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Synthesis and reactivity of hydridotris(1-pyrazolyl)borate tungsten(VI) amido alkylidyne complexes

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Dedicated to Professor R.R. Schrock

Abstract

The synthesis of a series of tungsten(VI) amido alkylidyne complexes containing the chelating ligands Tp (hydridotris(1-pyrazolyl)borate) and Tp′ (hydridotris(3,5-dimethyl-1-pyrazolyl)borate) is described. Complexes of general formula, $TpW(CC(CH_3)_3)(Cl)(NHR)$ [R = C_6H_5, 4-Br–C_6H_4, 3,5-$(CF_3)_2C_6H_3$, H], (**3**–**6**), were formed by reaction of $TpW(CC(CH_3)_3)(Cl)_2$ with the appropriate amide [M][NHR] (M = Li, K). In presence of excess [Li][NHPh], $TpW(CC(CH_3)_3)(NHPh)_2$ (**7**) was isolated. Sub-stoichiometric quantities of H_2O or HCl were found to catalyze the tautomerization of **3** to the corresponding imido alkylidene. Reaction of excess H_2O with **3** produced significant amounts of $TpW(O)(CHC(CH_3)_3)(Cl)$ (**10**) and $TpW(O)(CC(CH_3)_3)(Cl)$ (**11**) along with tautomerization. Attempted acid catalyzed tautomerizations of **4** and **5** with HCl resulted in loss of the amido ligands and recovery of $TpW(CC(CH_3)_3)(Cl)_2$. The complex $Tp'W(CC(CH_3)_3)(Cl)(NHPh)$ (**8**), was synthesized by reaction of $(CH_3)_3SiN(H)Ph$ with $(DME)W(CC(CH_3)_3)(Cl)_3$ followed by addition of KTp′. X-ray crystal structures have been obtained for compounds **7** and **8** and show that the amido groups are *syn* with respect to the neopentylidyne ligand probably due to the steric demands of the chelating Tp and Tp′ ligands.

Keywords: Tungsten(VI) complexes; Amido alkylidyne complexes; Alkylidyne complexes; Acid catalyzed tautomerization; Acid induced cleavage

1. Introduction

The chemistry of transition-metal–ligand multiple bonds is a subject of broad interest that crosses the lines of inorganic and organometallic chemistry [1]. Complexes that contain double and triple bonds between a high-oxidation-state transition metal atom and carbon are of special interest because many of these complexes have demonstrated the ability to catalyze olefin [2] or acetylene [3] metathesis, respectively. Transition metal alkylidynes are also known to undergo metathesis-like reactions with isocyanates [4], and Wittig-type reactions with nitriles [5]. Additionally, alkylidyne complexes have been frequently employed in the preparation of alkylidene complexes via intra- or intermolecular protonation of the metal–carbon triple bond [6].

Our group has been investigating the chemistry of W(VI) and Mo(VI) alkylidynes that contain tridentate hydridotris(pyrazolyl)borate ancillary ligands [7]. The complexes $TpW(CC(CH_3)_3)Cl_2$ and $Tp'W(CC(CH_3)_3)Cl_2$ (Tp = hydridotris(1-pyrazolyl)borate; Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate) have been converted to oxo alkylidenes by stirring over neutral alumina presumably via a mechanism that involves an intra- or intermolecular proton transfer [7a,8]. These complexes have proven to be remarkably inert to protonation by either triflic acid, tetrafluoroboric acid, or hydrochloric acid. In this paper, we report the synthesis of several amido alkylidyne complexes as well as studies of acid catalyzed proton transfer reactions that can be used to convert the amido alkylidyne complexes to imido alkylidene complexes.

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2. Experimental

2.1. General details

All procedures were performed using standard Schlenk techniques under argon, or were carried out in a nitrogen filled dry box. Diethyl ether (Et_2O), tetrahydrofuran (THF), C_5H_{12}, and hexanes were distilled from sodium benzophenone ketyl. Toluene was deolefinated by washing twice with cold H_2SO_4 followed by water and bicarbonate. It was then dried by distillation from potassium metal. Dichloromethane (CH_2Cl_2) was distilled from CaH_2. After collection, all solvents were stored in an argon atmosphere over molecular sieves. Glassware was oven dried before use. The compounds (DME)W(CC(CH_3)$_3$)Cl_3 [3e,9], potassium hydridotris(1-pyrazolyl)borate (KTp) [10], potassium hydridotris-(3,5-dimethyl-1-pyrazolyl)borate (KTp′) [10], TpW(CC(CH_3)$_3$)Cl_2 (**1**) [8], and Tp′W(CC(CH_3)$_3$)Cl_2 (**2**) [7a,8] were synthesized according to published procedures. All NMR solvents were degassed and stored over molecular sieves in an N_2 filled drybox prior to use.

^{1}H and ^{13}C NMR spectra were measured using either a General Electric QE 300 or a Varian VXR-300 spectrometer. Chemical shifts were referenced relative to the residual protons in the deuterated solvents and are reported relative to Me_4Si. Elemental analyzes were performed by either the University of Florida Analytical Services or by Atlantic Microlabs, Norcross, Ga. Repeated recrystallization of the samples were necessary to remove unreacted **2** from compounds **3**–**7**. High-resolution mass spectra were obtained by the UF Department of Chemistry Analytical Services and were measured in FAB mode using *p*-nitrophenyloctyl ether as the matrix material. Parent ions were calculated using the most abundant isotopes for each element.

2.2. Photolyses

All photolyses were performed on solutions of the compounds in NMR tubes with a teflon joint. A 275 W tungsten lamp was used as broad band irradiation source and the sample was cooled to −10 °C in an ice/$CaCl_2$ bath that was refreshed every 5 min to maintain a constant temperature.

2.3. TpW(CC(CH_3)$_3$)(NHPh)Cl (**3**)

TpW(CC(CH_3)$_3$)Cl_2 (0.15 g, 0.27 mmol) was dissolved in 20 ml Et_2O and cooled to −78 °C. To this solution was slowly added an Et_2O solution of LiNHPh (0.05 g, 0.54 mmol). An immediate color change from purple to green was observed. The reaction mixture was allowed to warm to room temperature (r.t.) and was stirred for up to 12 h giving a dark orange solution. After solvent removal, and dissolution in ether, recrystallization from a minimum of Et_2O/C_5H_{12} at −78 °C gave **3** as an orange powder. Typically, repeated recrystallizations were necessary to remove traces of TpW(CC(CH_3)$_3$)Cl_2 still present due to incomplete reaction. ^{1}H NMR (25 °C in C_6D_6): δ 1.2 (s, 9H, C(CH_3)$_3$), 5.69, 5.78, 5.82 (t, 1H each, Tp ring H's, 4-position), 6.9 (t, 1H, *p*-Ph), 7.32, 7.35, 7.76, 7.79, 8.4 (d, 1H each, Tp ring H's, 3,5-position, one overlaps with solvent), 7.2 (t, 2H, *m*-Ph, other phenyl H's overlap with solvent), 10.5 (broad s, 1H, N–H). ^{13}C NMR (25 °C, C_6D_6): δ 32.4 (C(CH_3)$_3$), 49.43 (C(CH_3)$_3$), 105.92, 106.60, 123.38, 124.23, 128.74, 131.73, 135.44, 142.63, 144.99, 147.07, 157.08 (Tp, Ph), 306.80 (CC(CH_3)$_3$). *Anal.* Calc. for: $C_{20}H_{26}BClN_7W$: C, 40.4; H, 4.41; N, 16.5. Found: C, 39.9; H, 4.22; N, 16.3%. High Res. MS. Calc. for: $C_{20}H_{26}BClN_7W$, 594.154117. Found: 594.153641. The compound, TpW(^{15}NHPh)(CC(CH_3)$_3$)Cl (**1a**) was prepared in a similar manner using K^{15}NHPh: ^{1}H NMR (25 C in C_6D_6) δ 10.5 (d, N–H, $^1J_{15N-H} = 70$ Hz).

2.4. TpW(CC(CH_3)$_3$)(NH-4-Br-C_6H_4)Cl (**4**)

A solution of *p*-bromoaniline (0.09 g, 0.75 mmol) in 10 ml THF was cooled to −78 °C and slowly added to a −78 °C THF suspension of KH (0.03 g, 0.75 mmol). The reaction mixture was allowed to warm to r.t. and stirred for approximately 40 min until the evolution of H_2 ceased. The color of the solution became yellow upon warming to r.t. At this time, the solution was cooled to −78 °C and was added slowly to a −78 °C solution of TpW(CC(CH_3)$_3$)Cl_2 (0.26 g, 0.5 mmol) in 20 ml THF. An immediate color change to green was observed. As the reaction was left to stir and warm to r.t. over the course of 10 h, the color changed to orange. Recrystallization from a minimum volume of Et_2O/C_5H_{12} at −40 °C gave **4** as an orange solid. ^{1}H NMR (25 °C, C_6D_6): δ 1.19 (s, 9H, C(CH_3)$_3$), 5.7, 5.75, 5.86 (t, 1H each, Tp H's 4-position), 6.98, 7.32 (d, 2H each, phenyl ring H's), 7.2, 7.5, 7.79, 8.35 (d, 1H each, four out six of Tp H's 3,5-positions, the other two masked by solvent), 10.15 (broad s, 1H, N–H). ^{13}C NMR (25 °C, C_6D_6): δ 31.92 (C(CH_3)$_3$), 49.18 (C(CH_3)$_3$), 106.20, 106.80, 123.87, 124.38, 128.50, 128.87, 135.23, 143.10, 145.40, 148.10, 154.42, 156.08 (Tp, Ph), 297.15 (CC(CH_3)$_3$). *Anal.* Calc. for: $C_{20}H_{25}BBrClN_7W$: C, 35.7; H, 3.74; N, 14.6. Found: C, 34.4; H, 3.65; N, 14.2%. High Res. MS. Calc. for: $C_{20}H_{25}BBrClN_7W$, 672.064640. Found: 672.062891.

2.5. TpW(CC(CH_3)$_3$)(NH(3,5-(CF_3)$_2$$C_6H_3$))Cl (**5**)

The same procedure was followed as in **4**. Immediate color change of the reaction mixture from blue to brown was observed which became lighter as the reaction was allowed to warm to r.t. and stirred for 10 h. Recrys-

tallization from minimum Et_2O/C_5H_{12} at −40 °C gave an orange crystalline material. ^1H NMR (25 °C, C_6D_6): δ 1.19 (s, 9H, $C(CH_3)_3$), 5.65, 5.67, 5.9 (t, 1H each, Tp H's 4-position), 7.1, 7.3, 7.56, 7.6, 7.79, 8.2 (d, 2H each, Tp H's 3,5-positions), 7.5 (s 2H, *o*-phenyl H's, *p*-H probably overlaps with solvent), 9.79 (broad s, 1H, N–H). *Anal.* Calc. for: $C_{22}H_{24}BClF_6N_7W$: C, 36.2; H, 3.31; N, 13.4. Found: C, 35.1; H, 3.15; N, 12.9%. High Res. MS. Calc. for: $C_{22}H_{24}BClF_6N_7W$, 730.128885. Found: 730.128456.

2.6. $TpW(CC(CH_3)_3)(NH_2)Cl$ (**6**)

$TpW(CC(CH_3)_3)Cl_2$ (0.15 g, 0.3 mmol) was dissolved in 20 ml THF and a suspension of $NaNH_2$ (0.035 g, 1.5 mmol, 5 equiv.) in THF was added dropwise. No immediate color change was observed. The reaction mixture was left to stir and warm up to r.t. overnight. At this point the reaction mixture had turned light green and when the solvent was removed under reduced pressure, a pale yellow solid was recovered. The solid was recrystallized from minimum Et_2O/C_5H_{12} at −40 °C giving a yellow crystalline material. ^1H NMR (25 °C, C_6D_6): δ 1.3 (s, 9H, $C(CH_3)_3$), 5.7, 5.75, 5.8 (t, 1H each, Tp H's 4-position), 7.29, 7.7.8, 7.86 [d, 1H each, three out six of the Tp H's at 3,5-position, (others probably overlap with solvent)], 8.6, 8.9 (broad s, 1H each, NH_2 protons). ^{13}C NMR (25 °C, C_6D_6): δ 31.53 ($C(CH_3)_3$), 49.13 ($C(CH_3)_3$), 106.18, 106.37, 134.42, 134.61, 135.28, 142.02, 144.95, 147.14, 147.80 (Tp C's), 303.53 ($CC(CH_3)_3$. *Anal.* Calc. For: $C_{14}H_{22}BClN_7W$: C, 32.4; H, 4.27; N, 18.9. Found: C, 29.7; H, 4.21; N, 18.5%. High Res. MS. Calc. for: $C_{14}H_{22}BClN_7W$, 518.122816. Found: 518.122091.

2.7. $TpW(CC(CH_3)_3)(NHPh)_2$ (**7**)

To a cold Et_2O solution of $TpW(CC(CH_3)_3)Cl_2$ (0.2 g, 0.77 mmol) 3.3 equiv. of LiNHPh (0.25 g, 2.54 mmol) in Et_2O was slowly added. The reaction mixture was allowed to warm to r.t. and changed from blue to bright orange almost immediately. After stirring for 3 h, Et_2O was removed under reduced pressure and the orange solid was extracted once with $C_6H_5CH_3$ and once with CH_2Cl_2. The solvent was removed from the combined extracts and the resultant solid was recrystallized from a r.t. CH_2Cl_2/C_5H_{12} mixture to afford an orange crystalline solid. X-ray quality crystals were obtained by slow diffusion of C_5H_{12} into a r.t. saturated CH_2Cl_2 solution of **7**. ^1H NMR (25 °C, C_6D_6): δ 1.29 (s, 9H, $C(CH_3)_3$), 5.73 (t, 2H, Tp H's 4-position), 5.82 (t, 1H, Tp H, 4-position), 6.90 (t, 2H, *p*-Ph), 7.23 (d, 2H, Tp H, 3,5-position), 7.26 (t, 4H, *m*-Ph), 7.28 (d, 1H, Tp proton, 3,5-position), 7.31 (d, 1H, Tp proton 3,5,-position), 7.45 (d, 4H, *o*-Ph), 7.82 (s, 2H, N–H), 7.99 (d, 2H, Tp H's 3,5-positions). ^{13}C NMR (25 °C, C_6D_6): δ 32.47 ($C(CH_3)_3$), 50.71 ($C(CH_3)_3$), 105.88, 106.68, 120.61, 121.43, 128.76, 134.74, 135.31, 140.72, 144.96, 157.08 (Tp, Ph), 295.37 ($CC(CH_3)_3$). High Res. MS. Calc. for: $C_{26}H_{31}BN_8W$, 650.227463. Found: 650.228286.

2.8. $Tp'W(CC(CH_3)_3)(NHPh)Cl$ (**8**)

$(CH_3)_3Si–N(H)Ph$ (0.19 ml, 1.1 mmol) in 10 ml THF was added to a cold THF solution of (DME)W-$(CC(CH_3)_3)Cl_3$ (0.5 g, 1.1 mmol). An immediate color change from purple to green was observed. The color of the reaction mixture became lighter as it warmed to r.t. After 30 min, the reaction mixture was cooled to −78 °C and a solution of KTp′ (0.37 g, 1.1 mmol) in 20 ml THF was slowly added. The color of the reaction mixture continued becoming lighter until it was bright orange. After stirring for 2 more hours at r.t., the solvent was removed under reduced pressure. Recrystallization from minimum Et_2O at −40 °C gave bright orange, X-ray quality crystals of **8**. ^1H NMR (25 °C, C_6D_6): δ 1.38 (s, 9H, $C(CH_3)_3$), 2.0, 2.12, 2.17, 2.28, 2.4, 3.1(s, 3H each, Tp′ CH_3, 3,5-positions), 5.57, 5.59, 6.1 (t, 1H each, Tp′ H's, 4-position), 6.9 (t, 1H, *p*-Ph), 7.2 (t, 2H, *m*-Ph), 7.3 (d, 2H, *o*-Ph), 10.62 (broad s, 1H, N–H). ^{13}C NMR (25 °C, C_6D_6): δ 12.09, 12.81, 13.47, 18.48, 18.77 (Tp′ CH_3's, overlapping), 32.62 ($CC(CH_3)_3$), 49.66 ($CC(CH_3)_3$), 107.31, 107.65, 143.06, 144.78, 145.44, 152.46, 153.18, 153.84, 157.29 (Tp′ ring C's), 123.94, 124.55, 128.47 (Ph C's). 310.17 ($CC(CH_3)_3$). *Anal.* Calc. for $C_{26}H_{37}ClN_7W$: C, 46.8; H, 5.55; N, 14.7. Found: C, 46.5; H, 5.46; N, 14.4%.

2.9. X-ray experimental details

Compound **7**: data were collected at 173 K on a Siemens CCD SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using the entire data set. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was $< 1\%$). ψ-Scan absorption corrections were applied based on the entire data set. Compound **8**: data were collected at room temperature on a Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). Thirty-two reflections with $20.0 < 2\theta < 22.0°$ were used to refine the cell parameters. The ω-scan method was used for data collection. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was $< 1\%$).

Both structures were solved by the Direct Method in SHELXTL-5 [11], and refined using full-matrix least-squares on F^2. The non-H atoms were refined with

anisotropic thermal parameters. The H atoms of **8** were all refined in a riding mode on their parent atoms except those bonded to boron, which were refined without constraint. The structure also contains a disordered half ether molecule. It was refined with isotropic thermal parameters in three parts with site occupation factors of 0.25, 0.15 and 0.10, respectively. Compound **7** had all H atoms riding on their parent atoms except the one on Boron. For compound **8**, 411 parameters were refined in the final cycle of refinement using 4274 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 5.53 and 11.16, respectively. For compound **7**, 179 parameters were refined in the final cycle of refinement using 2978 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.04 and 7.56, respectively. Refinement was done using F^2.

3. Results and discussion

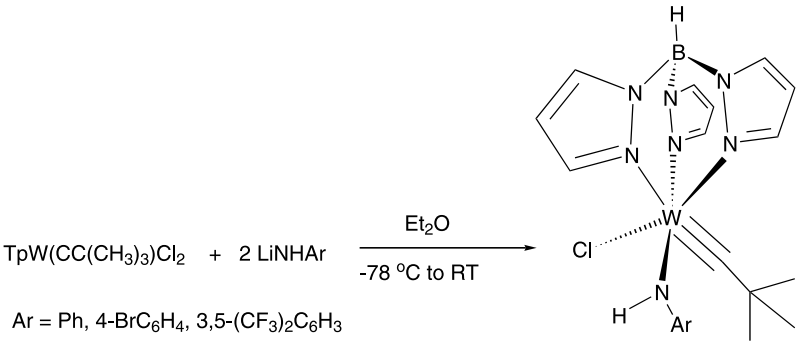
The coordinative saturation of the alkylidyne compounds $TpW(CC(CH_3)_3)Cl_2$ (**1**), and $Tp'W(CC(CH_3)_3)Cl_2$ (**2**), render them somewhat unreactive with respect to chemistry initiated at the metal center. Thus, attempted acetylene metathesis with diphenyl acetylene gave only unreacted starting materials. In order to create a vacant site in the coordination sphere, we added a Lewis acid (e.g. $AlCl_3$, $GaBr_3$) to these reaction mixtures, with no observable change. Attempted substitution of one or both of the chloride ligands of **1** or **2** met with mixed results. While both of these compounds react with lithium alkyls, Grignard or, other carbanion sources, only intractable mixtures of alkyl substituted products were observed. Reaction of **1** with lithiated amines however, gives a number of amido complexes in moderate yields.

Addition of 2–2.5 equiv. of Li[NHPh] to a THF solution of **1** results in a slow color change from purple to dark orange. Recrystallization of the reaction product from an ether/pentane solution gave $TpW(CC(CH_3)_3)(NHPh)Cl$ (**3**), Eq. (1), as a dark orange powder. The ^1H NMR spectrum is consistent with the formation of the monoamide alkylidyne complex. The amido N–H proton appears as a broad singlet at 10.50 ppm, while the lack symmetry renders all the Tp ring protons inequivalent.

The compounds, $TpW(CC(CH_3)_3)(N(H)4\text{-}Br(C_6H_3)Cl$ (**4**), and $TpW(N(H)(3,5\text{-}(CF_3)_2C_6H_3)(CC(CH_3)_3)Cl$ (**5**), were prepared from in situ generated K[anilide] and a THF solution of **1**. Removal of THF and subsequent recrystallization from Et_2O/pentane at −40 °C afforded **4** and **5** as orange solids. The ^1H NMR spectra of **4** and **5** display inequivalent resonances arising from the protons of the Tp rings confirming the asymmetric structures of the compounds. The amide protons appear as broad singlets at 10.15 ppm, **4**, and 9.79 ppm, **5**. Compound **4** is moisture sensitive both in solution and in the solid state and decomposes, forming a brown oil after extended exposure to air. Complex **5** is also relatively air and moisture sensitive and slowly decomposes forming a dark orange solid when exposed to air. In both cases, the hydrolysis products were shown to be mixtures of $TpW(O)(C(H)C(CH_3)_3)Cl$ and $TpW(O)_2(CH_2C(CH_3)_3)$ by ^1H NMR.

The reaction of 5 equiv. of $NaNH_2$ with $TpW(CC(CH_3)_3)Cl_2$ in THF, at ambient temperature overnight gave pale yellow–green $TpW(NH_2)(CC(CH_3)_3)Cl$ (**6**) upon recrystallization from ether. The ^1H NMR spectrum of **6** has inequivalent Tp proton resonances, while the amido protons are inequivalent and appear as broad singlets at 8.59 and 8.90 ppm, respectively. The inequivalence of the two protons is consistent with slow rotation about the W–N bond on the NMR time scale.

When 3.3 equiv. of [Li][NHPh] was added to $TpW(CC(CH_3)_3)Cl_2$, extraction of the reaction mixture



(1)

3; Ar = Ph
4; Ar = 4-BrC_6H_4
5; Ar = 3,5-$(CF_3)_2C_6H_3$

with toluene followed by recrystallization from CH_2Cl_2/pentane gave bright orange, crystalline $TpW(NHPh)_2(CC(CH_3)_3)$ (**7**). The ^1H NMR spectrum of the crude reaction mixture also shows formation of a small amount of free aniline and an unidentified compound that appears to arise from partial decomposition of the Tp ligand. In the room temperature ^1H NMR spectrum of recrystallized **7**, the protons of the pyrazole rings of the Tp ligand appear in a 2:1 ratio indicating the existence of a mirror plane in the molecule. The amide protons appear as a broad singlet at 7.8 ppm indicating either rapid rotation of the amide groups or possibly hindered rotation that gives a single conformation that retains the mirror plane in the molecule.

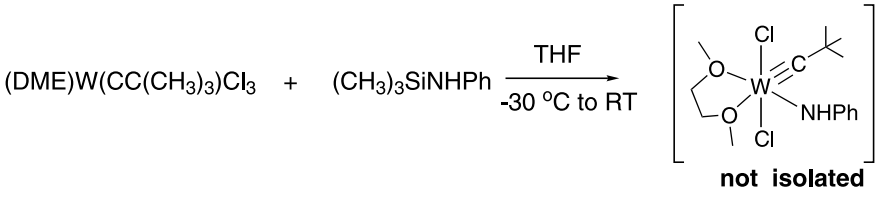
The reaction of 1 equiv. of [K][NHPh] with $Tp'W(CC(CH_3)_3)Cl_2$ in THF gave intractable products. An alternative route for the synthesis of the monoanilide Tp′ complex is shown in Eqs. (2) and (3). In this reaction sequence, $(CH_3)_3SiNHPh$ was allowed to react with $(DME)W(CC(CH_3)_3)Cl_3$ to generate the amide complex, $(DME)W(CC(CH_3)_3)Cl_2(NHPh)$. Addition of 1 equiv. of KTp′ in THF to the resultant reaction mixture completed the reaction. Removal of the solvent under reduced pressure and recrystallization from Et_2O at −40 °C afforded bright orange crystals of $Tp'W(CC(CH_3)_3)(NHPh)Cl$ (**8**). The product of the reaction between $(CH_3)_3SiNHPh$ and $(DME)W(CC(CH_3)_3)Cl_3$ has not been isolated, but we assume that it is the species $(DME)W(CC(CH_3)_3)Cl_2(NHPh)$ since $(DME)W(CC(CH_3)_3)Cl_2(N(H)–2,6\text{-}C_6H_3–i\text{-}Pr_2))$ has been isolated from the reaction between $Me_3SiN(H)–2,6\text{-}i\text{-}Pr_2C_6H_3$ and $(DME)W(CC(CH_3)_3)Cl_3$ [6d]. Synthesis of **3** was also possible using the same method used to prepare **8** by substituting KTp for KTp′, but with no significant improvement in yield or purity.

The room temperature ^1H NMR spectrum of **8** displays six inequivalent methyl groups and three inequivalent pyrazole ring protons. The amide peak appears as a broad singlet at 10.62 ppm.

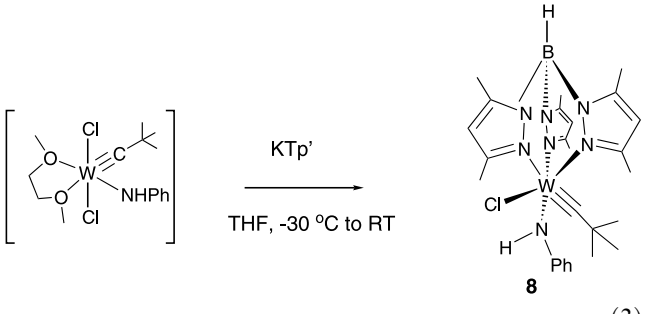
Compound **8** is air and moisture stable and does not decompose when heated in solution. The air and thermal stability of this compound is comparable to that of other W–Tp′ complexes [7a,8] and suggests that the increased steric bulk of the Tp′ ligand relative to the Tp ligand is responsible for the enhanced kinetic stability of **8**.

The presence of two distinct amido proton resonances in the ^1H NMR spectrum of **6** implies a rather rigid W–N bond. No change in the two amido proton resonances of **6** was observed up to 120 °C (decomposition of **6** began at higher temperatures), indicating a very high activation barrier for rotation ($\Delta G^{\ddagger} > 26$ kcal mol^{-1}). If restricted rotation about the W–N bond is a general phenomenon for these compounds, two possible isomers could exist for complexes **3**–**5**, **7**, and **8** (The phenyl group could be oriented *syn* or *anti* with respect to the alkylidyne ligand). However, in the variable temperature proton NMR spectra of **3**–**5**, **7**, and **8** only one isomer was observed between −100 and 100 °C. This observation can be explained if a single structure exists with slow rotation on the NMR time scale, or if the amido groups are undergoing rapid rotation on the NMR timescale.

Further information on the orientation of the amide groups in compounds **3** and **7** was obtained from proton



(2)



(3)

difference nOe studies. Irradiation of the t-butyl peak in **3** produced positive enhancement of the *meta* and *ortho* phenyl protons of the amido ligand, and of two Tp resonances at 7.79 and 8.37 ppm. No enhancement of the N–H proton was observed. Alternatively, when the amido proton was irradiated, positive enhancement was measured for the *ortho* phenyl protons of the amido ligands and for the Tp proton resonance at 7.76 ppm. These results allow us to conclude that **3** is the *syn* isomer in solution.

For complex **7** irradiation of the t-butyl peak produced enhancement of the *ortho* phenyl protons

and the Tp resonance at 7.99 ppm whereas irradiation of the N–H proton resulted in a positive enhancement of the *ortho* phenyl protons and of the Tp resonance at 7.28 ppm. These results suggest that the N–H protons of **7** point away from the alkylidyne group, and we suggest that only the *syn* isomer of **7** is present in the solution. Although nOe studies were not carried out for the rest of the aryl amido compounds we expect that they also possess similar conformations in solution.

We propose that in the amido alkylidyne complexes under discussion (where R = Ph, Ar), a combination of the sterically demanding Tp and Tp′ ligands together with a strong W–N bond disfavors the rotational isomerization. Contrary to these observations, the related complex TpMo(CC(CH_3)$_2$Ph)(NH(2,6-C_6H_3–i-Pr_2))(OCH_3) exists as a mixture of two rotamers in solution as observed in the room temperature ^{1}H NMR spectrum [7d]. In the case of the Mo complex, π-donation from the methoxy group competes with the amido N–Mo π interaction and lowers the barrier to rotation about the Mo–N bond enough to allow the formation of *syn* and *anti* isomers.

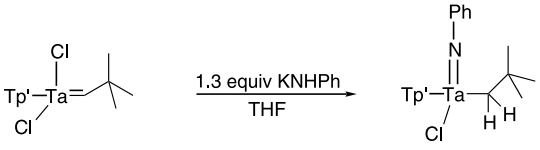
3.1. Crystal structure determination of 7 and 8

A single crystal of **7** suitable for an X-ray diffraction study was obtained by slow diffusion of pentane into a saturated, CH_2Cl_2 solution of **7** at room temperature. A thermal ellipsoid plot of **7** is found in Fig. 1. The data collection parameters are summarized in Table 1, while selected bond distances and angles are presented in Table 2. The coordination geometry about the metal center can best be described as a distorted octahedron with the Tp ligand occupying facial sites. The structure confirms the presence of a mirror plane that contains one of the pyrazole rings and the neopentylidyne ligand. The phenyl rings of the imido groups of **7** adopt a *syn* conformation with respect to the alkylidyne ligand. The W–C(14) bond length (1.790 Å) is within the expected range for d^0 tungsten–carbon triple bonds [1]. The W–C(14)–C(10) angle is 166.6°, which minimizes the interaction between the t-butyl group and the two phenyl rings, and is somewhat less than expected for the sp hybridized α-carbon atom. The N–W bond lengths to the pyrazole rings range from 2.354 to 2.237 Å and are consistent with the decreasing *trans* influence of the ligands alkylidyne > amido. The amido N–W bonds are slightly longer than similar mono amido compounds probably because of competition between the nitrogen lone pairs for donation into the vacant metal dπ orbital.

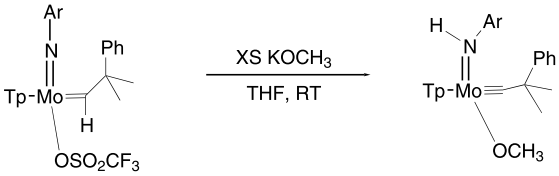
The crystal structure of **8** was also determined by X-ray diffraction, a thermal ellipsoid plot of is **8** is shown in Fig. 2. Information on the data collection parameters is presented in Table 1, and selected bond distances and angles are summarized in Table 3. The geometric constraints of the Tp′ ligand force the neopentylidyne, amido, and chloride ligands to be mutually *cis*. Complex **8** is formally a 18-electron species with the neopentylidyne ligand donating electron density into two metal d orbitals of π symmetry. The hindrance imposed by the size of the Tp′ ligand forces the amido ligand to assume the *syn* conformation with the phenyl ring tilted towards the alkylidyne ligand. The *syn* orientation of the phenylamido ligand allows the complex to achieve maximum N-pπ to W-dπ-bonding [1], accounting for the short (1.946 Å) length of the W–N(HPh) bond, and bringing the electron count at W to 18 e$^-$. The pyrazole N–W bonds range from 2.392 to 2.175 Å showing that the *trans* influence trend observed for **8** is alkylidyne > amide > chloride. The sp hybridization of the neopentylidyne α-carbon is evident from the 1.766 Å W–C(1) bond length and the nearly linear W–C(1)–C2 angle (174.5°).

3.2. Tautomerization studies

There are a number of examples involving intramolecular α-hydrogen transfers, in which the ultimate proton acceptor is itself another multiply bonded ligand. Such examples include proton transfers between amido/imido [2c,12] amido/alkylidyne [6,13], hydroxo/oxo [14], and alkylidene/oxo ligands [15]. In the tungsten and molybdenum amido/alkylidyne systems, the transfer can be thermal, and is usually catalyzed by bases. Although not directly observed, a base induced proton transfer may also be operative in the synthesis of Tp′Ta(NPh)($CH_2C(CH_3)_3$)Cl (Eq. (4)) [16]. In the complex, TpMo(NAr)(OCH_3)(CHC(CH_3)$_2$Ph), a base catalyzed proton transfer has been observed, in which the alkylidene proton is transferred to the imido ligand in the presence of excess methoxide (Eq. (5)) [7d].



(4)



(5)

Our initial studies of the tautomerization of TpW(CC(CH_3)$_3$)(NHPh)Cl (**3**), to give the imido/alkylidene complex TpW(NPh)(CHC(CH_3)$_3$)Cl (**9**) [7c], indicated that this reaction was possible, but was not consistently reproducible. In some cases, conversion of **3**–**9** was readily achieved at room temperature, while in

others no proton transfer was observed even upon heating a sample of **3** at 70 °C for 2 days. Complexes **4** and **5** also displayed inconsistent behavior with respect to proton transfer upon heating, while in no case was the corresponding imido alkylidene observed when **6**–**8** were subjected to the same conditions. We suspected that the inconsistent behavior was the result of an impurity (most likely water) that might have been present in varying amounts.

Because base catalyzed proton transfer between the alkylidyne and amido ligands is well documented, we attempted to catalyze the tautomerization by adding base to the samples of **3** that did not thermally convert to **9**. Addition of up to 10 equiv. of NEt_3 or $PhNH_2$ to a sample of **3** did not produce any change even upon heating to 70 °C. The choice of $PhNH_2$ was obvious given the possibility of its presence as an impurity in these samples. Moreover, since $TpW(CC(CH_3)_3)(NHPh)_2$ (**7**) instead of $TpW(NPh)(CHC(CH_3)_3)Cl$ (**9**), was isolated by addition of 3 or more equivalents of [Li][NHPh] to **2**, we concluded that the proton transfer is not base promoted even in the presence of a strong base such as anilide. A similar conclusion can be made for the other Tp amido complexes as well, since an excess of amide was also used in their synthesis with no observable formation of imido/alkylidene complexes.

A close examination of the ^1H NMR spectra of the samples of $TpW(CC(CH_3)_3)(NHPh)Cl$ (**3**) that underwent tautomerization, revealed the presence of trace amounts (approximately 1–3%) of the oxo alkylidene $TpW(O)(CHC(CH_3)_3)Cl$ (**10**) and sometimes the dioxo alkyl complex $TpW(O)_2(CHC(CH_3)_3)$ (**11**). The presence of these impurities suggests the presence of traces of H_2O in the reaction medium. Indeed, addition of catalytic amounts of H_2O (approximately 0.1 equiv.) to a sample of **3** that had not tautomerized upon previous heating at 80 °C for 10 h resulted in a slow color change from orange to yellowish-olive, and the ^1H NMR spectrum showed the formation of **9**. Heating this sample accelerated the formation of **9**. When larger amounts of H_2O were added, the hydrolysis products, **10** and **11** were also observed. This suggests that hydrolysis competes with the tautomerization to form **9** (Scheme 1).

Since proton transfer in **3** is H_2O catalyzed and not base catalyzed, we suspected that H_2O was behaving as an acid, or generating an acid. To further test this hypothesis, a trace amount of HCl (1.0 M in Et_2O approximately 0.05 equiv.) was added to a C_6D_6 solution of **3** at room temperature. A rapid color change from orange to olive green ensued and the ^1H NMR spectrum showed complete conversion of **3**–**9**. Addition of larger quantities of HCl resulted in complete protonation of the amido ligand and formation of $TpW(CC(CH_3)_3)Cl_2$ (**2**) (Scheme 2).

When H_2O (approximately 0.05 equiv.) was added to a sample of $TpW(CC(CH_3)_3)(NH_2)Cl$ (**6**), no compound that could be identified as $TpW(NH)(CHC(CH_3)_3)Cl$ was detected even upon heating. Larger quantities of H_2O resulted in the formation of the oxo complexes, **10** and/or **11**. This result implies that if $TpW(NH)(CHC(CH_3)_3)Cl$ forms, it is rapidly hydrolyzed. Compounds **4** and **5** react very rapidly with H_2O. Upon addition of H_2O to complex **4**, complete hydrolysis to $TpW(O)(CHC(CH_3)_3)Cl$ and $TpW(O)_2(CH_2C(CH_3)_3)$ occurred within minutes at room temperature. The addition of even small quantities of water gives imido hydrolysis products. Compound **5** reacts with water within minutes giving **11** as the major product along with $TpW(=N(3,5\text{-}(CF_3)_2C_6H_3)(CHC(CH_3)_3)Cl$ (**12**). After 3 days, the only compounds evident in this sample were **10** and **11**. Attempts to use HCl to catalyze the tautomerization of complex $TpW(CC(CH_3)_3)(NH_2)Cl$ (**6**) were not successful because even trace amounts of HCl displaced the amido ligands giving the dichloride, **2**.

The acid catalyzed proton transfer in **3** is unusual because such proton transfer reactions (from amide to alkylidyne) are typically base catalyzed [6,13]. Similar acid catalyzed proton transfer has been observed in the oxo/hydroxy species $Re(O)(^{18}OH)(RCCR)_2$ [17]. In this rhenium complex, proton transfer between the oxo and hydroxy ligands is slow (half-life of $\sim$11 h), but is rapid in the presence of trifluoromethanesulfonic acid (HOTf). The acid catalysis is believed to occur by initial protonation of the oxo ligand and formation of a symmetrical bis-hydroxide species. This mechanism was proposed because HOTf was shown to protonate the oxo ligand of the related complex $[Re(O)Et(MeCCMe)_2]$ [17].

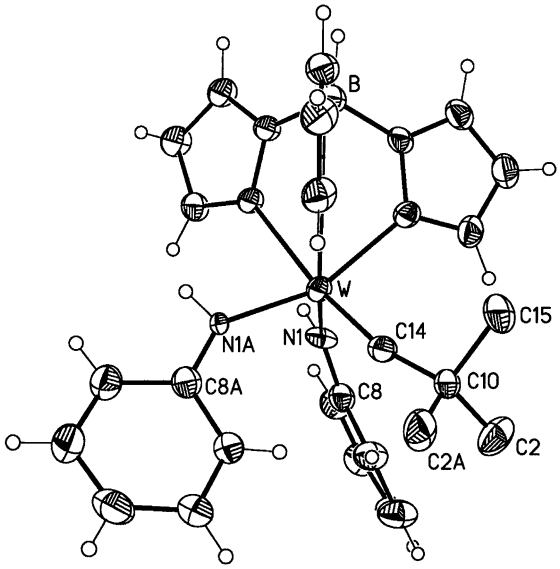


Fig. 1. Thermal ellipsoid plot of compound **7**.

Table 1
Data collection parameters for compounds **7** and **8**

	7	**8**
Crystal parameters		
Empirical formula	$C_{26}H_{31}BN_8W$	$C_{26}H_{37}N_7W \cdot 1/2[C_4H_{10}O]$
Formula weight	650.25	714.80
T (K)	173(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_{(1)}/m$	$P2_{(1)}/c$
a (Å)	7.6125(2)	11.731(2)
b (Å)	16.3776(4)	17.315(3)
c (Å)	10.5398(2)	17.754(4)
β (°)	98.705(1)	108.56(2)
V (Å^3)	1298.91(5)	3418.7(11)
Z	2	4
Crystal size (mm^3)	0.24 × 0.16 × 0.14	0.24 × 0.25 × 0.20
D_{calc} (g cm^{-3})	1.663	1.389
F(000), electrons	644	1436
Data collection		
Radiation, λ, (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Mode	ω-scan	ω-scan
Scan width and rate	0.3°/frame and 30 s/frame	
2θ Range (°)	1.95–27.50	1.69–25.00
Range of hkl	$-6 \le h \le 10$, $-18 \le k \le 22$, $-14 \le l \le 14$	$0 \le h \le 13$, $0 \le k \le 20$, $-21 \le l \le 20$
Total reflections measured	9523	6215
Unique reflections	3087	5911
Absolute coefficient, μ(Mo Kα) (mm^{-1})	4.478	3.485
Min/max transmission	0.411–0.543	0.410–0.550
Structure refinement		
Refinement method	full-matrix least-squares on F^2	
S, Goodness-of-fit	1.111	1.152
Variables	179	411
R_1/Reflections	3.04	5.53
wR_2/Reflections	7.56	11.16
R_{int} (%)	3.38	4.19
Max. shift/esd	0.001	0.001
Minimum peak in difference Fourier map (e Å^{-3})	−2.44	−0.77
Maximum peak in difference Fourier map (e Å^{-3})	1.387	0.97

$R_1 = \Sigma(||Fo|-|Fc||)/\Sigma|Fo|$. $wR_2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$. $\Sigma = [\Sigma[w(Fo^2-Fc^2)^2]/(n-p)]^{1/2}$. $w = 1/[\sigma^2(Fo^2)+(0.0370*p)^2+0.31*p]$, $p = [\max(Fo^2,0)+2*Fc^2]/3$.

For compound **3**, two pathways could lead to **9** depending on where protonation occurs first (Scheme 3). The first step in pathway **A** involves protonation of the anilide ligand. Proton transfer to the alkylidyne from the coordinated aniline in **13** followed by proton loss from the amido group in **14** would complete the reaction sequence. Pathway **B** involves direct protonation of the neopentylidyne ligand **14**. Subsequent loss of a proton from the amido group would give **9**.

The observation that higher concentrations of acid result in loss of the amido groups from these complexes

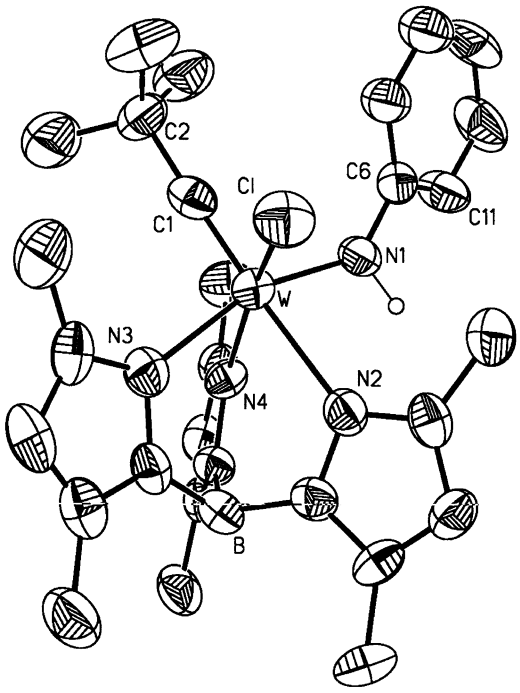


Fig. 2. Thermal ellipsoid plot of compound **8**.

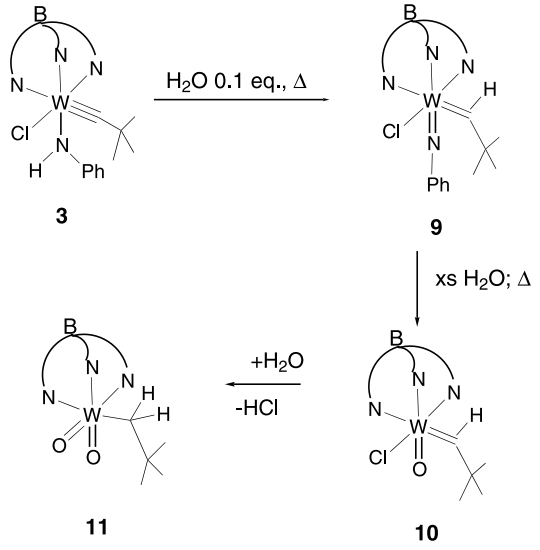
suggests that the first step in these reactions is protonation of the amide group. Furthermore, the qualitative reactivity of these complexes with water or HCl is **6** > **5** > **4** > **3**. It is possible that this reactivity trend reflects the lability of the amine in the intermediate, **13**. Thus, the weaker donors (3,5-$(CF_3)_2C_6H_3NH_2$, p-$FC_6H_4NH_2$ and NH_3) dissociate from the metal center before the proton transfer to the alkylidyne ligand can occur giving starting material with HCl or **10** and **11** with water.

Table 2
Bond lengths (Å) and angles (°) for the Non-H atoms of compound **7**

1	2	3	1–2	1–2–3
C(14)	W	N(1)	1.789(5)	100.66(14)
C(14)	W	N(1A)		100.66(14)
C(14)	W	N(2)		171.8(2)
C(14)	W	N(3)		93.2(2)
C(14)	W	N(3A)		93.2(2)
N(1)	W	N(1A)	2.034(3)	102.7(2)
N(1)	W	N(2)		84.39(11)
N(1)	W	N(3)		88.65(13)
N(1)	W	N(3A)		159.96(12)
N(1A)	W	N(2)	2.034(3)	84.39(11)
N(1A)	W	N(3)		159.96(12)
N(1A)	W	N(3A)		88.65(13)
N(2)	W	N(3)	2.356(4)	80.31(11)
N(2)	W	N(3A)		80.31(11)
N(3)	W	N(3A)	2.239(3)	76.1(2)
N(3A)	W		2.239(3)	
C(8)	N(1)	W	1.353(5)	140.5(3)
C(8A)	N(1A)	W	1.353(5)	140.5(3)
C(10)	C(14)	W	1.512(7)	166.5(4)

Table 3
Bond lengths (Å) and angles (°) for the non-H atoms of compound **8**

1	2	3	1–2	1–2–3
Cl	W	N(1)	2.401(3)	97.6(2)
Cl	W	N(2)		84.9(2)
Cl	W	N(3)		87.4(2)
Cl	W	N(4)		163.1(2)
N(1)	W	N(2)	1.943(7)	80.7(3)
N(1)	W	N(3)		161.7(3)
N(1)	W	N(4)		91.0(3)
N(1)	W	C(1)		96.5(4)
N(2)	W	N(3)	2.393(8)	82.2(3)
N(2)	W	N(4)		82.1(3)
N(2)	W	C(1)		176.6(3)
N(3)	W	N(4)	2.223(8)	80.2(3)
N(3)	W	C(1)		100.7(4)
N(4)	W	C(1)	2.169(7)	100.1(3)
C(1)	W	Cl	1.773(10)	93.5(3)
C(2)	C(1)	W	1.512(13)	174.7(8)
C(6)	N(1)	W	1.407(11)	139.5(6)



Scheme 1.

It is well known that photolysis of imido alkylidene complexes can induce rotational isomerization of the alkylidene ligand [18]. For example, the Schrock type catalyst systems undergo the interconversion of *syn* and *anti* isomers in this fashion. When a sample of **9**, that was generated by the proton catalyzed tautomerization of **3**, was photolyzed at −5 °C, a photostationary state was established between **9** and **3**. Experiments performed with **9**-^{15}**N**, produced by acid addition to **3**-^{15}**N**, confirmed that the compound generated from **9** was indeed **3**. Thus, while the photolysis of **9** probably induces rotational isomerization of the alkylidene ligand, proton transfer to the imido N atom also occurs.

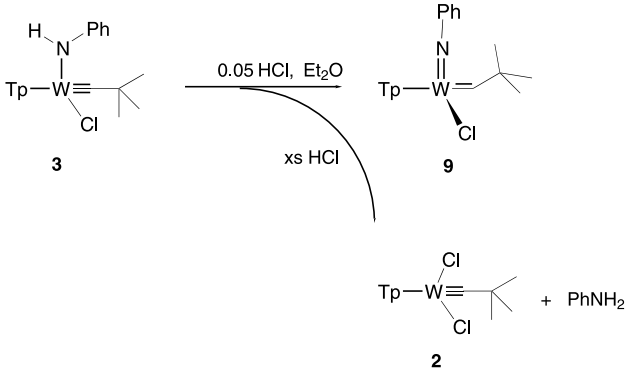
4. Summary and conclusions

The tungsten amido alkylidyne complexes reported here tautomerize to the thermodynamically favored imido alkylidene complexes only in the presence of a source of protons. The nOe studies of complexes **3** and **7** suggest that the only isomer present in solution is the *syn* isomer. This conformation orients the amide proton away from the alkylidyne and renders the tautomerization impossible without prior amide rotation or catalysis. A similar argument has been proposed to explain why the phosphide proton in the complex, $W(CC(CH_3)_3)(PHPh)(PEt_3)Cl_2$, does not spontaneously transfer to the alkylidyne carbon atom. In this case, the proton, although pointing towards the alkylidyne carbon, is too far away to engage in direct transfer because of the long W–phosphido bond [6b].

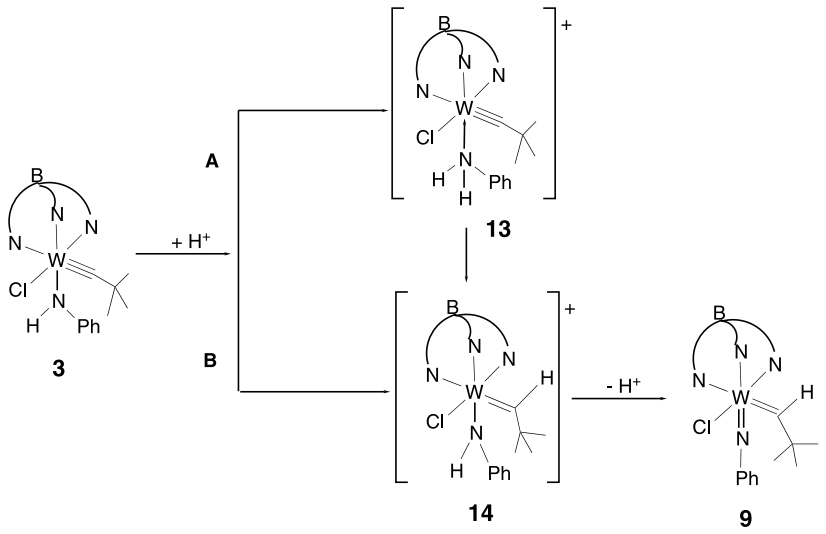
Although the mechanism of the acid catalyzed proton transfer in **3** has not been elucidated in detail, protonation of the amido ligand followed by proton transfer (Scheme 3, **B**) is a viable pathway. We also believe that the electronics of the amido ligands account for some of the observed differences in reactivity. Protonation of amido ligands containing electron withdrawing groups on the phenyl ring gives aniline complex intermediates that lose the amine more readily. In this case, loss of the aniline ligand can compete to a significant extent with subsequent proton transfer and would explain the observation that tautomerization is not observed with these complexes. Finally, it is likely that the electron donating nature of the Tp ligand systems used in these complexes renders the amide nitrogen basic enough to be protonated which causes the tautomerization to be acid rather than base catalyzed.

5. Supplementary material

Tables of crystal data, thermal parameters, bond distances, bond angles and atomic coordinates for



Scheme 2.



Scheme 3.

compounds **7** and **8** (19 pages) are available from the authors on request.

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References

[1] W.A. Nugent, J.M. Mayer, Metal-Ligand Multiple Bonds, Wiley Interscience, New York, 1988.
[2] (a) L.K. Johnson, S.C. Virgil, R.H. Grubbs, J. Am. Chem. Soc. 112 (1990) 5384;
(b) R.R. Schrock, R.T. De Pue, J. Feldman, K.B. Yap, D.C. Yang, W.M. Davis, L. Park, M. DiMare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Kruger, P. Betz, Organometallics 9 (1990) 2262;
(c) J. Kress, J.A. Osborn, R.M.E. Greene, K.J. Ivin, J.J. Rooney, J. Am. Chem. Soc. 109 (1987) 899;
(d) J.C. Bryan, J.M. Mayer, J. Am. Chem. Soc. 112 (1990) 2298;
(e) P. Legzins, E.C. Phillips, L. Sanchez, Organometallics 8 (1989) 940.
[3] (a) J.H. Wengrovius, J. Sancho, R.R. Schrock, J. Am. Chem. Soc. 103 (1981) 3932;
(b) J. Sancho, R.R. Schrock, J. Mol. Catal. 15 (1982) 75;
(c) L.G. McCullough, R.R. Schrock, J. Am. Chem. Soc. 106 (1984) 4067;
(d) S.F. Pedersen, M.R. Churchill, H. Wasserman, R.R. Schrock, J. Am. Chem. Soc. 104 (1982) 6808;
(e) L.G. McCullough, J.C. Dewan, J.C. Murdezk, R.R. Schrock, J. Am. Chem. Soc. 107 (1985) 5987.
[4] K. Weiss, U. Schubert, R.R. Schrock, Organometallics 5 (1986) 397.
[5] J.H. Freudenberger, R.R. Schrock, Organometallics 5 (1986) 398.
[6] (a) R.R. Schrock, Acc. Chem. Res. 19 (1986) 342;
(b) S.M. Rocklage, M.R. Churchill, H.J. Wasserman, R.R. Schrock, Organometallics 1 (1982) 1332;
(c) J.H. Freudenberger, R.R. Schrock, Organometallics 4 (1985) 1937;
(d) C.J. Schaverien, J.C. Dewan, R.R. Schrock, J. Am. Chem. Soc. 108 (1986) 2771.
[7] (a) L.L. Blosch, K.A. Abboud, J.M. Boncella, J. Am. Chem. Soc. 113 (1991) 7066;
(b) L.L. Blosch, A.S. Gamble, K.A. Abboud, J.M. Boncella, Organometallics 11 (1992) 2342;
(c) A.S. Gamble, J.M. Boncella, Organometallics 12 (1993) 2814;
(d) W.M. Vaughan, K.A. Abboud, J.M. Boncella, Organometallics 14 (1995) 1567.
[8] L.L. Blosch, A.S. Gamble, J.M. Boncella, J. Mol. Catal. 76 (1992) 229.
[9] D.N. Clark, J. Sancho, J.H. Wengrovius, S.M. Rocklage, S.F. Pedersen, R.R. Schrock, Organometallics 1 (1982) 1645.
[10] S. Trofimenko, Acc. Chem. Res. (1971) 17.
[11] G.M. Sheldrick, SHELXTL-5, Siemens Analytical Instrumentation, Madison, WI, USA, 1995.
[12] (a) T.E. Glassman, M.G. Vale, R.R. Schrock, Organometallics 10 (1991) 4046;
(b) D.M.-T. Chan, W.C. Fultz, W.A. Nugent, C.D. Roe, T. Tulip, J. Am. Chem. Soc. 107 (1985) 251;
(c) W.A. Nugent, R.L. Harlow, Inorg. Chem. 19 (1980) 777.
[13] (a) R.R. Schrock, J. Organomet. Chem. 300 (1986) 249;
(b) R.R. Schrock, R.T. DePue, J. Feldman, C.J. Schaverien, J.C. Dewan, A.H. Liu, J. Am. Chem. Soc. 110 (1988) 1423;
(c) R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M. O'Regan, J. Am. Chem. Soc. (1990) 3875.
[14] H. Arzoumanian, H. Krentzien, H. Teruel, J. Chem. Soc., Chem. Commun. (1991) 55.
[15] D.M. Hoffman, D.A. Wierda, J. Am. Chem. Soc. (1990) 7056.
[16] M.L. Cajigal, K.A. Abboud, J.M. Boncella, Organometallics 15 (1996) 1905.
[17] T.K.G. Erikson, J.M. Mayer, Angew. Chem., Int. Ed. Engl. 27 (1988) 1527.
[18] (a) J.H. Oskam, R.R. Schrock, J. Am. Chem. Soc. 115 (1993) 11831;
(b) W.J. Feast, V.C. Gibson, K.J. Ivin, A.M. Kenwright, E. Khosravi, J. Chem. Soc., Chem. Commun. (1994) 1399;
(c) J.H. Oskam, R.R. Schrock, J. Am. Chem. Soc. 114 (1992) 10680;
(d) J.H. Oskam, R.R. Schrock, J. Am. Chem. Soc. 114 (1992) 7588;
(e) R. Toreki, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 114 (1992) 3367.