# Tungsten(II) Alkylimido Complexes from Insertion of Nitriles into Tungsten Hydride: Alkylideneamido Intermediate Stage and Nitrene Group Transfer to Isocyanide

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Ⓢ *Supporting Information*

ABSTRACT: The tetrahydrido complex $[WH_4(\kappa^4\text{-}\mathbf{P4})]$ ($\mathbf{P4}$ = *meso-o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$) reacted with aliphatic nitriles AkCN at 80 °C in toluene to afford a series of the imido complexes, $[W(NCH_2Ak)(\kappa^4\text{-}\mathbf{P4})]$ (**2**). Similar reactions with aromatic nitriles ArCN proceeded stepwise, leading to formation of the hydrido−alkylideneamido complexes $[WH(N=CHAr)(\kappa^4\text{-}\mathbf{P4})]$ (**3**) at the first stage and a subsequent isomerization into the imido complexes $[W(NCH_2Ar)(\kappa^4\text{-}\mathbf{P4})]$ (**4**). Conversion of **3** into **4** was accelerated by electron-rich Ar groups such as *p*-$CH_3OC_6H_4$, while it was

completely inhibited when Ar was the considerably electron-deficient *p*-$CF_3C_6H_4$. An X-ray crystallographic study on **2** (Ak = *p*-$ClC_6H_4CH_2$) and **4** (Ar = *p*-tolyl) has disclosed a distorted-square-pyramidal coordination geometry, in which the apical position is occupied by the imido ligand with a W^{II}−N triple bond. An almost linear W^{II}=N=C linkage of **3** (Ar = *p*-tolyl) has also been determined. Complex **2** was capable of nitrene group transfer to isocyanide to produce carbodiimide.
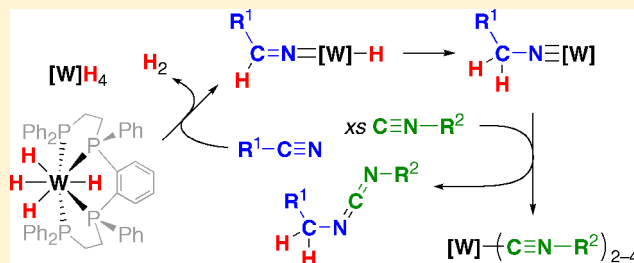
Hydrogenation of nitrile is a vital method to prepare primary amines, and the heterogeneous processes under hydrogen pressure using transition-metal catalysts have great industrial importance.[1] In comparison, homogeneous hydrogenation based on transition-metal catalysts has attracted little interest because of side reactions producing secondary and tertiary amines etc.,[2] whereas a number of complex catalysts that selectively give primary amines have been developed.[3] The first step in hydrogenation is insertion of a nitrile molecule into a metal−hydrogen bond. Stoichiometric reactions of this type have been observed for some hydride complexes and result in either an alkylideneamido (−N=CHR) or iminoacyl (−C(= NH)R) ligand, the former of which is common for mononuclear complexes.[4] Also in heterogeneous systems, these species are hypothesized to be present on the catalyst surface, and imido/nitrene (=N−CH_2R) and carbene (= C(NH_2)R) intermediate structures are proposed in addition.[5]

We have recently developed the synthesis of the tungsten tetrahydride complex $[WH_4(\kappa^4\text{-}\mathbf{P4})]$ (**1**; $\mathbf{P4}$ = *meso-o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$) and its use in the conversion of unsaturated organic molecules.[6,7] By virtue of the linear tetraphosphine coligand **P4**, **1** is much more reactive than the closely related $[WH_4(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$). This is presumed to be mainly due to the particular coordination geometry brought by **P4** as well as labile bonding between terminal PPh_2 groups and the metal center. Previous studies have shown the remarkable hydride-donating ability of **1**, which facilitates conversion of CS_2 into a methanedithiolato ligand ($CH_2S_2{}^{2-}$) and hydrodesulfurization of aryl isothiocyanates to *N*-arylmethylamines. Such reactivity toward polar

unsaturated bonds prompted us to investigate reactions with organonitriles, leading to the discovery of not only conventional alkylideneamido formation but also further conversion into the imido stage. Here we report this new synthetic route to imido ligands as well as the structures and reactions of the resulting imido complexes of W^{II}.

Various aliphatic nitriles AkCN (Ak = 1°−3° alkyls) reacted with **1** on heating in toluene to form the imido complexes $[W(NCH_2Ak)(\kappa^4\text{-}\mathbf{P4})]$ (**2**) accompanied by formation of 1 equiv of H_2 (eq 1). Reactions using 3-fold molar AkCN were
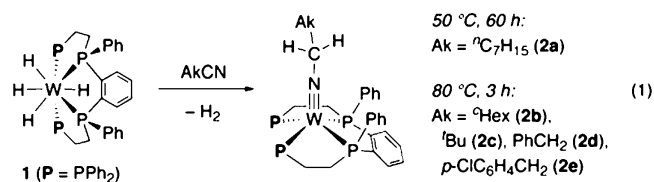
complete within 3 h at 80 °C without giving any other complexes, as determined by NMR, while those with *n*-C_7H_{15}CN proceeded even at 50 °C. Among the series of compounds **2**, that with Ak = *p*-$ClC_6H_4CH_2$ (**2e**) was isolated as air-sensitive brownish-purple crystals in 89% yield, while other derivatives could not be crystallized due to their high solubility in common organic solvents.

The molecular structure of **2e** was established by X-ray crystallography (Figure 1A). The metal center has a distorted-
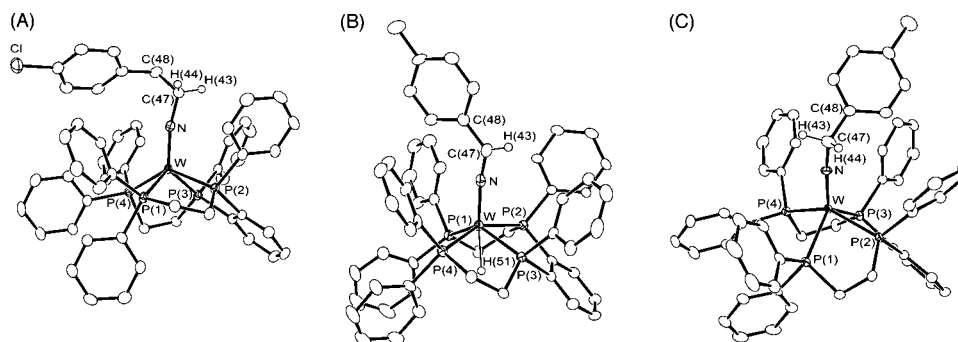
Figure 1. Molecular structures of **2e** (A), **3a** (B), and **4a** (C) showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity, except for those attached to the α-carbon atoms of organonitrogen ligands and the hydrido ligand. Some important bond lengths (Å) and angles (deg) not appearing in the text: N–C = 1.436(4), N–C–C = 112.7(2) for **2e**; W–H = 1.88(4), N–W–H = 174(1), P(1)–W–P(3) = 133.38(4), P(2)–W–P(4) = 154.45(4) for **3a**; W–N = 1.794(2), N–C = 1.449(4), W–N–C = 169.9(2), N–C–C = 114.4(2), P(1)–W–P(3) = 113.13(2), P(2)–W–P(4) = 140.25(2) for **4a**.

square-pyramidal geometry with the imido ligand at the apical position. The transoid P–W–P angles are 122.82(2)° for P(1)–W–P(3) and 135.31(2)° for P(2)–W–P(4), which are indicative of slight distortion toward a trigonal bipyramid. The closely related (*N*-piperidinyl)imido complex [W(NNC$_5$H$_{10}$)-(dppe)$_2$] has been reported to have a distorted-trigonal-bipyramidal geometry, in which the axial sites are occupied by two P atoms with a P–W–P angle of 157.1(1)° (equatorial P–W–P = 107.7(1)°).[8] This difference presumably arises from steric regulation due to three consecutive chelate rings of tetradentate **P4**. The W–N distance of 1.785(2) Å in **2e** is typical for a triple bond, which is consistent with the linear W–N–C linkage (168.4(2)°) due to the sp-hybridized N atom as well as the 18-electron count around the five-coordinate W^{II} center. In comparison with the six-coordinate W^{IV} complexes bearing one **P4**[9] or two dppe ligands,[10] the W–N bond of the imido ligand is slightly long (vs 1.72—1.76 Å) and the W–P distances are short for **2e**. These features are similarly seen in [W(NNC$_5$H$_{10}$)(dppe)$_2$] (W–N = 1.781(5) Å), while the six-coordinate W^{II} complex *fac*-[W(NNMe$_2$)(dppe)(CO)$_3$] has a considerably long W–N bond (2.12(1) Å) and bent W–N–N moiety (139(1)°), reflecting a W=N(sp^2) character.[11] The ^{31}P{^{1}H} NMR spectra of **2** displays two signals at about δ 85 and 117, corresponding to the outer and inner P atoms of **P4**. The proton signal due to the NCH$_2$ moiety is unambiguously assigned according to the vicinal coupling with the Ak group for each derivative of **2**.

Treatment of **1** with TolCN (Tol = *p*-tolyl) under the same conditions as for aliphatic nitriles (3 equiv of nitrile, 80 °C, 3 h) resulted in release of H$_2$ (0.88 equiv to **1**) and deposition of brown crystals from the reaction mixture, which were identified as the hydrido–alkylideneamido complex [WH(N=CHTol)-(κ^4-**P4**)] (**3a**, 37% yield) (Scheme 1). Prolonged heating of the above reaction mixture gradually decreased the amount of **3a**,

and the imido complex [W(NCH$_2$Tol)(κ^4-**P4**)] (**4a**) became predominant after 20 h, which was isolated as brown cubic crystals in 29% yield. As for NMR spectra, **4a** closely resembled its analogues **2**. For **3a**, the existence of the hydride ligand was confirmed by the ^{1}H NMR signal, which was observed at δ −3.42 as a broad quintet (J_{HP} = 38 Hz). The azomethine (N=CH) proton appeared at δ 4.43, weakly coupling with P nuclei (∼2 Hz). The ^{31}P{^{1}H} NMR spectrum showed two signals at δ 62.0 and 83.4 assignable to the outer and inner P atoms of **P4**, respectively. The experiment to heat a toluene solution of isolated **3a** at 80 °C unambiguously confirmed that **4a** was produced via isomerization of **3a**. This conversion was remarkably facilitated by a catalytic amount of [Et$_3$NH][BPh$_4$] to progress even at 28 °C (see the Supporting Information).

A crystallographic study on **3a** and **4a** has discriminately revealed the structures of their organonitrogen ligands (Figure 1B,C). The imido complex **4a** was ascertained to be essentially identical with that of **2e**, except for the organic moiety of the imido ligand. The coordination geometry of **3a** is a highly distorted octahedron, where four P atoms constitute an equatorial plane. With respect to this plane, the hydrido ligand is located at the side that the *o*-phenylene group of **P4** is directed, while the alkylideneamido ligand occupies the wider side of its opposite. The N–C distance at 1.305(6) Å and the N–C–C angle of 126.7(4)° in **3a** are diagnostic of an N=C(sp^2) system. The W–N bond length of 1.863(3) Å, which is longer by ∼0.07 Å than those of the imido complexes **2e** and **4a**, suggests a double-bond character, expected from the 18e rule. The sp hybridization of the N atom is supported by the linear W–N–C linkage (169.7(3)°). These bond distances and angles of the alkylideneamido ligand are comparable to those of other W complexes.[14,15]

Insertion of nitrile into an M–H bond has been known for a number of mononuclear complexes.[13–16] However, to the best of our knowledge, the formation of imido ligands via stepwise transfer of two hydrides to a nitrile carbon on a single metal center is unprecedented.[17] In the case of the dinuclear hydride [Cp′TaCl$_2$H]$_2$ (Cp′ = η^5-C$_5$Me$_4$Et), [(Cp′TaCl$_2$)$_2$(μ-H)(μ-NCHMe)] was given by reaction with MeCN, which degrades by addition of ethylene into the mononuclear [Cp′TaCl$_2$(NCH$_2$Me)] and [Cp′TaCl$_2${(CH$_2$)$_4$}].[18] However, the mononuclear dihydride complex [Cp*$_2$ZrH$_2$] (Cp* = η^5-C$_5$Me$_5$) undergoes insertions of two TolCN molecules to result in the bis(alkylideneamido) complex [Cp*$_2$Zr(N=CHTol)$_2$].[19] Photolysis of [Tp′W(CO)$_3$H] (Tp′ = hydrotris-

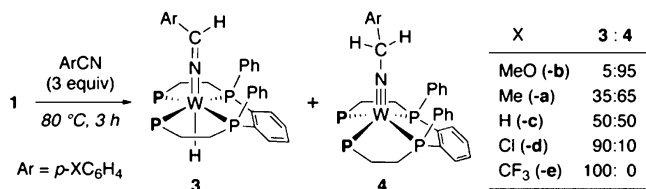**Scheme 1. Reaction of the Tetrahydrido Complex 1 with *p*-Tolunitrile**
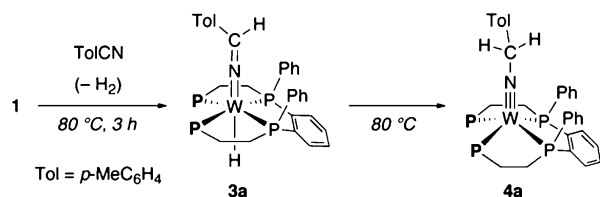
(3,5-dimethylpyrazolyl)borate) with RCN (R = Me, Et, CH_2Ph) provides the insertion products $[Tp'W(CO)_2(N=CHR)]$, subsequent protonation of which by HBF_4 gives the W^{IV} imido complexes $[Tp'W(CO)_2(NCH_2R)][BF_4]$.[12] Other transformations of a nitrile into an imido ligand demonstrated with mononuclear complexes include double protonation at the carbon atom of nitrile coordinated to Mo^0, W^0, or Re^I [10,20] and those presumed to proceed via hydrogen transfer from a methanol to a nitrile ligand in Mo^{II} and Cr^{II} complexes.[21]

The alkylideneamido ligand is probably formed via generation of an open site by dissociation of H_2 or one of the terminal P atoms in **P4**, followed by insertion of nitrile into a W–H bond. Possible pathways for the isomerization of **3a** to **4a** are roughly classified into intra- and intermolecular hydrogen shifts, although the former seems less probable because of the mutually trans location of the alkylideneamido and the hydride ligands. From the reaction of tetradeuterido complex **1**-d_4 with TolCN was prepared $[WD(N=CDTol)(\kappa^4$-**P4**$)]$ (**3a**-d,d), whose D atom enrichments were estimated at 93 and 87 atom % for the hydrido ligand and the azomethine group, respectively. Complex **4a** formed by heating this sample at 80 °C for 20 h in toluene bore predominantly the NCD_2Tol ligand (**4a**-d_2, 59% isotopic purity) containing totally 77 atom % D at the imido ligand. When a 1:1 mixture of **3a**-d,d and nondeuterated **3a** was treated under the same conditions, the mixture of isotopomers produced was in the ratio **4a**-d_2:**4a**-d:**4a**-d_0 = 14:46:40. This low content of **4a**-d_2 unequivocally excluded intramolecular mechanisms.

It was spectroscopically confirmed that various aromatic nitriles ArCN reacted with complex **1** to give the corresponding species **3**, which then converted into **4** in most cases (Scheme 2). While the reactivity of these nitriles toward **1** was not

speculated not to occur bimolecularly for steric reasons but rather to be mediated by proton carriers such as a trace of H_2O. This may be responsible for the observed D atom contents in the above labeling experiments being lower than the theoretical level.

Although imido complexes of W are ubiquitous, most of their oxidation states are from +4 to +6.[22] Imido ligands bound to low-valent centers such as W^{II} are very rare and are in general highly reactive,[8,11,23,24] while the reactivity of **2** and **4** seems dissimilar because these are relatively stabilized by the strong W–N triple bond. Complex **2e** reacted with 2,6-dimethylphenyl isocyanide (XyNC) at 80 °C to produce the asymmetric carbodiimide p-$ClC_6H_4CH_2CH_2N=C=NXy$ (**5**) in 75% yield via the coupling of the nitrene functionality and isocyanide (Scheme 3). The complex part was retrieved as a mixture of W^0

Scheme 3. Reaction of the Imido Complex 2e with XyNC

L = XyNC

NMR yields based on W atom are shown in parentheses.

Scheme 2. Reactions of the Tetrahydrido Complex 1 with Various Aromatic Nitriles under the Same Conditions

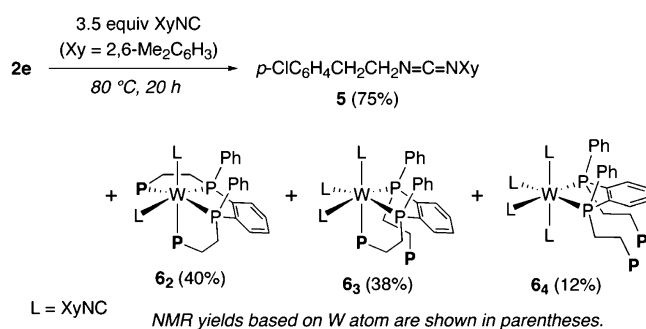| X	3 : 4
MeO (-b)	5:95
Me (-a)	35:65
H (-c)	50:50
Cl (-d)	90:10
CF_3 (-e)	100 : 0

significantly different, a tendency was observed that isomerization of **3** into **4** was accelerated by an electron-rich Ar group. Among the examined nitriles, the formation of **4** was fastest for Ar = p-$MeOC_6H_4CN$, while **3e** with Ar = p-$CF_3C_6H_4$ was never converted into **4** at 80 °C. In contrast, the amido-type complex was not detected at all along the reactions with aliphatic nitriles. Conversion to the imido complex is presumably very fast by virtue of highly electron-donating alkyl groups.

Taking into consideration of these results, conversion of **3** into **4** is proposed to proceed via the following mechanisms. The alkylideneamido ligand is reversibly protonated at the azomethine carbon atom to give the imido ligand. If the resulting cationic W^{IV} complex releases the hydrido ligand as a proton, the neutral imido complex **4** will be generated. The accelerating effect of an added proton source supports this hypothesis, and some imido complexes have been prepared via protonation pathways (vide supra).[10,12,20] The initial protonation step is probably rate determining and depends on the electron density at the azomethine carbon, which is influenced by the adjacent organic group. Proton-transfer steps are

isocyanide complexes $[W(CNXy)_n(\kappa^{6-n}$-**P4**$)]$ (**6**$_n$, n = 2—4) in high gross yield. Nitrene group transfer to isocyanide has been known for group 8—10 metals[25] but is exceptional for early transition metals.[26] It is noticeable that this reaction proceeds in a reverse direction in comparison with those of $[MCl_2(PMeR_2)_4]$ (M = Mo, W; R = Me, Ph) with $^tBuN=C=N^tBu$ to give imido–isocyanide complexes of the type $[WCl_2(N^tBu)(CN^tBu)(PMeR_2)_2]$.[27] The ratio of three W isocyanide complexes **6**$_n$ was almost constant during the reaction course, and transient species were not detected spectroscopically. Because it has been confirmed that bis(isocyanide) complex **6**$_2$ does not react with excess XyNC under these conditions,[6] **6**$_3$ and **6**$_4$ presumably result from the pathway that several numbers of XyNC displace the terminal P atom(s) of **P4** prior to liberation of carbodiimide. The dangling PPh_2 groups in these complexes remain unaffected, although these P atoms are susceptible to O and S atom transfer from heterocumulenes under certain conditions.[28] Some W and Mo complexes have been reported to transfer the nitrene group to tertiary phosphines.[24b,29]

In summary, a tetrahydrido complex of W bearing a tetradentate phosphine coligand undergoes insertion of nitrile, leading to an imido complex via the alkylideneamido intermediate. The resulting five-coordinated W^{II} system is unique in copious imido complexes and performs nitrene group transfer. Not only the strong hydridic character but also the ability to create a stable W–N multiple bond may be responsible for imido ligand formation from nitrile, and **1** is therefore promising for converting other nitrogen-containing molecules.

■ ASSOCIATED CONTENT

S **Supporting Information**

Text, a table, a figure, and CIF files giving experimental procedures, characterization data, and results of the crystallographic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.
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■ ACKNOWLEDGMENTS

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