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C–H activation of pendant alkoxides by tungsten imide complexes

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Abstract

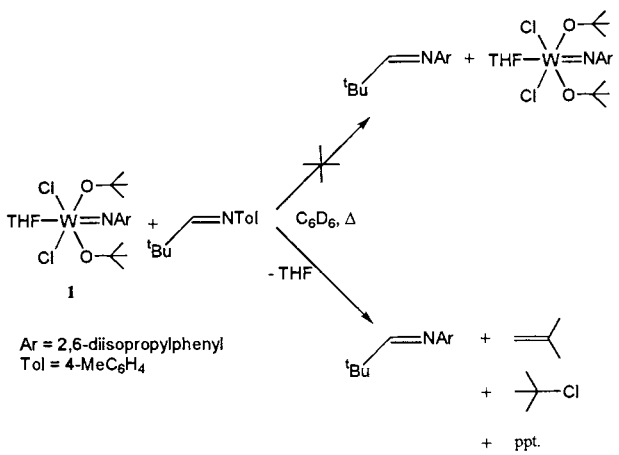
The tungsten complex W(=NAr)(O-*t*-Bu)$_2$Cl$_2$(THF) (**1**, Ar = 2.6-diisopropylamine) reacts with an imine substrate at 80°C in C_6D_6 to give an *N*-aryl imine product. A Chauvin [2 + 2] type mechanism was excluded when **1** was found to be thermally unstable. Decomposition of **1** yielded isobutylene, *t*-butyl chloride, 2,6-diisopropylphenylamine and precipitates that exhibited an IR absorbance for M=O. There was no evidence for the intermediacy of radical or cationic species. Imide-mediated C–H activation of the *t*-butoxide ligand was proposed as the most likely pathway. The tetraalkoxide W(=NAr)(O-*t*-Bu)$_4$ was also found to decompose at 80°C, but at a slower rate. The fluorinated alkoxide complexes, W(=NPh)((OC(CF$_3$)$_2$(CH$_3$))$_2$Cl$_2$(THF) and W(=N-*t*-Bu)$_2$((OC(CF$_3$)$_2$(CH$_3$))$_2$ did not decompose under similar conditions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Imide; Alkoxide; C–H activation

1. Introduction

Imide complexes with supporting alkoxide ligands are good candidates for imine metathesis catalysts because competitive π-donation from the alkoxide can potentially activate the extremely stable metal–nitrogen bond [1,2]. This hypothesis, combined with the electronic tuneability of the OR group, motivated us to study the imine reactivity of alkoxide and mixed alkoxide/chloride derivatives of the type W=(NR)(OR)$_n$Cl$_{4-n}$.

W(=NAr)(O-*t*-Bu)$_2$Cl$_2$(THF) [3] (Ar = 2,6-diisopropylphenyl) (**1**), previously prepared by Schrock et al. reacted with imine to give the predicted organic exchange product. However, in contrast to the previously reported behavior of (DME)Cl$_2$Mo(=NR)$_2$ [4–6], there was an initiation period, side products, and no evidence for the expected tungsten imido complex (Scheme 1). In this account, we describe evidence that the observed =NR exchange product does not arise from a [2 + 2] imide/imine metathesis, like that observed by Bergman and co-workers for Cp*CpZr(=N-*t*-Bu)(THF) [7–9], but rather from a reactive intermediate or intermediates produced from the alkoxide-mediated decomposition of **1**.



Scheme 1.

2. Results

Initially, reactions of **1** with imine appeared to be imide/imine metathesis reactions. In an NMR tube, **1** was heated in the presence of one (*p*-Tol)N=CH(*t*-Bu) (Tol = 4-MeC$_6$H$_4$), in C_6D_6 for 15 days at 55–75°C. The expected product imine ArN=CH(*t*-Bu) was first observed by ^{1}H-NMR spectroscopy after 5 days. In addition, however, the ^{1}H- and ^{13}C-NMR spectra contained resonances for free THF, *t*-butyl chloride, and

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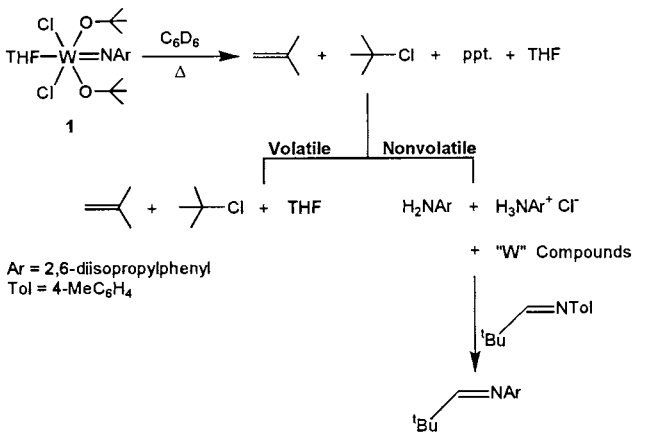


Scheme 2.

isobutylene (Scheme 1). Moreover, there were precipitated solids and no resonances consistent with the expected product imide.

The anomalous nature of this reaction was confirmed by the subsequent observation that all of the organic compounds, except ArN=CH(*t*-Bu), were present when tungsten imide **1** was heated in the absence of imine (Scheme 2). After 4 days at 70°C in C_6D_6, **1** decomposed to give a precipitate and solution color change that paralleled that observed in the presence of imine. As observed by ^{1}H-NMR, the first step in the process was the release of coordinated THF. Intermediate species then appeared and disappeared as *t*-butyl chloride and isobutylene were released. Concurrently, for high initial concentrations of **1**, broad singlets appeared ca. δ 9 and 12.

The reaction appeared to be independent of concentration, both of imine and **1**. Decompositions performed in the absence of imine, in the presence of stoichiometric imine, and in the presence of excess imine, all proceeded on a similar time scale (3–4 days) and gave *t*-butyl chloride and isobutylene as products. Nor were significant rate differences noted when the concentration of **1** was increased fivefold.

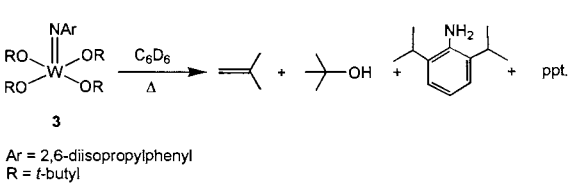
By NMR spectroscopy, the non-volatile components of the decomposition, isolated by removal of volatiles in vacuo, comprised of 2–3 different NAr-containing species (Scheme 2). Diisopropylphenylamine and/or the ammonium salt were amongst these compounds [10]. In addition, these residues exhibited the higher frequency singlets ca. δ 9 and 12 that were observed in the original reaction mixture. IR spectra of the nonvolatile compounds exhibited an absorbance at 750 cm^{-1} (Nujol), consistent with a W=O functionality. Repeated attempts to obtain a full crystal structure of the precipitate were unsuccessful. Treatment of the nonvolatile compounds from the decomposition with imine (*p*-Tol)N=CH(*t*-Bu) in C_6D_6 gave imine ArN=CH(*t*-Bu). Volatile components were also collected and consisted of isobutylene, *t*-butylchloride, THF, and the standard, anisole.

No evidence in the reaction mixtures for the presence of free *t*-butyl cation or for the presence of free radicals was observed. Free cation could result in the production of the Friedel–Crafts C_6D_6 alkylation product, $C_6D_5C(CH_3)_3$ [11]. This alkylation product was not present nor did the addition of excess benzyltriethylammonium chloride significantly decrease the amount of isobutylene produced as might be expected if such a cation were trapped by chloride anion [12]. A free radical pathway should give coupling products such as 2,2,3,3-tetramethylbutane and 2-methylpropane. These products were not observed nor did addition of dihydroanthracene (DHA), a radical trap, change the course of the reaction [13].

Trace amine did not affect the decomposition of **1**. Although the *n*-butylamine reacted slowly with imine (*p*-Tol)N=CH(*t*-Bu) to give (*n*-Bu)N=CH(*t*-Bu), upon heating, **1** decomposed as previously described yielding imine ArN=CH(*t*-Bu), with no further incorporation of the *n*-butylamine into any product. The isopropyl groups on the imide are apparently not directly involved in the reaction as is shown by the fact that W(=NPh)(O-*t*-Bu)$_2$Cl$_2$(THF) (**2**) decomposed (3 days, $\sim$ 70°C) to give the same distribution of product types as **1**.

The decomposition of the tetraalkoxide derivative W(=NAr)(O-*t*-Bu)$_4$ (Ar = 2,6-diisopropylphenyl) (**3**) proceeded more slowly than **1** (Scheme 3). Imide complex **3** required approximately 1 month at 80°C in C_6D_6 to give significant quantities of precipitate, isobutylene, *t*-butyl alcohol, and 2,6-diisopropylphenylamine. Decomposition of **3** in the presence of imine PhN=CH(*t*-Bu) gave imine ArN=CH(*t*-Bu). The decomposition rate was dramatically accelerated from 1 month to 4 days, the time previously associated with **1**, by the addition of trace amounts of W(=NAr)Cl$_4$(THF) (Ar = 2,6-diisopropylphenyl) (**4**) to **3**.

The decomposition of the tetrachloride complexes, **4** and W(=NPh)Cl$_4$(THF) [14] (**5**), was also investigated. Upon heating in C_6D_6 at 80 and 60°C, respectively, for more than 2 weeks, a small amount of precipitate formed, but the total concentration of the imides remained nearly constant and no new resonances were observed.



Scheme 3.

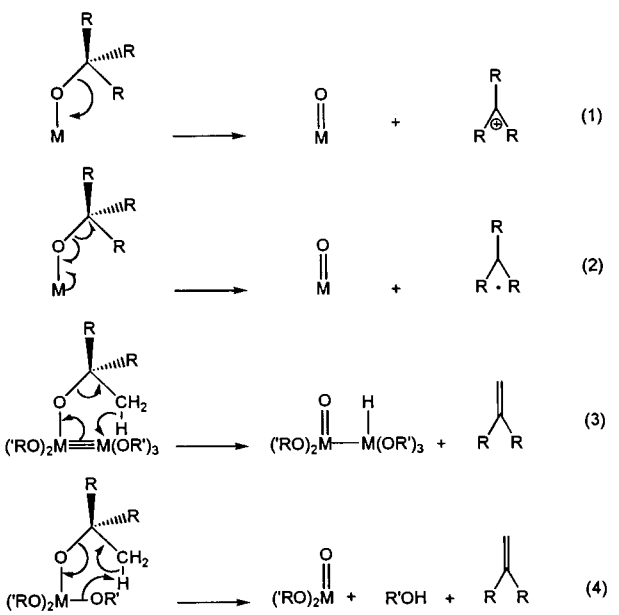
The fluorinated alkoxide derivatives W(=NPh)-$((OC(CF_3)_2(CH_3))_2Cl_2(THF)$ [15] (**6**) and W(=N-*t*-$Bu)_2((OC(CF_3)_2(CH_3))_2$ (**7**) did not decompose after weeks at elevated temperatures nor did they react significantly ($< 5\%$) with added imine.

Decomposition behavior similar to that observed for the tungsten alkoxide **1** was also observed for a related molybdenum compound. The complex $Mo(=NAr)_2(O$-*t*-$Bu)_2$ (**8**) decomposed to yield isobutylene and diisopropylphenylamine when heated for prolonged periods (100°C, 45 days). Moreover, when the non-volatile components of the decomposition reaction mixture were heated in the presence of (*n*-Pr)N=CHPh and PhN=CH(*t*-Bu) both imine/imine and imine/imide =NR exchange products were observed.

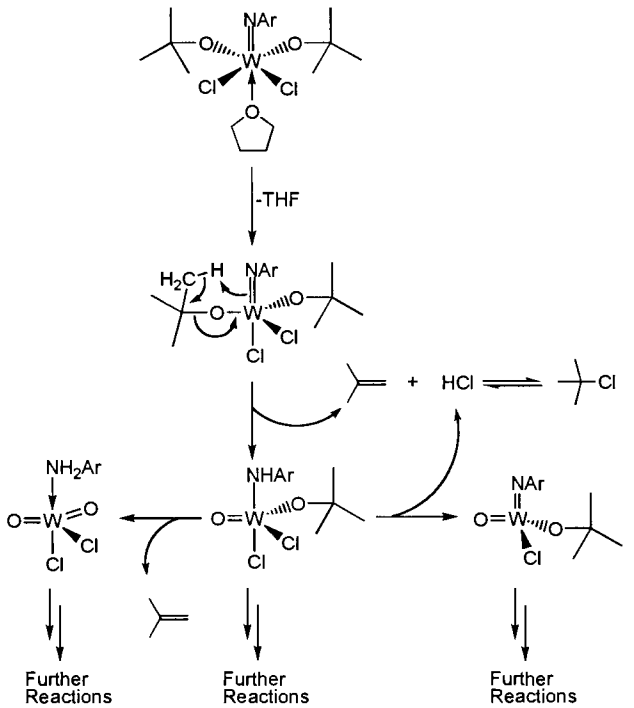
3. Discussion

Metal complexes used for the catalysis of polymers and the formation of metal oxide compounds often utilize alkoxide supporting ligands [16]. However, alkoxide ligands are not always innocent ancillary groups in transition metal complexes [16]. Several mechanisms have been proposed for their decomposition including heterolytic cleavage of the C–O bond (Eq. (1)) [11], homolytic cleavage of the C–O bond (Eq. (2)) [17], and C–H activation (Eq. (3) [18], Eq. (4) [19]) (Scheme 4).

Heterolytic cleavage was described by Wolczanski and co-workers in zirconium tritox systems that form the trityl cation in solution along with the metal oxide [11]. Cummins and co-workers established homolytic cleavage as the mechanism of decomposition for (*t*-



Scheme 4.



Scheme 5.

$BuO)_3Mo[\mu$-N]Ti$(NRAr)_3$ [17]. Chisholm and co-workers invoked C–H activation to explain the conversion of a ditungsten *t*-butoxide complex to a hydrido-oxo compound [18]. Similarly, Sen and co-workers proposed C–H activation as an explanation for the products obtained in the flash vacuum pyrolysis of $Ti(OR)_4$ compounds [19,20]. In both of these last two systems the alkoxide's γ-hydrogen was accessible for removal.

We propose that intramolecular C–H activation represents the most probable of these pathways for the decomposition of the tungsten imide alkoxide complexes (Scheme 5) [21]. The precedent is strong. The imide functional group is known to mediate C–H activation [22]. The mechanism is plausible. The six-membered transition state should be energetically accessible and relatively low in energy by analogy to organic ene-type reactions. The pathway does not require cations or radicals. None of the experiments or controls yielded evidence to support the presence of these high energy species in the reaction mixtures.

Imide-mediated C–H activation, along with the further reactions of the first-formed products, also explains all of the spectroscopic observations. After the loss of THF, the initial C–H activation should produce isobutylene and a metal complex with both oxo and amido groups. A subsequent α-hydride elimination from the amide, a reaction that is well-known for complexes of this class, should give HCl and reform the imido linkage. Amongst other reactions, we can postulate that the HCl can react with isobutylene to give the observed *t*-butyl chloride. It is, of course, possible to

propose direct abstraction of the *t*-butoxide hydrogen by chloride or alkoxide, but these reactions are less likely given the relative basicities of the ligands.

After both metal amide and HCl are present in the reaction mixture many new pathways open. For example, the amine can be produced either by C–H activation of another *t*-butoxide ligand or by reaction of HCl with amide. Ammonium salts could also be expected to form under these conditions. Amido groups and/or ammonium salts are the likely species responsible for the δ 9 and 12 resonances in the ^{1}H-NMR spectra [23]. Moreover, the now sterically unsaturated oxo compounds can dimerize or exchange ligands to give species that would precipitate from solution. It is probable that the reaction represents a mixture containing some or all of these species.

The cascade of reactions initiated by the C–H activation can account for the exchange of =NR groups with added imine since amine, ammonium salts, amides or imides are all potentially capable of mediating this type of reaction. Finally, the lack of dependence of the initiation period on added imine, amine or substrate concentration is consistent with a monomolecular rate determining step.

The role of the ancillary chloride ligand is intriguing. There are several possible explanations for the dramatic difference in decomposition rate between the tetraalkoxide **5** and the dichlorodialkoxide **1**. Electronic arguments are not persuasive since any activation of the alkoxide induced by the removal of electron-density from the metal center would be accompanied by a concomitant decrease in imide basicity. Steric arguments are slightly more satisfactory in that the tetraalkoxide may not be able to assume the appropriate geometry for facile imide C–H activation. There is a third, more probable, explanation for the role of Cl, however. HCl produced from amide elimination, which is not trapped by isobutylene, can act as a catalyst for further decomposition of both starting material and products. The latter explanation seems particularly appealing since the decompositions proceed rapidly after the initiation period. In addition, the initiation period for tetraalkoxide **3** decreases dramatically in the presence of trace amounts of tetrachloride **4** [24].

Finally, the findings of this study allow us to explain the anomalous reactivity observed for the analogous *t*-butoxide supported molybdenum complex **8**. As we established in a prior communication [5], this compound reacts with imine to produce the =NR exchange product that would be predicted based on an imine metathesis scheme. After further study, however, it became clear that the reaction did not belong to the general class of imide/imine exchange reactions in which it was originally grouped. In particular, resonances for isobutylene were always present. Controlled decomposition followed by addition of imines confirmed that the observed reactions paralleled those that we have described for the tungsten alkoxides in this report.

4. Experimental

4.1. General

Manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk techniques or a Vacuum Atmospheres glovebox. The solvents used were dry and oxygen free. Reagent grade ether and toluene were prepared by distillation from sodium benzophenone ketyl under nitrogen. Reagent grade hexane was washed with sulfuric acid, passed through a column of activated alumina, and distilled from sodium benzophenone ketyl under nitrogen. Benzene-d_6 was distilled from sodium benzophenone ketyl and stored in a glass vessel equipped with a Teflon stopcock. Chloroform-*d* and methylene chloride-d_2 were prepared by distillation from P_2O_5 and stored in glass vessels equipped with Teflon stopcocks. Methylene chloride was prepared by distillation from P_2O_5. Reagents were purified by standard methods unless otherwise noted. NMR spectra were recorded on a Bruker AF 300 MHz spectrometer at 25°C.

Tungsten hexachloride (Strem) and hexamethyldisiloxane (Acros) were used as received. Benzyltriethylammonium chloride salt was dried overnight under vacuum before using. 9,10-Dihydroanthracene was recrystallized twice from ethanol and dried under vacuum before using. *N*-butylamine was purified by distillation after stirring over calcium hydride.

Imines were prepared using an analogous procedure to that described in Ref [25]. In general, the procedure consisted of condensing the parent aldehyde and an amine in benzene over molecular sieves. Purification by vacuum distillation gave pure imine.

The following compounds were prepared as described in the literature procedures (Ar = 2,6-diisopropylphenyl): W(=NAr)Cl_4(THF) [3], W(=NAr)(O-*t*-Bu)$_2$$Cl_2$(THF) [3], W(=NPh)$Cl_4$(THF) [14], W(=NPh)-(OC(CH$_3$)(CF$_3$)$_2$)$_2$$Cl_2$(THF) [15], and Mo(=NAr)$_2$(O-*t*-Bu)$_2$ [26].

Significant ^{1}H-NMR resonances for commonly encountered compounds. *t*-Butyl chloride ^{1}H (C_6D_6): δ 1.32 (s, 9, (C*H*$_3$)$_3$CCl), ^{13}C{^{1}H} (C_6D_6): δ 67.1 ((CH$_3$)$_3$*C*Cl) and 34.3 ((*C*H$_3$)$_3$CCl); isobutylene ^{1}H (C_6D_6): δ 4.74 (s, 2, H_2C=C(CH$_3$)$_2$) and 1.58 (s, 6, H$_2$C=C(C*H*$_3$)$_2$), ^{13}C{^{1}H} (C_6D_6): δ 111.3 (H$_2$*C*=C-(CH$_3$)$_2$) and 24.1 (H$_2$C=C(*C*H$_3$)$_2$); THF, ^{1}H (C_6D_6): δ 3.55 (s, 4, (OC*H*$_2$)$_2$) and 1.4 (s, 4, (C*H*$_2$)$_2$); *t*-butyl alcohol ^{1}H (C_6D_6): δ 4.3 (s, 1, (CH$_3$)$_3$CO*H*) and 1.04 (s,

9, (CH_3)$_3$COH)). In some cases the presence of *t*-butyl chloride and *t*-butyl alcohol was verified by the addition of an authentic sample to the NMR experiment.

4.1.1. W(=N-t-Bu)$_2$(OC(CH$_3$)(CF$_3$)$_2$)$_2$

Bis(*t*-butylimido)bis(*t*-butylamido)tungsten (1.05 g, 2.238 mmol) was stirred with hexafluro-2-methylisopropanol (0.80 g, 4.40 mmol) overnight to give a red–orange mixture. The solvent was removed in vacuo to give a red oil. The oil was purified by trap-to-trap distillation to yield colorless crystals and a light orange liquid. Both the crystals and the oil were produced by ^{1}H-NMR spectroscopy. Unoptimized yield, 4.3%. ^{1}H-NMR (C_6D_6): δ 1.43 (s, 3, (OC(CH_3)(CF$_3$)$_2$)$_2$) and 1.23 (s, 18, (NC(CH_3)$_3$)$_2$). ^{13}C{^{1}H}-NMR (C_6D_6) tentative assignments: δ 124.1 (q, (OC(CH$_3$)(CF_3)$_2$)$_2$), 68.2 (s, (NC(CH$_3$)$_3$)$_2$), 33.2 (s, (NC(CH$_3$)$_3$)$_2$), and 18.8 (s, (OC(CH$_3$)(CF$_3$)$_2$)$_2$). ^{19}F-NMR (C_6D_6): δ −78.8 (s, 12, (OC(CH$_3$)(CF_3)$_2$)$_2$).

4.1.2. W(=NAr)(O-t-Bu)$_4$

A −40°C solution of lithium *t*-butoxide (0.26 g, 4.4 equivalents) in ether (10 ml) was added dropwise to a −40°C solution of tetrachloro(2,6-diisopropylimido)tungsten (0.42 g, 0.74 mmol, one equivalent) in THF (15 ml) and ether (10 ml). As the reaction warmed the color changed from dark green, to red, to orange, to a cloudy yellow color. After 2 days at 25°C, the mixture was filtered through Celite and the solvent was removed in vacuo leaving a light yellow solid. The solid was recrystallized from hexanes at −40°C. Unoptimized yield, 11.8%. ^{1}H-NMR (C_6D_6): δ 4.36 (sept, 2, ((2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)), 1.46 (s, 36, (OC(CH_3)$_3$)$_4$), and 1.39 (d, 12, ((2,6-((CH_3)$_2$CH)$_2$C$_6$H$_3$))).

4.1.3. W(=NPh)(O-t-Bu)$_2$Cl$_2$(THF)

A −40°C solution of lithium *t*-butoxide (0.23 g, 2.87 mmol) in ether (10 ml) was added dropwise to a −40°C solution of tetrachloro(phenylimido)tungsten (0.64 g, 1.3 mmol, one equivalent) in THF (15 ml) and ether (20 ml). As the reaction warmed the color changed from dark green, to red, to orange, to finally a cloudy yellow color. After several hours at 25°C, the mixture was filtered through Celite and the solvent was removed in vacuo leaving a light yellow solid. The solid was dissolved in hexanes and filtered again through Celite. The solid was recrystallized from hexanes at −40°C. The preparation of this compound was attempted many times, but the solid was never pure by ^{1}H-NMR. The lack of purity of the dissolved sample was due to Cl/OR ligand exchange. ^{1}H-NMR (C_6D_6): δ 7.28 (d, 2, *o*-H, NPh), 7.01 (t, 2, *m*-H, NPh), 6.58 (t, 1, *p*-H, NPh), 4.23 (br s, 4, (OCH_2)$_2$), 1.48 (s, 18, (OC(CH_3)$_3$)$_2$), and 1.41 (s, 4, (CH_2)$_2$).

4.2. NMR experiments

Reactions that produced equilibrium mixtures of reagents and multiple products were performed in NMR tubes. In most cases the isolation of individual organometallic products was not possible. NMR assignments are reported for significant species, but aromatic region overlap prevents complete assignments in many cases. Although hexamethylbenzene and anisole were used as internal standards, reliable quantification of the products after decomposition was inhibited in most cases by product volatility and by unfortunate overlap of resonances. Standard solutions of imine were typically prepared by weighing the imine ($\sim$100–200 mg) into a 2 ml volumetric flask and diluting to 2 ml with C_6D_6. Standard solutions of internal standards were prepared analogously.

4.2.1. Decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (1) in the presence of one equivalent of (p-Tol)N=CH(t-Bu)

A solution of **1** (6.2 mg, 0.0096 mmol, one equivalent) in C_6D_6 (480 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Anisole was added as an internal standard (40 μl of a 0.3 M soln) along with (*p*-Tol)N=CH(*t*-Bu) (ca. one equivalent, 13.5 μl of a 0.71 M soln). The sample was maintained at 25°C for 1 day to verify the stoichiometry and the stability of the reaction mixture. The sample was heated and maintained at 55–65°C for approximately 16 h and at 65–75°C for a total of 14 days. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Decomposition was observed after 4 days at elevated temperatures. While heating, solids precipitated and the color changed from yellow to red–brown. Isobutylene, *t*-butyl chloride, and dissociated THF were observed. After 5 days at elevated temperatures the product imine ArN=CH(*t*-Bu) was first observed. There was a 60% conversion of starting material imine (*p*-Tol)N=CH-(*t*-Bu) to product imine ArN=CH(*t*-Bu), but resonances consistent with the new imide W(=N-*p*-Tol)(O-*t*-Bu)$_2$Cl$_2$(THF) were not observed. ^{1}H-NMR (C_6D_6) of (2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)N=CH(*t*-Bu) (unisolated): δ 7.26 (s, 1, (CH(*t*-Bu)), 3.05 (m, 2, (2,6-((CH$_3$)$_2$CH)$_2$-C$_6$H$_3$)N), 1.16 (d, 12, (2,6-((CH_3)$_2$CH)$_2$C$_6$H$_3$)N), and 1.05 (s, 9, (CH(*t*-*Bu*)). Aromatic resonances could not be definitively assigned due to the complexity of the spectrum in this region.

4.2.2. Decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (1)

A solution of **1** (8.7 mg, 0.013 mmol) in C_6D_6 (500 μl) was prepared in an NMR tube. Anisole was added as an internal standard (40 μl of a 0.3 M soln) and the tube was flame sealed under vacuum. The sample was maintained at 65–75°C for a total of 7 days, and was

monitored by ^{1}H-NMR spectroscopy. Decomposition was observed after 4 days at elevated temperatures. During which time solids precipitated and the color changed from yellow to red–brown. Several resonances grew in and disappeared, the most prominent one at δ 1.04 (s) indicating that an intermediate, with additional resonances unassigned, could be present. Dissociated THF and two organic products, isobutylene and *t*-butyl chloride, were identified in the reaction mixture. Significant resonances from unidentified species were also observed: ^{1}H-NMR (C_6D_6): δ 6.92 (s), 6.75 (d), and 1.13 (br s).

4.2.3. Decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (1) in the presence of nine equivalents of (n-Pr)N=CHPh

A solution of **1** (5.5 mg, 0.0085 mmol, one equivalent) in C_6D_6 (600 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene was added as an internal standard (50 μl of a 0.4 M soln) along with imine (*n*-Pr)N=CHPh (ca. nine equivalents, 68 μl of a 0.868 M soln). The sample was maintained at 25°C for 1 day to verify the stoichiometry and the stability of the reaction mixture. The sample was heated and maintained at 55–65°C for approximately 1 day and at 65–75°C for a total of 48 days. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Decomposition was observed after 3 days at elevated temperatures. During this time solids precipitated and the color did not change to red–brown, but remained yellow. Product imine ArN=CHPh was observed, but due to overlapping signals it was not possible to quantify the amount of imine produced. Isobutylene, *t*-butyl chloride, and dissociated THF were observed in the ^{1}H-NMR spectrum. Resonances consistent with the new imide W(=N-*n*-Pr)(O-*t*-Bu)$_2$Cl$_2$(THF) were not observed. ^{1}H-NMR (C_6D_6) of (2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)N=CH(Ph) (unisolated): δ 3.12 (m, 2, (2,6-((CH$_3$)$_2$C*H*)$_2$C$_6$H$_3$)N) and 1.16 (d, 12, (2,6-((C*H*$_3$)$_2$CH)$_2$C$_6$H$_3$)N). Aromatic and methyne resonances could not be definitively assigned due to the complexity of the spectrum in these regions.

4.2.4. Concentration dependence of the decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (1)

Two solutions of different concentrations were prepared as follows: sample A consisted of **1** (5.6 mg, 0.0086 mmol), hexamethylbenzene (50 μl of a 0.4 M soln), and C_6D_6 (600 μl); sample B consisted of **1** (31.9 mg, 0.049 mmol), hexamethylbenzene (100 μl of a 0.4 M soln), and C_6D_6 (600 μl). Both samples were placed in NMR tubes equipped with Teflon stopcocks and maintained at 70°C for 9 days. The progress of the reactions was monitored by ^{1}H-NMR spectroscopy. Sample A decomposed after 4 days at elevated temperatures and sample B decomposed after 5 days. The spectra of both samples contained resonances for the organic products *t*-butyl chloride, isobutylene, and dissociated THF. The spectra were complex but a prominent resonance at δ 6.9 (s) was observed in both samples. Sample B also contained significant resonances at δ 12.88 (s) and 8.13 (br s).

4.2.5. Reaction of (p-Tol)N=CH(t-Bu) with the nonvolatile components after decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (1)

A solution of **1** (30.5 mg, 0.047 mmol) in C_6D_6 (260 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Anisole was added as an internal standard (300 μl of a 0.3 M soln). The sample was heated and maintained at 75–85°C for approximately 1 day during which time **1** decomposed, solids precipitated, and the color changed from yellow to brown–yellow. The reaction was monitored by ^{1}H-NMR spectroscopy. Several resonances grew in and disappeared the most prominent one at δ 1.07 (s) indicating that an intermediate, with additional resonances unassigned, could be present. The volatile compounds of the sample were vacuum transferred to another NMR tube. ^{1}H-NMR of the volatiles showed the presence of isobutylene, *t*-butyl chloride, and free THF. The nonvolatile compounds were redissolved (undissolved solids remained). Significant ^{1}H-NMR (C_6D_6) of non-volatile compounds: δ 12.4 (s), 8.5 (br s), 1.38 (v br s), 1.05 (d), and 1.00 (d). Partial ^{13}C{^{1}H}-NMR (C_6D_6) of non-volatile compounds: δ 141, 124.9, 29.1, and 24.3.

The imine, (*p*-Tol)N=CH(*t*-Bu) (66 μl of a 0.71 M soln, one equivalent) was added to the non-volatile components of the sample. After 2 h at 75–85°C, 35% of starting material imine (*p*-Tol)N=CH(*t*-Bu) was converted to product imine ArN=CH(*t*-Bu). There were no resonances for imide W(=N-*p*-Tol)(O-*t*-Bu)$_2$Cl$_2$(THF). The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. ^{1}H-NMR (C_6D_6) of (2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)N=CH(*t*-Bu) (unisolated): δ 7.25 (s, 1, C*H*(*t*-Bu)), 3.04 (m, 2, (2,6-((CH$_3$)$_2$C*H*)$_2$C$_6$H$_3$)N), 1.16 (d, 12, (2,6-((C*H*$_3$)$_2$CH)$_2$C$_6$H$_3$)N), and 1.06 (s, 9, CH(*t*-*Bu*)). Aromatic resonances could not be definitively assigned due to the complexity of the spectrum in this region.

4.2.6. Decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (1) in the presence of two equivalents of benzyltriethylammonium chloride salt

To a solution of complex **1** (6.7 mg, 0.0103 mmol), hexamethylbenzene (50 μl of a 0.4 M soln), and C_6D_6 was added benzyltriethylammonium chloride (ca. two equivalents, 4.7 mg, 0.021 mmol) in an NMR tube. Although the salt did not completely dissolve, the sample immediately changed in color from yellow to orange. The sample remained at 25°C for a total of 6 days and progress of the reaction was monitored periodically

by ^{1}H-NMR spectroscopy. After 3 days **1** decomposed, and although, the resonances are shifted from those observed in pure C_6D_6, isobutylene and *t*-butyl chloride were present. Dissociated THF was present along with significant resonances from unidentified species ^{1}H-NMR (C_6D_6): δ 10.3 (br s) and 1.27 (s).

*4.2.7. Decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (**1**) in the presence of nine equivalents of 9,10-dihydroanthracene*

A solution of **1** (6.1 mg, 0.0094 mmol, one equivalent) in C_6D_6 (500 μl) was prepared in an NMR tube. Anisole was added as an internal standard (100 μl of a 0.3 M soln) along with 9,10-dihydroanthracene (ca. nine equivalents, 0.0164 g) and the tube was flame sealed under vacuum. The sample was maintained at 25°C for 1 day to verify the stoichiometry and the stability of the reaction mixture. The sample was heated and maintained at 75–85°C for a total of 7 days. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. After 1 day at elevated temperatures **1** decomposed, solids precipitated, and the color changed from yellow–orange to red–orange. Several resonances grew in and disappeared the most prominent one at δ 1.04 (s) indicating that an intermediate, with additional resonances unassigned, could be present. No anthracene was observed in the ^{1}H-NMR spectra. Two organic products, *t*-butyl chloride and isobutylene were identified in the reaction mixture along with dissociated THF.

*4.2.8. Decomposition of W(=NAr)(O-t-Bu)$_2$Cl$_2$(THF) (**1**) in the presence of (p-Tol)N=CH(t-Bu) and n-butylamine*

A solution of **1** (7.3 mg, 0.011 mmol, one equivalent) in C_6D_6 (480 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Anisole was added as an internal standard (40 μl of a 0.3 M soln) along with imine (*p*-Tol)N=CH(*t*-Bu) (1.1 equivalents, 16 μl of a 0.71 M soln). The sample was maintained at 25°C for 1 day to verify the stoichiometry and the stability of the reaction mixture. *N*-butylamine (one equivalent, 1.1 μl) was added and the sample was maintained at room temperature for 21 days. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Although, the resonances are shifted slightly from those observed in pure C_6D_6, the resonances indicated that 2,6-diisopropylamine, *p*-tolylamine, and (*n*-Pr)N=CH(*t*-Bu) were present. The sample was heated and maintained at 55–65°C for approximately 1 day, at 65–75°C for 2 days, and at 75–85°C for a total of 17 days. After 5 days at elevated temperatures **1** decomposed. During this time, solids precipitated and the color changed from yellow to yellow–orange. There was a 40% conversion of starting material imine **2** to product imine ArN=CH(*t*-Bu). Resonances consistent with the imide W(=N-*p*-Tol)(O-*t*-Bu)$_2$Cl$_2$(THF) were not observed. ^{1}H-NMR (C_6D_6) of (2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)N=CH-(*t*-Bu) (unisolated): δ 7.25 (s, 1, C*H*(*t*-Bu)), 3.05 (m, 2, (2,6-((CH$_3$)$_2$C*H*)$_2$C$_6$H$_3$)N), 1.17 (d, 12, (2,6-((C*H*$_3$)$_2$-CH)$_2$C$_6$H$_3$)N), and 1.07 (s, 9, CH(*t-Bu*)). Aromatic resonances could not be definitively assigned due to the complexity of the spectrum in this region. In addition, *t*-butyl chloride, isobutylene, and dissociated THF were observed. The spectrum was complex but significant resonances from unidentified species were also observed. ^{1}H-NMR (C_6D_6): δ 8.52 (br s) and 0.663 (br s).

*4.2.9. Decomposition of W(=NPh)(O-t-Bu)$_2$Cl$_2$(THF) (**2**)*

A solution of **2** (14.9 mg, 0.0264 mmol) in C_6D_6 (700 μl) was prepared and sealed under vacuum in an NMR tube. The sample was maintained at 65–75°C for 3 days, during which time **2** decomposed, solids precipitated, and the color changed from yellow to orange. The progress of the reaction was monitored by ^{1}H-NMR. The organic products identified in the reaction mixture were isobutylene, *t*-butyl chloride, and free THF.

*4.2.10. Decomposition of W(=NAr)(O-t-Bu)$_4$ (**3**)*

A solution of **3** (9.4 mg, 0.014 mmol) in C_6D_6 (450 μl) was prepared in an NMR tube. Hexamethylbenzene was added as an internal standard (25 μl of a 0.4 M soln) and the tube was flame sealed under vacuum. The sample was maintained at 75–85°C for 27 days, during which time **3** decomposed and solids precipitated. The progress of the reaction was monitored by ^{1}H-NMR. Three organic products were obtained from the reaction mixture, isobutylene, *t*-butyl alcohol, and 2,6-diisopropylphenylamine. ^{1}H-NMR (C_6D_6) of 2,6-diisopropylphenylamine (unisolated): δ 3.5 (br s, 2, N*H*$_2$), 2.87 (m, 2, ((CH$_3$)$_2$C*H*)$_2$), and 1.15 (d, 12, ((C*H*$_3$)$_2$CH)$_2$). Partial ^{13}C{^{1}H}-NMR (C_6D_6) of *t*-butyl alcohol (unisolated): δ 31.6 ((*C*H$_3$)$_3$COH).

*4.2.11. Decomposition of W(=NAr)(O-t-Bu)$_4$ (**3**) in the presence of PhN=CH(t-Bu)*

A solution of **3** (7.9 mg, 0.012 mmol), C_6D_6 (450 μl), anisole, and imine PhN=CH(*t*-Bu) (10 μl of a 1 M soln, 0.010 mmol) was prepared in an NMR tube equipped with a Teflon stopcock. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. The sample was maintained at room temperature for 5 days, during which time there were some small changes in the NMR spectra but no decomposition products or reaction with imine was observed. The sample was maintained at 75–85°C for 35 days. During this time, yellow solids formed in the tube and **3** decomposed and reacted with imine PhN=CH(*t*-Bu). Approximately 100% of imine PhN=CH(*t*-Bu) was converted to the product imine

ArN=CH(*t*-Bu). In addition, isobutylene and *t*-butyl alcohol were observed in the NMR spectrum. There were no resonances consistent with the imide W(=NPh)(O-*t*-Bu)$_4$ observed in the spectrum. ^{1}H-NMR (C_6D_6) of (2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)N=CH(*t*-Bu) (unisolated): δ 8.00 (s, 1, C*H*(*t*-Bu)), 2.70 (sept, 2, (2,6-((CH$_3$)$_2$C*H*)$_2$C$_6$H$_3$)N), 1.26 (s, 9, CH(*t-Bu*)), and 1.16 (d, 12, (2,6-((C*H*$_3$)$_2$CH)$_2$C$_6$H$_3$)N). Aromatic resonances could not be definitively assigned due to the complexity of the spectrum in this region.

4.2.12. Decomposition of W(=NAr)(O-t-Bu)$_4$ (3) in the presence of W(=NAr)Cl$_4$(THF) (4)

A solution of **3** (5.2 mg, 0.00799 mmol), C_6D_6 (600 μl), **4** (1 mg, 0.002 mmol), and anisole (15 μl of a 1 M soln) was prepared in an NMR tube equipped with a Teflon stopcock. The sample was maintained at 25°C for 1 day and at 75–85°C for 4 days, during which time ligands exchanged, solids formed, and **3** decomposed. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. The volatile components of the sample were vacuum transferred to another NMR tube. ^{1}H-NMR of the volatile material showed the presence of isobutylene and *t*-butyl chloride. The non-volatile components were left behind in the original NMR tube. ^{1}H-NMR showed the presence of 2,6-diisopropylamine and/or 2,6-diisopropylammonium chloride, these are indistinguishable in a complex reaction mixture. Significant resonances ^{1}H-NMR (C_6D_6) of non-volatile components (unisolated): δ 2.86 (br s), 1.25 (m), 1.16 (d).

4.2.13. Thermal stability of W(=NAr)Cl$_4$(THF) (4)

A solution was prepared of **4** (5.4 mg, 0.00943 mmol) and C_6D_6 (700 μl) in an NMR tube that was flamed sealed under vacuum. The sample was heated and maintained at 75–85°C for over 1 month. A dark precipitate formed, but the total concentration of imide remained nearly constant. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy and no new signals appeared in the ^{1}H-NMR spectrum.

4.2.14. Thermal stability of W(=NPh)Cl$_4$(THF) (5)

A solution was prepared of **5** (15.7 mg, 0.0321 mmol) and C_6D_6 (700 μl) in an NMR tube that was flame sealed under vacuum. The sample was heated and maintained at 55–65°C for about 1 month. A dark precipitate formed, but the total concentration of imide remained nearly constant. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy and no new signals appeared in the ^{1}H-NMR spectrum.

4.2.15. Thermal stability of W(=NPh)(OC(CH$_3$)-(CF$_3$)$_2$)$_2$Cl$_2$(THF) (6) in the presence of (n-Pr)N=CHPh

A solution was prepared of **6** (5.1 mg, 0.00654 mmol), C_6D_6 (400 μl), and anisole (100 μl of a 0.3 M soln) in an NMR tube, equipped with a Teflon stopcock. The sample was maintained at 25°C for 1 day to verify the stoichiometry and the stability of the reaction mixture. The sample was heated and maintained at 55–65°C for 1 day, at 65–75°C for 2 days, and at 75–85°C for 3 days. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. No change was observed in the sample or its ^{1}H-NMR spectrum. The imine (*n*-Pr)N=CHPh (7.5 μl of a 0.8 M soln, one equivalent) was added to the NMR tube. The sample was maintained at 75–85°C for 62 days at which time product imine PhN=CHPh was present in $< 5\%$ yield and 35% of the THF dissociated. There were no resonances consistent with the imide W(=N-*n*-Pr)(OC(CH$_3$)(CF$_3$)$_2$)$_2$Cl$_2$(THF) in the spectrum, nor were there any resonances consistent with the decomposition of **6**. ^{1}H-NMR (C_6D_6) of PhN=CHPh (unisolated): δ 8.119 (s, 1, PhN=C*H*Ph). Aromatic resonances could not be definitively assigned due to the complexity of the spectrum in this region.

4.2.16. Thermal stability of W(=N-t-Bu)$_2$(OC(CH$_3$)-(CF$_3$)$_2$)$_2$ (7) in the presence of (n-Pr)N=CHPh

A solution of **7** (5.5 mg, 0.0421 mmol, one equivalent) in C_6D_6 (500 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene was added as an internal standard (240 μl of a 0.4 M soln) along with imine (*n*-Pr)N=CHPh (73 μl of a 0.8 M soln, 1.7 equivalents). The sample was maintained at 25°C for 1 day to verify the stoichiometry and the stability of the reaction mixture. The sample was heated and maintained at 55–65°C for 1 day, at 65–75°C for 2 days, and at 75–85°C for 18 days. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Only $< 5\%$ of imine (*n*-Pr)N=CHPh was converted to product imine (*t*-Bu)N=CHPh. There were no resonances consistent with (bis)imide W(=N-*t*-Bu)(=N-*n*-Pr)(OC(CH$_3$)(CF$_3$)$_2$)$_2$ observed in the spectrum, nor were there any resonances consistent with the decomposition of **7**. ^{1}H-NMR (C_6D_6) of (*t*-Bu)N=CHPh (unisolated): δ 8.12 (s, 1, (*t*-Bu)N=C*H*Ph). Aromatic and *t*-butyl resonances could not be definitively assigned due to the complexity of the spectrum in these regions.

4.2.17. Decomposition of Mo(=NAr)$_2$(O-t-Bu)$_2$ (8)

A solution of **8** (33 mg, 0.059 mmol) in C_6D_6 (750 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene was added as an internal standard and the sample was maintained at 100°C for 45 days at which time **8** decomposed. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Isobutylene and 2,6-diisopropylphenylamine were identified. ^{1}H-NMR (C_6D_6) of 2,6-diisopropylphenylamine (unisolated): δ 3.19 (s, 2, N*H*$_2$), 2.63 (sept, 2 ((CH$_3$)$_2$C*H*)$_2$) and 1.13 (d, 12, ((C*H*$_3$)$_2$CH)$_2$). Aromatic

resonances could not be definitively assigned due to the complexity of the spectrum in this region. Significant resonances from unidentified species were also observed: ^{1}H-NMR (C_6D_6): δ 4.47 (m), 4.30 (m), 3.96 (m), 1.46 (d), 1.37 (m) and 1.13 (m).

*4.2.18. Reaction of (n-Pr)N=CHPh and PhN=CH(t-Bu) with the nonvolatile components from the decomposition of Mo(=NAr)$_2$(O-t-Bu)$_2$ (**8**)*

A solution of **8** (33 mg, 0.059 mmol) in C_6D_6 (750 μl) was prepared in an NMR tube equipped with a Teflon stopcock. Hexamethylbenzene was added as an internal standard and the sample was maintained at 100°C for 45 days at which time **8** decomposed. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. Isobutylene and 2,6-diisopropylphenylamine were identified. ^{1}H-NMR (C_6D_6) of 2,6-diisopropylphenylamine (unisolated): δ 3.19 (s, 2, NH_2), 2.63 (sept, 2 ((CH$_3$)$_2$CH)$_2$) and 1.13 (d, 12, ((CH_3)$_2$CH)$_2$). Aromatic resonances could not be definitively assigned due to the complexity of the spectrum in this region. Significant resonances from unidentified species were also observed: ^{1}H-NMR (C_6D_6): δ 4.47 (m), 4.30 (m), 3.96 (m), 1.46 (d), 1.37 (m) and 1.13 (m).

The volatile compounds of the sample were vacuum transferred to another NMR tube. The nonvolatile components showed resonances for 2,6-diisopropylphenylamine and the unidentified species listed above. Imines (*n*-Pr)N=CHPh and PhN=CH(*t*-Bu) were added to the nonvolatile compounds and the reaction was maintained at 25°C for 24 h. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. ^{1}H-NMR (C_6D_6) PhN=CHPh (unisolated): δ 8.12 (s, 1, CHPh). ^{1}H-NMR (C_6D_6) (*n*-Pr)N=CH(*t*-Bu) (unisolated): 7.33 (s, 1, CH(*t*-Bu)), 3.26 (t, 2, CH$_3$CH$_2$CH_2N), 1.59 (m, 2, CH$_3$CH_2CH$_2$N), 1.03 (s, 9, CH(*t-Bu*), and 0.86 (t, 3, CH_3CH$_2$CH$_2$N). ^{1}H-NMR (C_6D_6) (2,6-((CH$_3$)$_2$CH)$_2$C$_6$H$_3$)N=CHPh (unisolated): δ 8.0 (s, 1, CHPh), 3.12 (sept, 2, ((CH$_3$)$_2$CH)$_2$), and 1.16 (d, 12, ((CH_3)$_2$CH)$_2$).

5. Conclusions

The reactions of the *t*-butoxide-supported imide complexes **1**, **3**, and **8** with imines do not proceed via a Chauvin-type [2 + 2] metathesis pathway. Experimental data establish that these complexes are unstable to the reaction conditions and that the products from the decomposition are the agents of =NR exchange. Although it is impossible to completely eliminate the intermediacy of cationic or radical species, no evidence for their presence was observed. We conclude that the imide-mediated C–H activation is the most probable first step in the decomposition reaction and that, generally, *t*-butoxide ligands are not inherently compatible with the imide functional group, especially under conditions of prolonged heating.

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