ORGANOMETALLICS

Oxo/Imido Heterometathesis Reactions Catalyzed by a Silica-Supported Tantalum Imido Complex

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Supporting Information

ABSTRACT: Grafting $Ta(=N^{t}Bu)(CH_{2}CMe_{2}Ph)_{3}$ onto the surface of silica partially dehydroxylated at 300 °C leads to the formation of the surface imido complex (\equiv SiO)₂Ta(= N^{t}Bu)(CH₂CMe_{2}Ph) as a major species, which was characterized with EXAFS, ¹³C CP/MAS NMR, diffuse reflectance FTIR, elemental analyses, and chemical reactivity. The obtained material acts as an efficient heterogeneous catalyst for various oxo/imido heterometathesis transformations: imidation of ketones and DMF with N-sulfinylamines and condensation of



N-sulfinylamines into sulfurdiimines and phenyl isocyanate into diphenylcarbodiimide.

INTRODUCTION

Catalytic *heterometathesis* (i.e., carbon–heteroatom and heteroatom–heteroatom multiple-bond metathesis) is quite a novel class of transition-metal-mediated reactions. Despite a plethora of stoichiometric metathetical reactions of various multiply bonded transition-metal–ligand units with heteroolefins and heterocumulenes being described,^{1–3} the examples of catalytic heterometathesis of the latter are still scarce. The only reports to date are metathesis of imines,^{4,5} carbodiimides,⁶ diphosphenes,⁷ and nitriles,⁸ condensation of isocyanates and *N*sulfinylamines into carbodiimides⁹ and sulfurdiimines,¹⁰ respectively, and metathetical imido-deoxygenation of aldehydes with isocyanates⁵ and iminophosphoranes.¹¹

Recently we have successfully combined two well-documented stoichiometric heterometathesis reactions—imidation of transition-metal oxo complexes with *N*-sulfinylamines¹² and imido group transfer from imido complexes to oxo compounds^{1-3,5,13-16}—into a catalytic cycle (Scheme 1). The overall transformation, catalyzed by vanadium and molybde-num oxo and imido complexes (MOCl₃, M = V, Mo; Mo(= NAr)₂Z₂, Z = OR, Alk, etc.), results in oxo/imido heterometa-thesis between *N*-sulfinylamines and aldehydes (X = CHR) to afford aldimines.¹⁷

The low activity of the molybdenum and vanadium catalysts and quite limited scope of reactive oxo substrates stimulated us to seek more efficient catalysts based on other transition metals. It is well-known that the reactivity of transition-metal imido complexes toward the C==O unit of carbonyl compounds (X = CR^1R^2), isocyanates (X = CNR), carbon dioxide (X = CO), etc. increases to the left and to the down across the d block of the periodic table, which could be explained in terms of Scheme 1. Oxo/Imido Heterometathesis between N-Sulfinylamines and Oxo Compounds



nucleophilicity of the imido group¹⁸ or oxophilicity of the metal atom. Thus, among the most reactive are the group 4 and heavy group 5 metal imides (Ti,^{3,15} Zr,¹⁶ Ta^{1,14}). However, the pronounced tendency of their terminal oxo derivatives to form catalytically inactive oligomers with bridging oxo ligands prevents their application as catalysts. The only example has been reported recently^{9c} and utilized a Ti=O species stabilized with a bulky phthalocyanine ligand.

Meanwhile, the stabilization of terminal M=O fragments could be simply achieved by the fixation of the catalytically active species on the surface of the support. Indeed, the possibility of in situ generation of isolated Ta=O species on silica and even its stoichiometric heterometathetical imidation

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with *tert*-butyl isocyanate has been already demonstrated by Basset.¹⁹ Thus, we suppose that application of modern techniques of the rational design of well-defined heterogeneous catalysts, such as *Surface Organometallic Chemistry*,²⁰ to the reactive imido complexes of Ti, Zr, Hf, and Ta provides an opportunity to develop a new generation of highly efficient heterogeneous oxo/imido heterometathesis catalysts. Herein we report the preparation, characterization, and catalytic performance of a silica-supported tantalum imido complex— the first tantalum-based oxo/imido heterometathesis catalyst.

RESULTS AND DISCUSSION

Catalyst Preparation and Characterization. Grafting $Ta(=N^{t}Bu)(CH_{2}CMe_{2}Ph)_{3}$ (5 mol % to SiO₂) onto the surface of silica partially dehydroxylated at 300 °C (SiO₂-300) was accomplished via addition of a heptane solution of the complex to a suspension of silica and stirring at ambient temperature overnight. Subsequent filtering, washing with heptane, and drying in vacuo gave a pale yellow solid (Ta/SiO₂-300). The elemental analysis of several independently prepared samples of Ta/SiO₂-300 (Table 1) showed that the

Table 1. Elemental Analysis Data for the Independently Prepared Samples of Ta/SiO₂-300

sample	Ta (wt %) ^{<i>a</i>}	mmol of Ta/g	$Ta/N/C^{a,c}$
1	10.5	$0.58^a (0.61^b)$	1/1/16
2	9.2	0.51 (0.64)	1/0.8/17
3	10.2	0.56 (0.60)	1/0.9/17
		h	-

^{*a*}According to elemental analysis. ^{*b*}Maximum value expected at total chemisorption of the complex. ^{*c*}Atomic ratio.

composition of the obtained material was reproducible, the tantalum content (~10 wt %) was only slightly lower than that expected at total chemisorption of the complex, and the Ta/N/C ratio was close to 1/1/14, corresponding to the bis-grafted surface complex with an imido group and one alkyl ligand remaining. Elimination of *tert*-butylbenzene during grafting was confirmed using NMR spectroscopy. When grafting was carried out in the presence of the internal standard (C_6Me_6), the amount of *tert*-butylbenzene in the filtrate was estimated from ¹H NMR as ~1.6 equiv per Ta atom. The mass balance during grafting was also consistent with the elimination of 1.5–1.7 Ph^tBu/Ta. Thus, these data suggest the preliminary formulation of the surface complex as (\equiv SiO)₂Ta(=N^tBu)(CH₂CMe₂Ph) (Scheme 2).²¹

The presence of the $[N^tBu]$ group was confirmed by the stoichiometric heterometathesis reaction of Ta/SiO₂-300 with 5 equiv of PhCHO that gave 57% (to Ta) of spectroscopically identified PhCH=N^tBu after 3 h of reflux in heptane and subsequent washing of the solid with Et₂O (Scheme 3a). It

should be also noted that no olefin was observed in this reaction, which excludes the formation of a surface alkylidene complex.

In order to retrieve information on the number of atoms and interatomic distances within the first and second coordination spheres of the Ta atoms in Ta/SiO₂-300, extended X-ray absorption fine structure (EXAFS) spectroscopy was applied. The Fourier transform (FT) of the experimental EXAFS spectrum together with the best-fit theoretical curve are shown in Figure 1, whereas the best-fit parameters corresponding to the structural model are summarized in Table 2. The EXAFS spectrum of the sample is fully compatible with the bis-grafted structure A (Scheme 2) described above. The short Ta=N bond (at ca. 1.81 Å, which is close to values observed in other similar surface complexes 22a,b) is clearly attributable in the experimental spectrum, which strongly supports the notion that the imido ligand survived grafting. Three neighbors at ca. 1.95 Å are assigned to oxygen and carbon atoms of the siloxy and alkyl ligands, respectively (not resolved), the observed distance lying between the literature values of Ta-O (~ 1.9 Å)²² and Ta-C $(\sim 2.1 \text{ Å})^{22c}$ bond lengths in similar surface complexes. Finally, long nonbonded Ta-Si contacts are observed at ca. 3.26 Å.

The structure of the surface complex was also investigated with solid-state ¹³C CP/MAS NMR spectroscopy (Figure 2). The assignments of the peaks observed in the ¹³C NMR spectrum of Ta(=N^tBu)(CH₂CMe₂Ph)₃ (C₆D₆) and the solid-state spectrum of Ta/SiO₂-300 are juxtaposed in Table 3. All of the resonances in the solution spectrum of the initial complex are clearly attributable. The solid-state spectrum of Ta/SiO₂-300 shows two series of peaks in the region of CH₃ groups (28–36 ppm) and aromatic CH atoms (124–132 ppm), three distinct resonances of quaternary carbons with chemical shifts practically identical with those of the molecular complex at 41.8 (CMe₂Ph), 68.1 (NCMe₃), and 153.5 ppm (Ph_{ipso}), and an additional peak at 53.4 ppm.

It is worth noting that no CH_2 resonance was observed in the spectrum of the solid sample. This observation seems to suggest that the Ta atom in the surface complex is no longer bearing the alkyl ligands, all three of them being eliminated as Ph^tBu and not washed out completely. However, a series of observations and additional experiments strongly supports the presence of the organometallic fragment on the surface.²³ First, almost constant Ta/N/C ratios and reproducible elemental analyses, consistent with elimination of nearly two alkyl groups, for the independently prepared samples could hardly result from a coincidence. Second, additional washing of the samples with a large excess of heptane, Et₂O, and CH₂Cl₂ did not affect the elemental analyses, thus confirming that the remaining "Ph^tBu" is somehow bound in the solid. Meanwhile, it is quantitatively washed out after treatment of the sample with









Figure 1. FT of the experimental Ta L_{III} -edge EXAFS spectrum of Ta/SiO₂-300 (solid line) compared to the best-fit model curve (open circles).

Table 2. Parameters of the Local Environment of Ta Atoms in Ta/SiO₂-300 Refined from EXAFS Data^a

sphere	CN^{b}	distance (Å)	Debye–Waller factor (Å ²)
=N ^t Bu	1	1.81	0.0021
$-OSi \equiv$, $-CH_2CMe_2Ph$	3 ^c	1.95	0.0021
–OSi≡	2	3.26	0.0074
		1	0

^{*a*}Fitting ranges: $k = 2.5-14.0 \text{ Å}^{-1}$, R = 0.8-3.2 Å; $\Delta E = 9 \text{ eV}$ common to all spheres, $R_{\rm f} = 0.025$. ^{*b*}Coordination numbers were fixed at anticipated values and not refined. ^{*c*}Not resolved.



Figure 2. Solid-state 13 C CP/MAS NMR spectrum of Ta/SiO₂-300. The asterisks mark the spinning sidebands.

methanol (~1.1 equiv of Ph^tBu per Ta according to ¹H NMR with internal standard). Furthermore, *tert*-butylbenzene turns out to be monodeuterated after treating the sample with methanol- d_4 (Scheme 3b), which is clearly evidenced by ¹H (triplet at 1.30 ppm, ² $J_{\rm HD} \approx 2$ Hz) and ¹³C (triplet at ~31.0

Table 3. ^{13}C Chemical Shifts of Ta(=N^tBu)(CH_2CMe_2Ph)_3 and Ta/SiO_2-300

δ (ppm)		
$Ta(=N^{t}Bu)(CH_{2}CMe_{2}Ph)_{3}$	Ta/SiO ₂ -300	assignment
33.8	20 6 22 6	NCMe ₃
34.4	50.0-55.0	CMe2Ph
41.4	41.8	CMe ₂ Ph
	53.4	NHCMe ₃
68.4	68.1	NCMe ₃
106.9	not observed	CH ₂
125.7		Ph _{meta}
125.9	126.4, 129.3	Ph_{para}
128.7		Phortho
153.3	153.5	Ph_{ipso}

ppm, ${}^{1}J_{\rm CD}$ = 19.3 Hz) NMR. Finally, the 13 C resonances that appear at δ 41.4 and 41.8 ppm in the spectra of the complex and Ta/SiO₂-300, respectively, are characteristic of the quaternary carbon in the TaCH₂CMe₂Ph moiety, whereas the corresponding atom of Ph^tBu has a chemical shift of 34.6 ppm (CDCl₃).

Thus, consistent with EXAFS, elemental analysis, and the literature, ¹³C NMR confirms the presence of the surface complex (\equiv SiO)₂Ta(=N^tBu)(CH₂CMe₂Ph). Meanwhile, the observation of the ¹³C resonance at 53.4 ppm and a series of multiple poorly resolved peaks in the methyl group region indicates the possible coexistence of other surface complexes. The signal at 53.4 ppm could arise from the quaternary carbon of a *tert*-butylamido ligand.²⁴ Indeed, application of diffuse reflectance FTIR (DRIFT) spectroscopy allowed us to confirm the presence of the surface amido species. In addition to the intense CH vibrations in the aliphatic (3000–2800 cm⁻¹) and aromatic regions (3088, 3062, and 3028 cm⁻¹) and broad Si–OH bands (3800–3300 cm⁻¹), the DRIFT spectrum of Ta/SiO₂-300 (Figure 3) clearly demonstrates distinct bands in the NH vibration region (at 3306 and 3250 cm⁻¹).

Thereby we can conclude that at least two different passways take place during grafting: the initially proposed substitution of two alkyl ligands by silanol groups leading to the surface imido complex A (Scheme 2) and the substitution of one alkyl ligand along with the direct addition of the SiO–H bond across the M=N linkage that results in the formation of the amido species B (Scheme 4). Such transformations of multiply bonded ligands during grafting (and the imido ligand particularly) have been reported previously.²⁵

The amount of form B could be tentatively estimated as 10-40 mol % on the basis of (a) the amount of Ph^tBu eliminated during grafting (~1.6 equiv/Ta) and after alcoholysis of Ta/SiO₂-300 (~1.1 equiv/Ta), (b) the amount of imine formed in the reaction with PhCHO (~0.6 equiv/Ta), and (c) the Ta/C ratio found by elemental analysis (the experimental value 1/17

(b)

(a)

4500

inactive.

molybdenum complexes.

4000

the nominal accuracy given by EXAFS.

3306

3500

3000

Wavenumber (cm⁻¹)

Figure 3. DRIFT spectra of (a) SiO₂-300 and (b) Ta/SiO₂-300.

lies between 1/14 and 1/24 expected for forms A and B, respectively, and corresponds to 70% A and 30% B). Unfortunately, EXAFS spectroscopy also used to identify the nature of the Ta active site cannot provide an accurate estimate of the fraction of the B form. The abundance of form B would decrease the effective coordination number for the shortest imido Ta=N bonds and slightly increase the coordination number for the Ta-O/Ta-C bonds to an extent that is beyond

It should be pointed out that according to our initial hypothesis (the catalytic cycle presented in Scheme 1) only form A is capable of participating in heterometathetical transformations, and the reaction with PhCHO seems to confirm this supposition. Thus, we believe that all the catalytic results which are presented below reflect the chemical behavior of the surface imido complex A, whereas form B remains

Imidation of Ketones with N-Sulfinylamines. The obtained material was tested in the oxo/imido heterometathesis reaction between N-sulfinyl-p-toluidine and acetophenone and compared to its molecular precursor and other previously developed homogeneous^{10,17} and heterogeneous^{26,27} catalysts (Table 4). As was earlier observed for vanadium²⁶ and molybdenum²⁷ systems, the grafted tantalum complex displayed activity significantly higher than that of its molecular analogue. Moreover, Ta/SiO₂-300 appears to be the most active to date among all tested homogeneous and heterogeneous catalysts, in full agreement with the higher imidating ability of tantalum imido complexes over vanadium and

2500

2000

Absorbance (Kubelka-Munk units)



	$N_{S}^{O} + O^{Ph} - \frac{\text{cat. (5 mol%M)}}{\text{heptane, } \Delta}$	N	Ph + SO ₂
	catalyst	time	$(\%)^a$
1	$Ta(=N^{t}Bu)(CH_{2}CMe_{2}Ph)_{3}/SiO_{2}-300$	20 min	≥95
2	$Mo(=NMes)_2(CH_2CMe_2Ph)_2/SiO_2-300^b$	1 h	≥95
3	2% VOCl ₃ /SiO ₂ -500 ^c	5 h	90
4	$Ta(=N^{t}Bu)(CH_{2}CMe_{2}Ph)_{3}$	5 h	82
5	$Mo(=NMes)_2(CH_2CMe_2Ph)_2$	5 h	37
6	$MOCl_3$ (M = V, Mo)		no reaction
	_		

^{*a*}Spectroscopically estimated. ^{*b*}Obtained via grafting Mo(=NMes)₂(CH₂CMe₂Ph)₂ onto SiO₂-300.²⁷ ^cObtained via grafting 2 mol % of VOCl₃ onto SiO₂-500.²⁶

Table 5. Imidation of Ketones with N-Sulfinylamines

		R'	Ta/SiC) ₂ -300) (5 mol%Ta)		R'
Rľ	N=S=O +	O≓(8"		heptane, Δ		RN=	(+SO ₂
				•		1-1	2
	Ketimine	Time	Yield (%) ^a		Ketimine	Time	Yield (%)
1	-∕⊂}-N }-Ph	20 min	97	7	N Ph Ph	7 h	68
2	F N→Ph Ph	20 min	86	8		1 h	86
3		1 h	90	9		3 h	96
4	OMe N Ph	l h	83	10	R Fe N	3.5 h	81
5	F F F F F	1 h	93	11	$\begin{array}{c} & & & \\ & & & \\ & & & \\ + & & & \\ 0 & & & 0 \end{array}$	1 h	83
6	N Ph Ph	7 h	90	12	$\operatorname{res}_{N} \xrightarrow{N} \operatorname{res}_{N}$	10 h	82
^a Is	olated vield						

To further investigate the catalytic performance of Ta/SiO₂-300 in the imidation of ketones, we studied the interaction of a range of N-sulfinylamines and ketones in the presence of the heterogeneous catalyst (Table 5). All reactions were carried out in refluxing heptane (98 °C) and followed with IR spectros-

Scheme 4. Formation of the Surface Amido Complex

copy. The method can be regarded as general for the derivatives of acetophenone, benzophenone, fluorenone, and acetylferrocene. It is particularly attractive in the case of electron-deficient anilines (2, 5, and 9) that are poorly reactive in the classical



Table 4. Catalytic Performance of Various Homogeneous and Heterogeneous Oxo/Imido Heterometathesis Catalysts

Article

Tabl	e 6.	Imidation	of DMF	with	N-8	Sulfiny	lamines
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	RN=S=O + 0 <u></u> N -	Ta/SiO₂-300 (5 mol%Ta) heptane, ∆	RN _≫ N + RN≈ _S ≈NR + S0	D ₂
			conversion of	f RNSO $(\%)^a$
entry no.	R	time (h)	into formamidine	into sulfurdiimine
1	$2-FC_6H_4$	3	100	
2	$4-MeC_6H_4$	5	45	10
3	$2-MeOC_6H_4$	5	32	36
^a Spectroscopically estima	ted.			

acid-catalyzed condensation of anilines and ketones. It is worth noting that even such sterically hindered substrates as *N*sulfinyl-2,4,6-trimethylaniline and *N*-sulfinyl-2,4,6-tribromoaniline react smoothly (**6** and **9**). Only in the case of *N*-sulfinyl-2,6-diisopropylaniline does the reaction not give quantitative conversion (7). Prolonged heating was also required in the case of substrates with pronounced coordinating ability: e.g., containing a pyridine core (**12**).

Imidation of DMF and Condensation of *N*-Sulfinylamines into Sulfurdiimines. Dimethylformamide can be used as a carbonyl source instead of a ketone, the corresponding formamidines being formed. Three *N*-sulfinylamines were tested as imidating agents (Table 6). The observed reactivity of *N*-sulfinylamines correlates with their electron deficiency, *N*-sulfinyl-2-fluoroaniline being remarkably more active than methyl- and methoxy-substituted species.

It was noticed that DMF imidation was accompanied by the formation of the corresponding sulfurdiimines as byproducts (Table 6). Analogously, this was reported earlier for the same reaction catalyzed by $Mo(=NMes)_2(CH_2CMe_2Ph)_2$.¹⁰ This observation reveals the occurrence of an alternative oxo/imido heterometathesis process, where *N*-sulfinylamine acts as both imidating and oxo component (Scheme 1, X = SNR). In the absence of a ketone, DMF, or any other oxo compound the reaction can be used as a preparative method for sulfurdiimine synthesis. Table 7 demonstrates the performance of Ta/SiO₂-300 in condensation of the same series of *N*-sulfinylamines. *o*-Fluoro-substituted sulfinylaniline was again found to be the most reactive.

Table 7. Condensation of N-Sulfinylamines into Sulfurdiimines

	Ta/SiO ₂ -300 (5 mol%Ta)			
2 RN=S=0	heptane,		$s = NR + SO_2$	
entry no.	R	time (h)	conversion (%)	
1 (13)	$2-FC_6H_4$	5	$94^{a} (66^{b})$	
2 (14)	4-MeC ₆ H ₄	24	72 (50)	
3 (15)	2-MeOC ₆ H ₄	24	87 (70)	
^a Spectroscopically estimated conversion. ^b Isolated yield.				

Condensation of Phenyl Isocyanate into Diphenylcarbodiimide. Condensation of isocyanates into carbodiimides with liberation of CO_2 catalyzed by transition-metal imido complexes is a mechanistic equivalent of the condensation of *N*-sulfinylamines. It was reported for several homogeneous catalysts, the reaction conditions being usually quite severe (140–190 °C).^{9a–c} We have investigated the catalytic capability of Ta/SiO₂-300 in the condensation of PhNCO into PhNCNPh (Scheme 5). Although the observed activity is rather low (only 25% conversion was achieved after Scheme 5. Condensation of PhNCO into PhNCNPh

	Ta/SiO ₂ -300 (5 mol%Ta)	
2 PNN=C=O	hontono A	$Pnn=C=nPn + CO_2$
	neptane, A	25% (24 h)

24 h of reflux in heptane), it is worth noting that the conditions are significantly milder than those reported.

CONCLUSION

In summary, we have shown that surface organometallic chemistry opens new possibilities for the design of oxo/imido heterometathesis catalysts due to the stabilization of in situ generated highly reactive terminal oxo complexes on the surface of the support. The simply prepared tantalum surface imido complex (\equiv SiO)₂Ta(=N^tBu)(CH₂CMe₂Ph) acts as an efficient heterogeneous catalyst for the imidation of ketones and dimethylformamide with *N*-sulfinylamines and catalyzes condensations of *N*-sulfinylamines into sulfurdiimines and phenyl isocyanate into diphenylcarbodiimide.

EXPERIMENTAL SECTION

General Considerations. If not otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. NMR spectra were recorded using Bruker AMX 400 and Avance 300 spectrometers. Chemical shifts are measured relative to residual ¹H and ¹³C resonances of the solvents: 7.24 (¹H, CDCl₃) and 7.16 (¹H, C₆D₆); 77.0 (¹³C, CDCl₃) and 128.0 (¹³C, C₆D₆). ¹⁹F spectra were referenced externally to TFA. Chemical shifts are given in ppm and coupling constants in Hz. Infrared spectra were registered with a Specord M82 spectrophotometer. Elemental analyses were performed in the Laboratory of Microanalysis of the INEOS RAS.

Reagent grade solvents were dried by refluxing over sodium/ benzophenone ketyl (tetrahydrofuran and diethyl ether), sodium (toluene and *n*-heptane), magnesium (methanol), phosphorus pentoxide (chloroform, DMF), or calcium hydride (dichloromethane) and distilled prior to use. Deuterated solvents were dried over sodium/ potassium alloy (C_6D_6) or phosphorus pentoxide (CDCl₃) and stored over activated 4 Å molecular sieves. Methanol- d_4 was used as received. *N*-Sulfinylamines were prepared according to the standard procedures^{17,28} using Merck SOCl₂ ("for synthesis" grade) and freshly distilled or recrystallized anilines.

Silica (Merck silica gel 60 for column chromatography; surface area, 480–540 m²/g; particle size, 63–200 μ m; mean pore size, 60 Å) was preheated in vacuo (10⁻² Torr) to 300 °C for 5 h and stored under argon.

Preparation of Ta(==N^tBu)(CH₂CMe₂Ph)₃. A 1.76 M solution of CMe₂(Ph)CH₂MgCl (13.9 mL, 24.5 mmol) in diethyl ether was added dropwise to a stirred suspension of Ta(==N^tBu)Cl₃(py)₂²⁹ (4.22 g, 8.2 mmol) in diethyl ether (100 mL) cooled to -78 °C. The reaction mixture was stirred at room temperature overnight, the resulting white suspension was filtered, and the residue was washed with diethyl ether (2 × 25 mL). The filtrate was evaporated and dried in vacuo to give 5.23 g (98%) of a yellow oil. ¹H NMR (400 MHz, C₆D₆): δ 7.31 (d, ³J

= 7.3, 6H, Ph_{ortho}), 7.22 (t, ³*J* = 7.3, 6H, Ph_{meta}), 7.08 (t, ³*J* = 7.3, 3H, Ph_{para}), 1.47 (s, 9H, NCMe₃), 1.39 (s, 18H, CMe₂Ph), 0.76 (s, 6H, CH₂). ¹³C NMR (100 MHz, C₆D₆): δ 153.3 (Ph_{ipso}), 128.7 (Ph_{ortho}), 125.9 (Ph_{para}), 125.7 (Ph_{meta}), 106.9 (CH₂), 68.4 (NCMe₃), 41.4 (CMe₂Ph), 34.4 (CMe₂Ph), 33.8 (NCMe₃).

Preparation of Ta/SiO₂-300. $Ta(=N^{t}Bu)(CH_{2}CMe_{2}Ph)_{3}$ (5.23 g, 8.0 mmol) was dissolved in heptane (30 mL) and added slowly to a stirred suspension of silica (9.78 g, 162.8 mmol) in heptane (100 mL). The mixture was stirred overnight at room temperature and then filtered, and the residue was washed twice with heptane and dried in vacuo to give 13.05 g of a pale yellow solid. Anal. Found: Ta, 10.5; N, 0.85; C, 11.72.

Alcoholysis of Ta/SiO₂-300. A vial was charged with Ta/SiO₂-300 (93 mg, 0.052 mmol Ta) and C₆Me₆ (0.043 mmol, internal standard), and methanol (~0.2 mL) was added. The vial was left open for several days to evaporate the excess methanol under atmospheric pressure. The solid was then washed with CDCl₃ (3 × 0.2 mL). The amount of *tert*-butylbenzene was estimated from ¹H NMR as 0.056 mmol (1.1 equiv/Ta). ¹H NMR (300 MHz, CDCl₃): δ 7.39 (d, ³J = 7.3, 2H, Ph_{ortho}), 7.30 (t, 2H, Ph_{metaa}), 7.16 (t, 1H, Ph_{para}), 1.32 (s, 9H, CMe₃). ¹³C NMR (100 MHz, CDCl₃): δ 151.0 (Ph_{ipso}), 128.1 (Ph), 125.4 (Ph), 125.2 (Ph), 34.61 (quat CMe₃), 31.36 (CMe₃). When methanol-d₄ was used, signals assigned to monodeuterated *tert*butylbenzene were observed. ¹H NMR (400 MHz, CDCl₃): δ 1.32 (s, 6H, CMe₂), 1.30 (t, ²J_{H-D} ≈ 2, 2H, CH₂D). ¹³C NMR (100 MHz, CDCl₃): δ 34.54 (quat CMe₂CH₂D), 31.34 (CMe₂), 31.04 (t, ¹J_{C-D} = 19.3. CH₂D).

Stoichiometric Reaction of Ta/SiO₂-300 with PhCHO. A Schlenk flask was charged with Ta/SiO₂-300 (140 mg, 0.087 mmol Ta), benzaldehyde (0.045 mL, 0.435 mmol, 5 equiv to Ta), and heptane (3 mL), and the mixture was stirred under reflux for 3 h. The solid was then filtered off and washed with diethyl ether (3 × 4 mL). C_6Me_6 (0.012 mmol, internal standard) was added to the filtrate. A 57% amount (to Ta) of *N*-benzylidene-*tert*-butylamine was identified in ¹H NMR (300 MHz, CDCl₃): δ 8.28 (s, 1H, CH=N), 1.30 (s, 9H, NCMe₃).

Ketimine Synthesis. A Schlenk flask was charged with Ta/SiO_2 -300 (5 mol % of Ta), ketone (1 equiv), *N*-sulfinylamine (1 equiv), and heptane (C = 0.15 M), and the mixture was stirred under reflux. The reaction was followed with IR spectroscopy by taking aliquots of the reaction mixture until total disappearance of the carbonyl band was achieved. The resulting solution was rapidly filtered in air through a glass filter. The filtrate was concentrated in vacuo and cooled to -20°C. The precipitated solid was separated by filtration. Spectral characteristics and elemental analysis data for ketimines 1-12 are given in the Supporting Information.

Sulfurdiimine Synthesis. A Schlenk flask was charged with Ta/ SiO₂-300 (5 mol % of Ta), *N*-sulfinylamine, and heptane (C = 0.30 M), and the mixture was stirred under reflux. The reaction vessel was purged several times with argon to remove the liberated SO₂. The conversion was determined from the NMR spectra of the aliquots of the reaction mixture. The catalyst was filtered off under argon. The filtrate was concentrated in vacuo and cooled to -78 °C. The precipitated solid was separated by filtration. Spectral characteristics and elemental analysis data for compounds 13–15 are given in the Supporting Information.

Imidation of DMF. A Schlenk flask was charged with Ta/SiO₂-300 (5 mol % of Ta), DMF (1 equiv), *N*-sulfinylamine (1 equiv), C_6Me_6 (internal standard), and heptane (C = 0.15 M), and the mixture was stirred under reflux for 3–5 h. The reaction was followed with IR spectroscopy by taking aliquots of the reaction mixture. The products of the reaction were identified through ¹H NMR spectroscopy by comparison with literature data.^{10,30} The conversion was determined relative to the internal standard.

Condensation of PhNCO. A Schlenk flask was charged with Ta/ SiO_2 -300 (170 mg, 0.10 mmol Ta, 5 mol % of Ta), and a 0.15 M solution of PhNCO (0.22 mL, 2.1 mmol) in heptane (14 mL) was added. The mixture was followed with IR spectroscopy by taking aliquots while being heated under reflux. A band at 2142 cm⁻¹ appeared and increased during the course of the reaction, indicating

the formation of carbodiimide. The conversion after 24 h of reflux was \sim 25% (GC).

Extended X-ray Absorption Fine Structure Spectroscopy (**EXAFS**). The Ta L_{III} -edge EXAFS spectrum for Ta/SiO₂-300 was measured at the Structural Materials Science beamline of the Kurchatov Synchrotron Radiation Center (Moscow, Russia).³¹ The measurements were performed in the transmission mode using a Si(111) channel-cut monochromator and two ionization chambers filled with appropriate N₂-Ar mixtures. Since the sample is susceptible to humidity, freshly prepared substance was used and all sample manipulation steps were performed under argon. Standard processing and quantitative analysis of the experimental spectrum were performed using the IFEFFIT software suite³² with the amplitude and phase functions calculated by FEFF as implemented therein.

Solid-State ¹³**C CP/MAS NMR Spectroscopy.** Solid-state ¹³**C** CP/MAS NMR spectra were recorded on a Bruker Avance-II 400 NMR spectrometer operating at a frequency of 100.4 MHz using a solid-state 7 mm H/X MAS probe. The sample was packed into a 7 mm zirconia rotor (in a glovebox) and spun at the magic angle at a rate of 5.0 kHz. A RAMP cross-polarization pulse sequence was used³³ with ramping of ¹H-channel power from 100 to 70% and 2 ms contact time. For high-power proton decoupling during the acquisition the SW-TPPM sequence ($\tau = 8 \, \mu s, \varphi = 15^{\circ}$) was used.³⁴ The recycle delay was 2 s, and the length of the proton 90° pulse was 5.5 μs . The number of transients collected for spectrum was 2048. The sweep width was 55 kHz, and the chemical shift scale was referenced relative to the CH₂ group of solid adamantane.³⁵

DRIFT spectroscopy. Diffuse reflectance FTIR spectra were recorded in the 6000–400 cm⁻¹ range at a data point resolution of 4 cm⁻¹ with a Nicolet "Protege" 460 spectrometer equipped with a diffuse reflectance attachment developed at IOC RAS.³⁶ The catalyst was placed in an ampule supplied with a CaF₂ window using a glovebag filled with argon. The ampule was then evacuated at ambient temperature for 10 min, and the spectra were recorded (500 scans per spectrum).

ASSOCIATED CONTENT

S Supporting Information

Text and figures giving spectral characteristics and analytical data for compounds 1-15. 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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