

Unprecedented Reactivity Initiated by Insertion of 2,6-Xylylisonitrile into the W–Alkyl Linkages of Cp*W(NO)(*n*-alkyl)(η^3 -CH₂CHCHMe) Complexes

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Summary: Treatment of the compounds $Cp^*W(NO)(R)(\eta^3 - CH_2CHCHMe)$ ($R = n - C_5H_{11}$, $n - C_7H_{15}$, $n - C_8H_{17}$) with 2,6xylylisonitrile first produces the expected complexes bearing η^2 -iminoacyl ligands arising from migratory insertion of the isonitrile into the tungsten-alkyl linkages, processes that result in the allyl ligands undergoing concomitant $\eta^3 \rightarrow \eta^1$ haptotropic shifts. These η^1 -allyl complexes then undergo subsequent intramolecular nucleophilic attacks by their allyl groups on the nitrogen atoms of the η^2 -iminoacyl ligands to form novel metallacyclic compounds that contain α -aminocarbene ligands.

The migratory insertion of organic isonitriles into metal– alkyl bonds is an important organometallic reaction that has received a fair amount of attention from various researchers over the years.^{1,2} Such insertions have been reported for most of the early transition metals as well as some lanthanides and actinides, and they lead to the formation of η^2 -iminoacyl ligands. Hence, it did not surprise us that during our recent investigation³ of the characteristic chemistry of the two Cp*W(NO)(R)(η^3 -CH₂CHCHMe) complexes having R = CH₂SiMe₃, CH₂C₆H₅ we found that they react with



 $\mathsf{R} = \mathsf{CH}_2\mathsf{SiMe}_3 \text{ or } \mathsf{CH}_2\mathsf{C}_6\mathsf{H}_5, \, \mathsf{R'} = 2,6\text{-}\mathsf{Me}_2\mathsf{C}_6\mathsf{H}_3$



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Figure 1. Solid-state molecular structure of A with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(2)-C(43) = 2.214(3), W(2)-N(4) = 2.170(2), W(2)-C(34) = 2.101(3), C(34)-N(4) = 1.267(4), W(2)-N(3) = 1.761(3); W(2)-N(4)-C(34) = 69.78(17), W(2)-C(34)-N(4) = 75.77(17).

2,6-xylylisonitrile by inserting the isonitrile into the tungsten-allyl linkages (Scheme 1).⁴

During an extension of these original studies we have now discovered that those members of this family of tungsten compounds that have R = n-alkyl exhibit an entirely different mode of reactivity involving their alkyl ligands when treated with 2,6-xylylisonitrile. It is these novel chemical transformations that we now wish to communicate in some detail.

As summarized in Scheme 2, treatment of Cp*W(NO)-(*n*-C₅H₁₁)(η^3 -CH₂CHCHMe) with the isonitrile first produces the expected compound **A**, containing an η^2 -iminoacyl ligand arising from migratory insertion of the isonitrile into

(10) See the Supporting Information for details.

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⁽⁴⁾ Klei, E.; Teuben, J. H.; de Liefde Meijer, H. J.; Kwak, E. J.; Bruins, A. P. *J. Organomet. Chem.* 1982, 224, 327–339 and references cited therein.
(5) For additional examples of η¹-allyl ligands functioning as nucleo-

⁽⁵⁾ For additional examples of η^{+} -allyl ligands functioning as nucleophiles, see: Rosenblum, M. Acc. Chem. Res. **1974**, 7, <u>1</u>22–128.

⁽⁶⁾ Crystal data for $\mathbf{A} + \mathbf{B}$: triclinic, space group $P\overline{1}$, a = 7.884(5) Å, b = 18.274(5) Å, c = 19.322(5) Å, $\alpha = 102.850(5)^{\circ}$, $\beta = 100.902(5)^{\circ}$, $\gamma = 93.820(5)^{\circ}$, V = 2648(2) Å³, Z = 2, R1 = 0.0409, wR2 = 0.0477, and GOF(F^2) = 1.020 for 12416 observed reflections and 700 variable parameters.

⁽⁷⁾ The molecular structure of \mathbf{B} exhibits some disorder of the pentyl ligand. Only one of the rotational isomers is shown in Figure 2.

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the tungsten-alkyl linkage,⁴ a process that results in the allyl ligand undergoing a concomitant $\eta^3 \rightarrow \eta^1$ haptotropic shift. Compound **A** then undergoes a subsequent intramolecular nucleophilic attack by the η^1 -allyl group⁵ on the nitrogen atom of the η^2 -iminoacyl ligand to form the unusual metallacyclic compound **B**, which contains an α -aminocarbene ligand. Interestingly, the conversion of **A** to **B** does not proceed to completion but rather continues only until an equilibrium is established between the two isomeric complexes (K = 1.15 at 20 °C) after approximately 24 h.

The solid-state molecular structures of **A** and **B** have been confirmed by an X-ray crystallographic analysis of a single crystal containing both complexes,⁶ and they are shown in Figures 1 and 2, respectively.

While the intramolecular metric parameters of **A** are as expected for a molecule of this type,⁴ those of **B** constitute a more fascinating story.⁷ The newly formed α -aminocarbene ligand is best viewed as functioning as a four-electron donor



Figure 2. Solid-state molecular structure of **B** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)-C(18) = 2.182(3), W(1)-C(17) = 2.163(3), W(1)-C(6) = 2.134(3), C(6)-N(2) = 1.317(4), N(2)-C(16) = 1.511(4), C(17)-C(18) = 1.438(5); C(16)-N(2)-C(6) = 116.7(2), W(1)-C(6)-N(2) = 118.4(2), C(17)-C(16)-N(2) = 106.2(2).

to the tungsten center that thus attains the favored 18e configuration. The four electrons are provided via a $C \rightarrow W$ dative interaction involving C(6) and synergic η^2 -(C=C)-W bonding involving C(17) and C(18). Consistent with this view are the following facts.

(1) The C(6)–N(2) and C(17)–C(18) bond lengths are 1.317(4) and 1.438(5) Å, respectively, and they are shorter than typical C–N and C–C single-bond distances of 1.469 and 1.514 Å, respectively.⁸

(2) The coordination geometries at C(6) and N(2) are essentially planar, consistent with these atoms being sp^2 -hybridized.

(3) The ¹³C NMR spectrum of **B** in C₆D₆ exhibits a downfield resonance attributable to C(6) at δ 258.9. For comparison, the carbene carbon signal for W{*C*(NHMe)-Me}(CO)₅ in C₆D₆ occurs at 255.6 ppm.⁹

The other spectroscopic properties of A and B indicate that they retain their solid-state molecular structures in solutions.¹⁰

The conversion depicted in Scheme 2 for the $n-C_5H_{11}$ reactant also occurs for the Cp*W(NO)(R)(η^3 -CH₂CH-CHMe) complexes having $R = n - C_7 H_{15}$ and $n - C_8 H_{17}$. The organometallic products in each case (i.e., \mathbf{A}' and \mathbf{B}' , and \mathbf{A}'' and $\mathbf{B}^{\prime\prime}$, respectively, in Scheme 2) have been characterized by conventional spectroscopic and analytical methods.¹⁰ Just as for the $R = n-C_5H_{11}$ case (vide supra), both reactions attain equilibrium in about 24 h, and from the variation of ln K vs $1/T \Delta H$ and ΔS can be estimated for these transformations. In the case of the *n*-pentyl reactant in C_6D_6 with an A/Bmixture concentration of ca. 0.05 M, such a plot (Figure 3) affords reasonable values for ΔH and ΔS of -19.70 ± 1.5 kJ/ mol and -65.4 ± 4.7 J/mol, respectively, which reflect both the stronger bonds and the more ordered nature of **B**. Finally, we have also established that the relatively pure metallacyclic complex B does not react with electrophiles such as B-chlorocatecholborane, whereas the comparably pure η^1 -allyl complex A undergoes electrophilic attack at the W-C bond while leaving the isonitrile-inserted unit intact (Scheme 3).

In summary, we have discovered that the allyl ligand can become involved in subsequent reactivity after Cp*W-(NO)(R)(η^3 -CH₂CHCHMe) (R = *n*-alkyl) complexes have undergone insertion of 2,6-xylylisonitrile into their W–R linkages. Specifically, the initially formed η^2 -iminoacyl ligands



Figure 3. Plot of $\ln K \operatorname{vs} 1/T$ for the equilibrium between A and B.



then undergo intramolecular nucleophilic attack by the allyl ligand that has undergone a concomitant $\eta^3 \rightarrow \eta^1$ haptotropic shift to form azametallacycles that involve olefin and carbene links from α -aminocarbene ligands to the tungsten centers. To the best of our knowledge, these transformations involving the methylallyl ligand are without precedent. However, given the central role that migratory insertion reactions play in transition-metal-catalyzed processes,² these results are of fundamental significance. Nevertheless. it remains to be ascertained whether

similar modes of reactivity are exhibited by other Cp*W(NO)-(alkyl)(η^3 -allyl) complexes with other isocyanides. Studies designed to provide these answers and to develop more fully the chemistry of the novel metallacyclic complexes are currently in progress.

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Supporting Information Available: Text and tables providing full details of experimental procedures and characterization data for all new complexes and a CIF file containing details of the crystallographic analysis of complexes **A** and **B**. This material is available free of charge via the Internet at http:// pubs.acs.org.