprotonation relative to reaction of the alkene with nucleophiles as the unprotonated complexes $\mathbf{2a-b}$ are not detected among the products of reactions of $\mathbf{2a-bH}^+$ with nucleophiles (vide infra). The deuterated complex $\mathbf{2aD}^+\text{TfO}^-$ in wet acetone- d_6 solution ($\sim 5\%$ H_2O) did not undergo measurable H–D exchange after 1 day at 25 °C. As for $\mathbf{1H}^+$,⁴ this low kinetic acidity is attributed to a combination of the bulkiness of the dimethylsilyl linkers in the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ bridging ligand and the rigidity of the molecule.

Reactions of $\mathbf{2a-bH}^+\text{BF}_4^-$ with amines (NH_3 , MeNH_2 , Me_2NH , morpholine, $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$) yield amine complexes $[\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_3(\text{NHR}_1\text{R}_2)\}]^+$ ($\text{NHR}_1\text{R}_2 = \text{NH}_3$, MeNH_2 ,

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(6) Crystal data: (173(2) K) $\text{C}_{10}\text{H}_{12}\text{BF}_4\text{O}_2\text{Ru}_2\text{Si}_2$, MW = 644.50, monoclinic, $P2_1/c$, $a = 18.2230(9)$ Å, $b = 15.9109(8)$ Å, $c = 17.2675(8)$ Å, $\beta = 108.5284(10)^\circ$, $Z = 8$, $V = 4747.1(4)$ Å³, $\mu = 1.423\text{ mm}^{-1}$, 9689 unique reflections, $R1 = 0.0511$ (0.0616 for all data), $wR2 = 0.1411$ (0.1485 for all data). Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162940 ($\mathbf{2aH}^+\text{BF}_4^-$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

(7) Details of the X-ray and neutron diffraction studies of $\mathbf{1H}^+$ will be published separately: Ovchinnikov, M. V.; Wang, X.; Schultz, A. J.; Angelici, R. J. Manuscript in preparation.

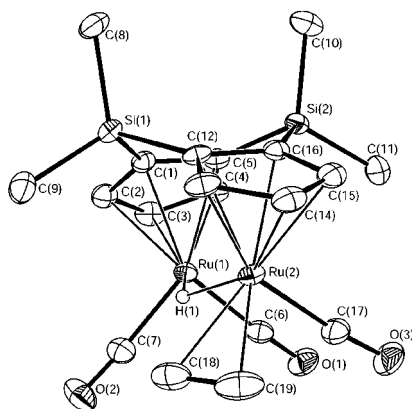


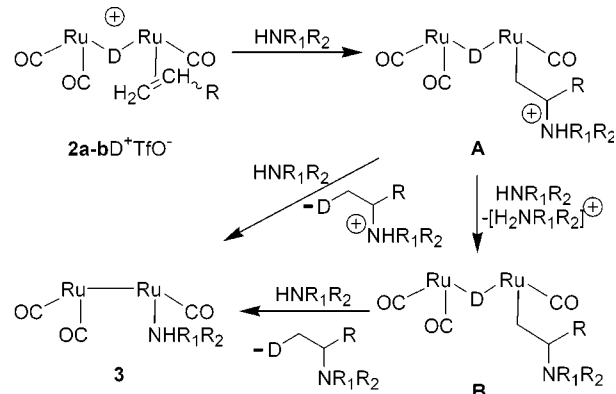
Figure 1. Thermal ellipsoid drawing, with 30% probability ellipsoids, of $[(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_3(\eta^2\text{-CH}_2=\text{CH}_2)(\mu\text{-H})]^+$ in $2\text{aH}^+\text{BF}_4^-$ showing the labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: Ru(1)–Ru(2), 3.1306(6); Ru(1)–H(1) = Ru(2)–H(1), 1.743(1); Ru(1)–C(6), 1.901(7); Ru(1)–C(7), 1.899(7); Ru(2)–C(17), 1.889(7); Ru(2)–C(18), 2.237(7); Ru(2)–C(19), 2.242(7); C(18)–C(19), 1.340(12); Ru(1)–Cp(centroid), 1.872(3); Ru(2)–Cp(centroid), 1.868(3); $\angle\text{Ru(1)–H(1)–Ru(2)}$, 128(1); $\angle\text{Ru(2)–Ru(1)–C(6)}$, 89.28(19); $\angle\text{Ru(2)–Ru(1)–C(7)}$, 101.6(2); $\angle\text{C(6)–Ru(1)–C(7)}$, 91.2(3); $\angle\text{Ru(1)–Ru(2)–C(17)}$, 88.8(2); $\angle\text{C(6)–Ru(1)–Ru(2)–C(17)}$, 5.5(3); $\angle\text{C(7)–Ru(1)–Ru(2)–C(17)}$, 96.5(3); $\angle\text{Cp(centroid)–Ru(1)–Ru(2)–Cp(centroid)}$, 3.16(17); $\angle\text{Cp–Cp fold angle (angle between the planes of the Cp rings)}$, 131.3(3).

Table 1. Hydrofunctionalization of Alkenes Promoted by 2a–bH^+ (R = H (a), CH₃ (b))

	Nucleophile	Ru-cont. Product	Organic Product(s) (ratio)
1	NHR_1R_2 (CDCl_3) (2 equiv.)		$\text{H–CH}_2\text{–CH(R)–NH}_2^+$
2	PMe_3 (CD_2Cl_2) (2 equiv.)		$\text{R–CH}_2\text{–CH(H)–PMe}_3^+$ (1.6) $\text{H–CH}_2\text{–CH(R)–PMe}_3^+$ (1)
3	NaOMe (C_6D_6) (1–5 equiv.)	Decomp. products	$\text{H–CH}_2\text{–CH(R)–OMe}$
4	NaSMe (C_6D_6) (1–5 equiv.)		–

Me_2NH)⁸ (**3**) and the corresponding alkylated amines in a 1:1 ratio as determined by ¹H NMR spectroscopy (Table 1; entry 1; Scheme 2). The reactions of $2\text{bH}^+\text{BF}_4^-$ give Markovnikov addition products with >95% regioselectivity. In contrast to reaction of 1H^+ (eq 2),⁴ even weakly nucleophilic amines (*p*-CH₃C₆H₄NH₂, $pK_a = 5.10$)⁹ react with $2\text{aH}^+\text{BF}_4^-$. Rates of reactions of $2\text{aH}^+\text{BF}_4^-$ with morpholine are approximately 10^2 – 10^3 times faster than those of complex 1H^+ ($t_{1/2} = 5$ min for 1H^+ , $t_{1/2} < 1$ s for $2\text{aH}^+\text{BF}_4^-$);⁴ the reaction of $2\text{aH}^+\text{BF}_4^-$ with *p*-CH₃C₆H₄NH₂ was found to be slowest ($t_{1/2} = 15$ min, 25 °C, CDCl_3) among the amines studied. The absence of the deprotonated complexes 2a–b and formamides among the products in these reactions is consistent with relatively slow rates of deprotonation of 2a–bH^+ and faster rates of nucleophilic attack on the coordinated alkene than on CO.²

Scheme 2. Proposed Mechanism for the Reaction of 2a–bD^+ with Amines^a



^a ($\eta^5\text{-C}_5\text{H}_3$)₂(SiMe₂)₂ ligands are omitted.

The scope of this reaction is relatively broad: complexes $2\text{a–bH}^+\text{BF}_4^-$ react with several representative nucleophiles (PMe_3 , ^-OMe , ^-SMe) to give the hydrofunctionalized alkenes and, in most cases (Table 1; entries 2, 4), readily identifiable Ru-containing products.¹⁰ Reactions of $2\text{a–bH}^+\text{BF}_4^-$ with these nucleophiles occur rapidly ($t_{1/2} < 1$ s) to give organic products with high Markovnikov regioselectivities (except PMe_3). Surprisingly, the reaction of complex $2\text{bH}^+\text{BF}_4^-$ with PMe_3 gives a mixture of *n*-Pr PMe_3^+ and *i*-Pr PMe_3^+ in a 1.6:1 ratio.

Although a detailed mechanism for the reactions of 2a–bH^+ with nucleophiles is yet to be established, on the basis of experiments with deuterium-labeled complex $2\text{aD}^+\text{TfO}^-$, we propose the mechanism shown in Scheme 2. It involves initial nucleophilic attack by the amine on the coordinated alkene to produce the cationic intermediate **A**, which is either deprotonated to **B** or undergoes reductive elimination of the alkylated ammonium salt to form an unsaturated diruthenium intermediate that coordinates an amine to give **3**. Intermediate **B** could also undergo reductive elimination of the alkylated amine. This mechanism is consistent with the reaction of the deuterium-labeled $2\text{aD}^+\text{TfO}^-$ with morpholine which gives *N*-ethylmorpholine ($\text{CH}_2\text{D–CH}_2\text{–N(CH}_2\text{CH}_2)_2\text{O}$) that is $\sim 93 \pm 5\%$ deuterated at the methyl position and no other. No intermediates were observed by FT-IR or ¹H NMR spectroscopy during the course of the reactions. Reductive eliminations involving a $\mu\text{-H}$ have only recently been characterized¹¹ in the formation of alkanes and arenes from $\text{Pd}_2\text{R}_2(\mu\text{-H})(\text{dppm})_2^+$ and proposed in the formation of formamides in reaction 2.⁴

In conclusion, we have demonstrated that the alkene complexes 2a–bH^+ , featuring a kinetically inert bridging proton on a metal–metal bond and a doubly linked dicyclopentadienyl ligand, react with a variety of nucleophiles to give hydrofunctionalized alkenes with predominantly Markovnikov regioselectivity. Future studies will be directed toward hydroamination and other hydrofunctionalization reactions of alkenes that are catalyzed by 2a–bH^+ and its derivatives.

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Supporting Information Available: Full experimental details, including the preparations of 2a–b and 2a–bH^+ and their reactions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(8) Complexes $\{(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\text{Ru}_2(\text{CO})_3(\text{NHR}_1\text{R}_2)$ (**3**) ($\text{NHR}_1\text{R}_2 =$ morpholine, *p*-CH₃C₆H₄NH₂) undergo rapid decomposition in CDCl_3 solution

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