

Umpolung of a Metal–Carbon Bond: A Potential Route to Porphyrin-Based Methane Functionalization Catalysts

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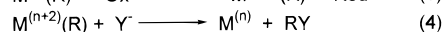
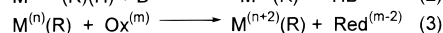
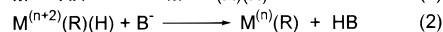
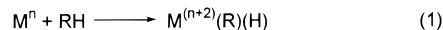
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Selective functionalization of otherwise unactivated alkanes is an important goal, since alkyl chains are ubiquitous and constitute one of the few functional groups for which there is not a highly developed chemistry.^{1,2} While several homogeneous late transition metal catalysts activate alkanes under relatively mild conditions, well-defined systems capable of efficient alkane functionalization are rare.^{3–7} At the most basic level, metal-based alkane functionalization is complicated by the need to catalyze heterolytic (ionic) and homolytic bond-making and bond-breaking events at a single metal center. A typical sequence, such as that proposed for the Pt-based Shilov oxidation process, is outlined in Scheme 1.⁸

The reactions outlined in eq 1–4 differ radically in their ionicity. Thus, if one can effectively change the electronegativity of a metal center while maintaining a model catalyst's coordination geometry, the effects on the thermodynamics of the relevant reactions can be predicted from first principles. In Pauling's valence-bond treatment, the strength of a chemical bond, as measured by its homolytic bond dissociation energy (BDE), is determined by covalent and ionic terms.⁹ According to this analysis, BDE is a function of the difference in electronegativity ($\Delta\chi$) of the two atoms; effectively decreasing $\Delta\chi$ will decrease BDE. Since transition metal atoms are more electropositive than hydrogen or carbon, it is expected that M–C and M–H BDEs will decrease as electron density is withdrawn from a given metal center's coordination sphere, decreasing the enthalpy for oxidative addition into a C–H bond (and M–C and M–H BDEs). However, from inspection of the thermodynamic cycle shown in Scheme 2, one can also conclude that M–C and M–H BDEs will be less sensitive, in terms of energy, than their respective heterolytic (or ionic) bond dissociation energies (eqs 2 and 4 above) as transition metal atoms are rendered more electrophilic.¹⁰

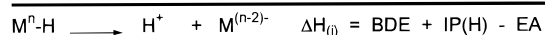
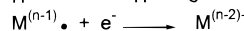
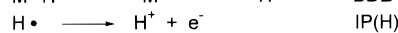
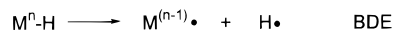
Elegant studies from Wayland's laboratories have shown that Rh(II) porphyrins activate methane reversibly.^{11,12} However, nucleophilic functionalization of the resulting methylrhodium complexes has not been demonstrated. Recently, the first syntheses and characterization of the extremely electron-deficient porphyrin F₂₈TPP¹³ and its transition metal chelates were reported.^{14–16} Electron-deficient porphyrin macrocycles offer the opportunity to stabilize the Rh(I) oxidation state dramatically, potentially

Scheme 1. Proposed Mechanism for Hydrocarbon Functionalization^a



^a The four steps shown are: (1) oxidative addition, (2) proton transfer, (3) oxidation of a metal center, and (4) nucleophilic attack on an organometallic species. M = complexed metal ion, RH = hydrocarbon, B[−] = base, O_x^(m) = oxidant, Red^(m−2) = reduced oxidant, Y[−] = nucleophile.

Scheme 2. Thermodynamic Cycle for Bond Heterolysis^a



^a BDE = bond dissociation energy, IP(H) = ionization potential for hydrogen atom, EA is the electron affinity of the metal (M) in the oxidation state (n − 1), and $\Delta H_{(i)}$ = is the enthalpy for the ionic (heterolytic) reaction shown.

switching on a key S_N2 reaction featuring an alkyrhodium electrophile.¹⁷ In accord with the above discussion, activating this ionic pathway need not compromise C–H activation, since the Rh–H and Rh–C BDEs should be less dependent upon metal electrophilicity than heterolysis of these same bonds. Therefore, the series of transformations outlined in Figure 1 should be feasible.

Syntheses of the rhodium complexes CH₃Rh(F₂₈TPP), HRh(F₂₈TPP), Rh(F₂₈TPP), and [Rh(F₂₈TPP)][−] relied on methodology established for analogous nonfluorinated derivatives.¹⁸ All of these compounds are stable to water, and only [Rh(F₂₈TPP)][−] is air sensitive.

Rh(F₂₈TPP) is sufficiently soluble in benzene (Bz) and chlorobenzene (ClBz) for ¹⁹F NMR experiments. The β-fluorine resonances show a substantial isotropic shift [Rh(F₂₈TPP) δ = −98.3, Co(F₂₈TPP) δ = −124.8, Zn(F₂₈TPP) δ = −145.4 ppm]¹⁶ and the line widths of the broad signals are insensitive to changing temperatures (20–60 °C), indicating that the metalloradical is largely monomeric in solution. This behavior contrasts with that observed for typical rhodium porphyrins, which readily form dimers possessing Rh–Rh bonds.¹⁹ The reversible activation of

(13) Abbreviations used in the paper are: F₂₈TPP - 5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin, Rh(F₂₈TPP)-[5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphinato]rhodium(II), HRh(F₂₈TPP)-[5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphinato][hydrido]rhodium(III), CH₃Rh(F₂₈TPP)-[5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphinato][methyl]rhodium(III), [Rh(F₂₈TPP)][−] - [5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphinato]rhodium(I) anion, Rh(OEP) - [2,3,7,8,12,13,17,18-octaethylporphinato]rhodium, Rh(TMP) - [5,10,15,20-tetramesitylporphinato]rhodium, CH₃Rh(OETAP) - [5,10,15,20-tetraaza-2,3,7,8,12,13,17,18-octaethylporphinato][methyl]rhodium(III).

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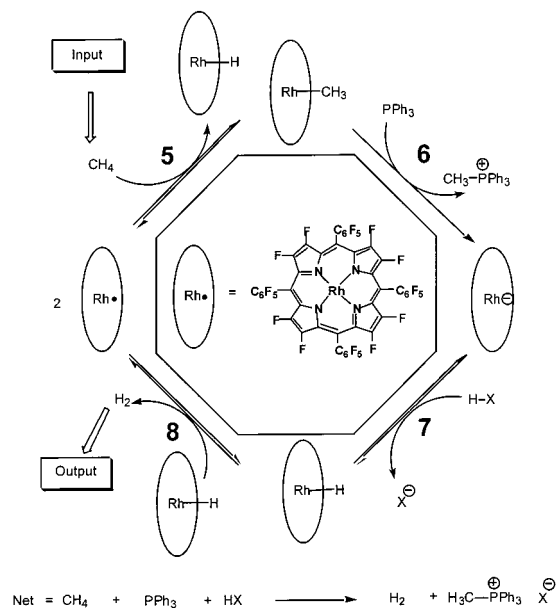


Figure 1. Proposed reaction sequence for methane functionalization. The net reaction is homogeneous alkane–hydrogen metathesis.

H₂ (5 atm) by Rh(F₂₈TPP) in Bz was followed by ¹⁹F NMR spectroscopy at 30–60 °C; only the paramagnetic Rh(F₂₈TPP) and diamagnetic HRh(F₂₈TPP) were observed. There was a marked solvent dependence upon the rate at which the equilibrium was established (30 min in ClBz, 1 d in Bz). By monitoring the equilibrium constant for the reaction as a function of temperature, the relevant thermodynamic quantities ($\Delta H = -11 (\pm 3)$ kcal/mol, $\Delta S = -20 (\pm 10)$ eu, BDE = 58 (± 2) kcal/mol) were determined. The Rh–H BDE observed with Rh(F₂₈TPP) compares to Rh(OEP) (Rh–H = 61.8 kcal/mol)¹⁹ and Rh(TMP) (Rh–H \approx 60 kcal/mol),²⁰ indicating that the Rh–H bond strength varies with metal electron density in the expected manner.

Similarly, the Rh(F₂₈TPP) metalloradical was observed by ¹⁹F NMR to activate methane (5 atm) to form CH₃Rh(F₂₈TPP) at 40 °C. The prohibitively slow rate of this process (15 d to reach 40% conversion in ClBz) and evolution of H₂ from the initially formed rhodium hydride precluded an accurate determination for the reaction enthalpy.

The CH₃Rh(F₂₈TPP) complex is robust and can be isolated by crystallization or benchtop chromatography. It is stable in toluene heated at reflux, and Bz solutions are unchanged by iodine, bromine, trifluoroacetic acid (TFA), or triflic acid (1 M). The ¹³C–¹H coupling constant ($J_{C-H} = 144.5$ Hz) is substantially larger than that reported for [¹³CH₃Rh(TMP)]₂, 141.5 Hz.¹¹ The reluctance of this complex to eliminate methane by protonolysis, and the large J_{C-H} value testify to the metal center's electrophilicity. The Rh–C bond length for CH₃Rh(F₂₈TPP) (2.027(4) Å), determined from an X-ray diffraction study of CH₃Rh(F₂₈TPP) (toluene solvate),²¹ is indistinguishable from that of CH₃Rh(OEP) (2.031(6) Å)²² and CH₃Rh(OETAP) (2.034(7) Å),²³ indicating that

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(21) Single crystals of [CH₃]Rh[NaC₂₀F₈(C₆F₅)₄]₂·5CH₃C₆H₅ obtained from toluene are, at -85 ± 2 °C, triclinic, space group *P*-*C* (No. 2) with $a = 13.0624(8)$ Å, $b = 13.7551(8)$ Å, $c = 16.1232(10)$ Å, $\alpha = 91.210(1)^\circ$, $\beta = 96.405(1)^\circ$, $\gamma = 106.739(1)^\circ$, $V = 2752.5(3)$ Å³ and $Z = 2$ formula units ($d_{\text{calcd}} = 1.767$ g cm⁻³; $\mu_a(\text{Mo K}) = 0.454$ mm⁻¹). A full description of the structure determination is included in the Supporting Information.

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this metrical parameter is relatively insensitive to large changes in porphyrin electronic structure, as is expected for a covalent bond with little ionic character.

In Bz or ClBz at 40 °C, the potent nucleophile triphenylphosphine (PPh₃) (0.1 M) attacks CH₃Rh(F₂₈TPP) at the methyl group, quantitatively forming methyltriphenylphosphonium cation [CH₃PPh₃]⁺ and displacing the [Rh(F₂₈TPP)]⁻ leaving group (reaction 6 in Figure 1). Remarkably, ion pair formation is sufficiently favorable for the reaction to occur in Bz, a relatively nonpolar solvent, although the reaction required 10 d to reach completion (12 h in ClBz). Evidence for extensive ion-pairing of the product salt is apparent in the ¹H NMR spectrum, where there are substantial upfield shifts of the phenyl and methyl proton resonances; the methyl doublet is shielded to the greatest extent ($\delta = -1$ ppm). (The product assignments were confirmed by NMR spectroscopy of independently synthesized [CH₃PPh₃]⁺ [Rh(F₂₈TPP)]⁻ and of [CH₃PPh₃]⁺ Cl⁻ extracted from the reaction mixture with NaCl/D₂O.) The success of this nucleophilic displacement confirms that the Rh(I) oxidation state is sufficiently stabilized by the perfluorinated porphyrin to make the metal complex a relatively good leaving group in comparison to typical Rh(I) porphyrins. To our knowledge, this is the first example of a bona fide nucleophilic displacement on a neutral organometallic complex leading to a stable ion pair product.

To quantify the stabilization of the Rh(I) oxidation state by the fluorinated porphyrin, the acidities of HRh(F₂₈TPP) and HRh(TPP) were measured in dimethyl sulfoxide against a series of standard acids.²⁴ At 25 °C the following data were obtained: HRh(F₂₈TPP), $pK_a = 2.1 (\pm 0.3)$; HRh(TPP), $pK_a = 11.0 (\pm 0.3)$; $\Delta pK_a = 8.9$. The large difference in acidity between the fluorinated and nonfluorinated complexes ($\Delta\Delta G^\circ = -12.1$ kcal/mol) confirms that the ionic reactions are much more sensitive to the electron-withdrawing nature of the perfluorinated porphyrin than are the Rh–C and Rh–H BDEs. In addition a sample of [CH₃PPh₃]⁺ [Rh(F₂₈TPP)]⁻ in benzene was titrated with TFA, and the relative acidities were measured by ¹⁹F NMR spectroscopy. The rhodium hydride is slightly more acidic than TFA ($\Delta pK_a = 0.6$) under these conditions. This acid–base reaction formally completes the reaction cycle shown in Figure 1.

Here we have demonstrated that a modified rhodium porphyrin complex performs each of the reactions shown in Figure 1. The key design principle, that ligand modification can so increase metal nucleofugacity that nucleophilic substitution can be activated without compromising alkane and hydrogen activation, is drawn directly from fundamental concepts of chemical bonding. Developing an efficient catalytic system from these or similar components requires dramatically accelerated rates of the methane activation and nucleophilic functionalization reactions; studies aimed at satisfying these kinetic requirements are currently underway.

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Supporting Information Available: Experimental procedures, ¹⁹F NMR spectra, and characterization data for Rh(F₂₈TPP) derivatives; X-ray structural information on CH₃Rh(F₂₈TPP) (PDF) and a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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