Selective Activation and Functionalization of Linear Alkanes Initiated under Ambient Conditions by a Tungsten Allyl Nitrosyl Complex

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Alkanes are difficult to convert directly to more valuable chemicals since they possess strong C–C and C–H bonds and lack Lewis acidic or Lewis basic sites of reactivity. They can be functionalized by highly reactive species such as free radicals, carbenes, and superacids, but these transformations are generally not selective and do not tolerate other functionalities. Consequently, a goal of researchers working in this area of chemistry has been the selective conversion of alkanes to functionalized molecules at ambient temperatures. While striving for this goal, investigators have expended considerable efforts in recent years to develop transition-metal complexes for the activation and functionalization of alkane C–H bonds, and they have achieved some notable successes. Particularly noteworthy in this regard are the selective oxidation of alkanes in aqueous solution in the presence of platinum salts first reported by Shilov and co-workers and the catalytic, regioselective functionalization of alkanes with borane reagents recently developed by Hartwig and co-workers. However, effecting such transformations for linear alkanes is particularly challenging since the activations of aliphatic C–H bonds at these transition-metal centers often require generation of the active species by high-energy thermal or photochemical means. Furthermore, the activations can be nonselective, and they frequently result in the formation of initial organometallic products that are unstable under the experimental conditions employed.

We now wish to report a new tungsten allyl nitrosyl complex, namely, Cp*W(NO)(η 2-C 3 H 5 CHCHMe)(CH 2 CMe 3 ) (1) (Cp* = η 5-C 5 Me 5 ; Me = CH 3 ), that initiates C–H activations and functionalizations of linear alkanes without any of the problems outlined above. Specifically, 1 selectively activates the terminal C–H bonds of n-alkanes under ambient conditions and forms thermally stable Cp*W(NO)(η 2-C 3 H 5 CHCHMe)(n-alkyl) compounds from which the n-alkyl ligand may be selectively released in a derivatized form of the unbound C–H bond. We have discovered is summarized in Scheme 1 with n-pentane being employed as the prototypical linear alkane.

Reagent 1 can be isolated in moderate yields as an orange-yellow solid from the reaction of Cp*W(NO)(CH 2 CMe 3 )Cl with 0.5 equiv of (MeCHCHCH 2 ) 2 Mg·x(dioxane) in Et 2 O at −78 °C. It has been fully characterized by conventional spectroscopic methods including single-crystal X-ray diffraction. Complex 1 is thermally unstable, and when dissolved in n-pentane at room temperature for 20 h, it loses CMe 3 and cleanly converts to the yellow-orange n-pentyl complex 2 (Figure 1) which has been isolated in 80% yield.

Monitoring the conversion of 1 into 2 by 1 H NMR spectroscopy reveals no detectable intermediate complexes. Consequently, it is not clear from these observations whether 2 results from exclusive activation of the most accessible terminal C–H bond of n-pentane or whether internal C–H bonds are also activated, but these latter products rearrange rapidly (and intramolecularly) to the final isolable products. Fortunately, an isotopic labeling experiment has proven to be informative in this regard. As shown in Scheme 1, exposure of 1 to n-pentane-d 2 results in the quantitative formation of Cp*W(NO)(η 2-C 3 H 5 CHCHMeD)(n-C 3 D 11 ) (2-d 12 ) as evidenced by the appearance of a 1:1:1 triplet at 17.7 ppm in the 13 C 1 H NMR spectrum of the crude product in C 6 D 6 and the absence of n-pentyl proton signals in its 1 H NMR spectrum. The lack of additional D or H incorporation into the allyl and pentyl ligands, respectively, in 2-d 12 is most consistent with 2 being formed by the exclusive activation of the terminal C–H bond of pentane.

Finally, exposure of 1 to an excess of PMe 3 leads to the formation of the 18e η 2 -dienyl complex, Cp*W(NO)(η 2-C 3 H 5 CH=CHCH=CH 2 )-(PMe 3 ) (3). No concomitant C–H activation of the phosphine occurs during this reaction. Compound 3 has been isolated as a light yellow crystalline material, and its solid-state molecular structure is shown in Figure 2. That this molecular structure is maintained in solution is indicated by the 1 H NMR spectrum of 3 in C 6 D 6 that displays diagnostic downfield resonances between 4.70 and 6.07 ppm for the protons on the uncoordinated H 2 C=CH unit and upfield resonances from 0.32 to 2.04 ppm for the protons on the bound H 2 C=CH unit. Similarly, in the 13 C 1 H NMR spectrum of 3 in the same solvent, the chemical shifts of the signals due to the unbound C=C linkage are much more downfield (102.5 and 132.4 ppm).
149.7 ppm for CH= and CH=CH, respectively) than are the chemical shifts for the signals attributable to the bound C==C group (42.7 and 31.4 ppm, for CH== and CH2==, respectively).

On the basis of the results from the deuteron-labeling and PMe5-trapping experiments outlined in the preceding paragraphs, we suggest that the C–H activation chemistry initiated by 1 proceeds via two distinct steps: (1) formation of the 16e intermediate η4-diene complex, Cp*W(NO)(η2-CH=CH=CH2) (A) via intramolecular β-H elimination of neopentane from 1, and (2) incorporation of n-pentane into A via intermolecular C–H bond activation to produce 2 (i.e., essentially the reverse of the first step but with n-pentane as the alkane reactant). The first step is somewhat surprising since it might have been expected that loss of a β-H from the allyl CH2 group in 1 and its metal-mediated transfer to the CH2CMe3 ligand resulting in the loss of CMe6, could lead to the formation of the 18e η4-diene complex, Cp*W(NO)-(η4-trans-CH2=CH=CH2). This complex is a thermally stable yellow compound that we have prepared previously by treating diethyl ether solutions of Cp*W(NO)(CH2SiMe3)2 at −78 °C with H2 in the presence of 1.3-butadiene.6 It is unlikely that the η4-trans-diene complex is formed during the C–H activation chemistry initiated by 1 since we have also established previously that such complexes are relatively kinetically inert to substitution by PMe5,7 a process that would be required for the formation of 3. Furthermore, it is highly unlikely that in the presence of n-pentane Cp*W(NO)-(η4-trans-CH2=CH=CH2) with its favored 18e configuration at the metal would open up the coordination position at the tungsten center required for C–H activation by spontaneously converting to the electronically unsaturated (16e) Cp*W(NO)(η2-CH=CH=CH2) (A in Scheme 1). Hence, we believe that it is A that is formed initially by loss of CMe3 from 1 and that A is the intermediate complex responsible for the selective activation of n-alkanes. Such a mechanism of C–H activation has not been established experimentally previously, and it may well be behind the unique C–H activating properties of 1. In that connection, it may be noted that alkane activation by 16e intermediate A results in the formation of a thermally stable allyl alkyl complex such as 2, whereas with many other transition-metal C–H activating systems both the C and H atoms remain attached to the metal center and the organometallic products are thermally unstable hydrido alkyl complexes.4 Such hydrido alkyl compounds are particularly prone to undergo reductive elimination of alkane or β-hydride elimination to form a complex containing η2-olefin and H ligands attached to the metal center.8

As shown in Scheme 1, the n-pentyl ligand can be released in 70% yield from 2 in a derivatized form as 1-iodopentane that may then be elaborated into other derivatives by utilizing established organic synthetic methodologies.9 The presence of the functional group at the terminal position is highly desirable since terminal alcohols and terminal amines are major commodity chemicals. In other words, the C–H activation chemistry initiated by 1 provides a synthetic route under very mild conditions for the stoichiometric conversion of n-pentane into 1-iodopentane. [For comparison, it may be noted that direct iodinations of pentane either by tert-butyl hypiodite10 or by HCl in the presence of solid NaNH11 are unselective and produce mixtures of iodocontanes.] Initial experiments indicate that other linear alkanes are transformed in an identical manner by 1. Thus, treatment of 1 with n-heptane affords Cp*W(NO)(η1-CH2CHCHMe)(CH2CH2CH2CH2CH2Me) (4) as the only organometallic product, and it has been definitively identified by its diagnostic 1H and 13C NMR spectra.5

In summary, we have discovered a unique tungsten allyl nitrosyl complex (1) that selectively activates the terminal C–H bonds of n-alkanes under ambient conditions and forms thermally stable n-alkyl complexes that may be isolated and fully characterized. In addition, we have found that the n-alkyl ligands can be selectively released from these complexes in a derivatized form with the functional group at the terminal position. Preliminary experiments suggest that 1 can initiate similar C–H bond activations and functionalizations even in the presence of functional groups containing N and O heteroatoms. These studies are currently in progress.

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Supporting Information Available: Experimental procedures and complete characterization data for compounds 1–4 (PDF), and full details of the crystal structure analyses of 1, 2, and 3 including associated tables (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


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Figure 2. Solid-state molecular structure of 3 with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)–C(1) = 2.221(4), W(1)–C(2) = 2.218(3), W(1)–P(1) = 2.4335(8), C(1)–C(2) = 1.453(5), C(2)–C(3) = 1.456(5), C(3)–C(4) = 1.306(5), C(1)–C(2)–C(3) = 121.4(3), C(2)–C(3)–C(4) = 126.7(4).