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Inorganica Chimica Acta 345 (2003) 173-184

Inorganica Chimica Acta

www.elsevier.com/locate/ica

## Amide derivatives of tantalum and a niobium-promoted ring opening of 3,5-lutidine

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Received 3 June 2002

Dedicated to our friend and colleague Professor Richard R. Schrock, whose pioneering work in early transition metal chemistry has been inspirational to our endeavors.

#### Abstract

Various tantalum amide compounds were prepared in an attempt to observe C-N bond activation. Addition of lithium amides to THF solutions of  $(silox)_2TaCl_3$  (3) in the presence of trace amounts of the corresponding amine afforded  $(silox)_2TaCl_2NR_2$  (NR<sub>2</sub> = NMe<sub>2</sub>, 4-NMe<sub>2</sub>; N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>, 4-pyrr; N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>, 4-pip). Treatment of 4-pyrr with EtMgCl and 4-pip with MeMgBr provided (silox)<sub>2</sub>TaEt<sub>2</sub>(N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>) (5-pyrr-Et<sub>2</sub>) and (silox)<sub>2</sub>TaMe<sub>2</sub>(N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>) (5-pip-Me<sub>2</sub>). Thermolysis of 5-pip-Me<sub>2</sub> generated CH<sub>4</sub> and  $\eta^2$ -imine complex (silox)<sub>2</sub>Ta(CH<sub>3</sub>)( $\eta^2$ -NC<sub>5</sub>H<sub>9</sub>) (6). In contrast, 5-pyrr-Et<sub>2</sub> thermally degraded to the ethylene adduct,  $(silox)_2(C_4H_8N)Ta(\eta^2-C_2H_4)$  (7-pyrr) and  $C_2H_6$ . Na/Hg reductions of 4-pyrr and 4-pip in the presence of 1 equiv.  $C_2H_4$  generated 7pyrr and  $({}^{t}Bu_{3}SiO)_{2}(C_{5}H_{10}N)Ta(\eta^{2}-C_{2}H_{4})$  (7-pip); under an excess of  $C_{2}H_{4}$ , tantallacyclopentane (silox)<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>N)TaCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C H<sub>2</sub> (8-pyrr) was prepared. With pyridine present, Na/Hg reduction of 4-pyrr and 4-pip provided  $\eta^2$ -pyridine complexes  $(silox)_2(C_4H_8N)Ta(\eta^2-(N,C)-NC_5H_5)$  (9-pyrr) and  $(silox)_2(C_5H_{10}N)Ta(\eta^2-(N,C)-NC_5H_5)$  (9-pip). Treatment of 9-pyrr and 9-pip with 1 equiv.  $CH_3NH_2$  in  $C_6D_6$  revealed the formation of tantalum imido derivatives  $(silox)_2(C_4H_8N)Ta=NMe$  (10-pyrr) and  $(silox)_2(C_5H_{10}N)Ta=NMe$  (10-pip), respectively, via the  $\alpha$ -pyridyl-methylimido complex,  $(silox)_2Ta(NMe)(NC_5H_4)$  (11). Na/Hg reduction of  $(silox)_3NbCl_2$  (13) in the presence of excess 3,5-lutidine afforded  $(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$  (2-3,5-Lut), which was heated for 4 days at 120 °C to give (silox)<sub>2</sub>NbN-cis-CH=CMe-cis-CH=CMe-trans-CH=CHCMe<sub>2</sub>Si<sup>t</sup>Bu<sub>2</sub>O (14), whose structure was confirmed by X-ray crystallography. The direct participation of a silox group in the ring opening is a rare occurrence for this typically ancillary ligand, and provides another pathway for C–N bond activation relevant to hydrodenitrogenation (HDN). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Amide derivatives; Tantalum; 3,5-Lutidine; Niobium; Pyridine; Ring-opening; Siloxide; Metallacycle

## 1. Introduction

The scission of carbon-heteroatom bonds is the cornerstone of crude oil purification that enables its use as fuel or as the raw material for commodity chemicals. Hydrodesulfurization (HDS) is imperative, and removal of additional nitrogenous and oxygenated functionalities is increasing in importance as the need to utilize coal derivatives and lower quality heavy crude

oils becomes crucial to the world's energy concerns. Hydrodenitrogenation (HDN) requires the breaking of carbon-nitrogen bonds during the course of hydro-treatment, and two general classes of nitrogen containing species are targeted: amines ( $R_x NH_{3-x}$  (x = 1-3)) and aromatics (pyridines, quinolines, etc) [1,2]. Aromatics represent the more difficult case as they may first require hydrogenation, which is costly in energy and dihydrogen [1-3]. A variety of conventional mechanistic schemes for HDN that include binding events, hydrogen/alkyl transfer processes, C-N cleavage steps, and substrate elimination have been proposed [1-8].

HDN typically occurs simultaneously with HDS on sulfided Co/Mo/Al<sub>2</sub>O<sub>3</sub> or Ni/Mo/Al<sub>2</sub>O<sub>3</sub> at  $\sim 400$  °C

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and 70 atm [1]. The presence of reduced metal sites operating in concert with a Lewis acidic support may promote the formation of nucleophilic hydrides or adsorbed hydrocarbyl species critical to catalysis [7,8]. Binding could occur at acidic sites through nitrogen lone pairs or at reduced metal sites through  $\pi$ -bonding/ backbonding [9–11]. Surface nucleophiles could cleave the C–N bond of a bound species through attack at the  $\alpha$ -carbon [1–8], reduced metal sites could oxidatively add C–N bonds [12–17], and organic fragments may be liberated via hydrogenation.

In order to model HDN transformations, the chemistry of  $(silox)_3M$  (M = Ta (1), NbL (2-L),  $silox = {}^tBu_3$ -SiO) and various nitrogen-containing substrates has been examined. The oxidative addition of N–H and Ar–NH<sub>2</sub> bonds to  $(silox)_3$ Ta (1) has been observed [12], and examples of the latter C–N bond cleavage reveal an alternative to current HDN mechanistic postulations [1–8]. In addition, thermolyses of  $(silox)_3Nb(\eta^2-N,C$ py) and related compounds [13,18,19] promote the ringopening of the bound heterocycles. Herein are reported various amide derivatives [20,21] that display β-activations [22–25], and an unusual lutidine ring opening germane to HDN.

### 2. Results and discussion

## 2.1. Amide derivatives

#### 2.1.1. $(silox)_2TaCl_2NR_2$

Slow addition of secondary lithium amides to THF solutions of  $(silox)_2TaCl_3$  (3) [26] in the presence of catalytic quantities (~0.1%) of the corresponding amine (HNMe<sub>2</sub>, pyrrolidine, piperidine) generated LiCl and the metal amides  $(silox)_2TaCl_2NR_2$  (NR<sub>2</sub> = NMe<sub>2</sub>, 4-NMe<sub>2</sub>;  $N(CH_2)_3CH_2$ , 4-pyrr;  $N(CH_2)_4CH_2$ , 4-pip) in moderate to excellent yields (Eq (1)). These reactions proceeded without added amine but gave

$$({}^{t}Bu_{3}SiO)_{2}TaCl_{3} (3) + R_{2}NLi \xrightarrow{1Hr} ({}^{t}Bu_{3}SiO)_{2}TaCl_{2}NR_{2} + LiCl \\ + ~0.1\% R_{2}NH \xrightarrow{23^{\circ}C, 4-24 h} NR_{2} = NMe_{2}, 4-Me_{2}, 48\% \\ = N(CH_{2})_{3}CH_{2}, 4-pyrr, 87\% \\ = N(CH_{2})_{4}CH_{2}, 4-pip, 91\%$$
(1)

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lower yields [27]. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these species revealed equivalent siloxides and amide substituents (Table 1), consistent with a trigonal-bipyramidal geometry with axial siloxides, or a squarepyramidal configuration with an apical amide. Given the dynamics intrinsic to five-coordinate d<sup>0</sup> species, fluxional processes leading to the symmetrization evident in the spectra are also plausible; variable temperature NMR spectral measurements were not undertaken.

## 2.1.2. $(silox)_2 TaR'_2 NR_2$ and thermolyses

Treatment of  $(silox)_2 TaCl_2(N(CH_2)_3 CH_2)$  (4-pyrr) and  $(silox)_2 TaCl_2(N(CH_2)_4 CH_2)$  (4-pip) with EtMgCl and MeMgBr in Et<sub>2</sub>O afforded the pyrrolidide and piperidyl alkyls,  $(silox)_2 TaEt_2(N(CH_2)_3 CH_2)$  (5-pyrr– Et<sub>2</sub>) and  $(silox)_2 TaMe_2(N(CH_2)_4 CH_2)$  (5-pip–Me<sub>2</sub>), respectively (Eq. (2)). Like the amide chlorides, <sup>1</sup>H NMR spectra exhibited resonances consistent with a single type of siloxide, and symmetric

$({}^{t}Bu_{3}SiO)_{2}TaCI_{2}NR_{2} + 2 R'MgX$	Et <sub>2</sub> O ( <sup>t</sup> Bu <sub>3</sub> SiO) <sub>2</sub> TaR' <sub>2</sub> NR <sub>2</sub> + MgXCI
4-pyrr	X = CI, R' = Et, NR <sub>2</sub> = N(CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> , 5-pyrr-Et <sub>2</sub>
<b>4-</b> pip	$X = Br, R' = Me, NR_2 = N(CH_2)_4CH_2, 5-pip-Me_2$
	(2)

amide and alkyl groups (Table 1) [28,29]. Carbonhydrogen coupling constants were normal (5-pyrr-Et<sub>2</sub>:  ${}^{1}J_{CH\alpha} = 123$ ,  ${}^{1}J_{CH\beta} = 127$  Hz; 5-pip-Me<sub>2</sub>:  ${}^{1}J_{CH} = 121$  Hz), hence agostic interactions [30] were ruled out.

Thermolyses of the amide alkyls were undertaken in an attempt to observe C–N bond cleavage, but the degradations did not occur smoothly. Piperidide (silox)<sub>2</sub>(C<sub>5</sub>H<sub>10</sub>N)TaMe<sub>2</sub> (**5**-pip–Me<sub>2</sub>) decomposed completely to a mixture of products after thermolysis in C<sub>6</sub>D<sub>6</sub> for 12 days at 130 °C. Production of methane was evident from a signal at  $\delta$  0.15 in the <sup>1</sup>H NMR spectrum, and the major organometallic product (~ 50%) was tentatively assigned as the  $\eta^2$ -imine complex (silox)<sub>2</sub>Ta(CH<sub>3</sub>)( $\eta^2$ -NC<sub>5</sub>H<sub>9</sub>) (**6**, Eq. (3)) [25]. A pair of inequivalent siloxide resonances ( $\delta$  1.17, 1.15) were observed among a number of smaller resonances in the <sup>1</sup>H NMR spectrum. Two

$$({}^{^{\prime}\text{Bu}_3\text{SiO}})_2{}^{^{\prime}\text{Ta}}_1 \longrightarrow N \xrightarrow{C_6D_6}_{130^\circ\text{C}, 12 \text{ d}} ({}^{^{\prime}\text{Bu}_3\text{SiO}})_2{}^{^{\prime}\text{Ta}}_1 \longrightarrow N \xrightarrow{+ \dots \dots} (3)$$
  
5-pip-Me<sub>2</sub> CH<sub>3</sub> - CH<sub>4</sub> 6 CH<sub>3</sub>

multiplets ( $\delta$  4.12, 't'd; 4.24, 't'd), each integrating as one proton, were assigned to the  $\alpha$ -methylene of the imine ligand. The coupling pattern may be explained as a combination of one small vicinal coupling ( ${}^{3}J_{\rm HH} \sim 3$ Hz) and a large vicinal coupling on the same order as the geminal coupling ( ${}^{3}J_{\rm HH} \sim {}^{2}J_{\rm HH} \sim 12$  Hz). A resonance observed at  $\delta$  3.01 (dd, 1H) was assigned to the imine CH. Unfortunately, the complexity of the spectrum prevented further assignments, and attempts to purify the compound by crystallization and sublimation failed. Of various mechanisms,  $\beta$ -abstraction of an amide  $\alpha$ hydrogen by one of the methyls to directly give methane and **6** seems most likely.

In contrast to the reactivity of piperidide 5-pip $-Me_2$ , thermal decomposition of pyrrolidide  $(silox)_2(C_4H_8N)$ -TaEt<sub>2</sub> (5-pyrr $-Et_2$ ) proceeded more rapidly (~60% after 2.5 h at

# Table 1 <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectral data ( $\delta$ , assignment, mult, J (Hz)) for the complexes in C<sub>6</sub>D<sub>6</sub> unless otherwise noted

Compound	<sup>1</sup> H NMR ( $\delta$ , mult, assignment, J (Hz))		<sup>13</sup> C{ <sup>1</sup> H} NMR ( $\delta$ , assignment, J (Hz))			
	((H <sub>3</sub> C) <sub>3</sub> C) <sub>3</sub> Other		C(CH <sub>3</sub> ) <sub>3</sub>	$C(CH_3)_3$	Other	
$(^{t}Bu_{3}SiO)_{2}TaCl_{2}(NMe_{2})$ (4-Me <sub>2</sub> ) $(^{t}Bu_{3}SiO)_{2}TaCl_{2}(N(CH_{2})_{2}CH_{2})$ (4-pyrr)	1.32 1.35	3.60, s, NMe <sub>2</sub> 1.19, m, (CH <sub>2</sub> ) <sub>2</sub> ; 4.64, m, N(CH <sub>2</sub> ) <sub>2</sub>	30.42 30.40	24.35 24.34	47.64, N(CH <sub>3</sub> ) <sub>2</sub> 26.63, (CH <sub>2</sub> ) <sub>2</sub> ; 59.24, N(CH <sub>2</sub> ) <sub>2</sub>	
$(^{t}Bu_{3}SiO)_{2}TaCl_{2}(N(CH_{2})_{4}CH_{2})$ (4-pip)	1.34	1.04, m, CH <sub>2</sub> ; 1.45, m, (CH <sub>2</sub> ) <sub>2</sub> ; 4.17, m, N(CH <sub>2</sub> ) <sub>2</sub>	30.46	24.33	23.32, (CH <sub>2</sub> ); 25.57, (CH <sub>2</sub> ) <sub>2</sub> ; 56.86, N(CH <sub>2</sub> ) <sub>2</sub>	
$(^{t}Bu_{3}SiO)_{2}TaEt_{2}(N(CH_{2})_{3}CH_{2})$ (5-pyrr-Et <sub>2</sub> )	1.27	1.48, m, (CH <sub>2</sub> ) <sub>2</sub> ; 1.82, m, Et <sub>2</sub> ; 3.77, m, N(CH <sub>2</sub> ) <sub>2</sub>	30.80	23.79	10.84, CH <sub>2</sub> CH <sub>3</sub> , <i>J</i> <sub>CH</sub> = 127; 26.75, (CH <sub>2</sub> ) <sub>2</sub> ; 49.53, N(CH <sub>2</sub> ) <sub>2</sub> , <i>J</i> <sub>CH</sub> = 138; 63.38, TaCH <sub>2</sub> Me, <i>J</i> <sub>CH</sub> = 123	
$({}^{t}Bu_{3}SiO)_{2}TaMe_{2}(N(CH_{2})_{4}CH_{2}) {}^{a,b}$ (5-pip-Me <sub>2</sub> )	1.30	1.16, s, TaMe <sub>2</sub> ; 3.40, m, N(CH <sub>2</sub> ) <sub>2</sub>	30.77	23.85	24.86, (CH <sub>2</sub> ); 26.90, (CH <sub>2</sub> ) <sub>2</sub> ; 47.33, N(CH <sub>2</sub> ) <sub>2</sub> , $J_{CH} = 136$ ; 57.60, TaMe <sub>2</sub> , $J_{CH} = 121$	
$({}^{t}Bu_{3}SiO)_{2}Ta(\eta^{2}-C_{2}H_{4})(NC_{4}H_{8})$ (7-pyrr)	1.13	1.64, m, (CH <sub>2</sub> ) <sub>2</sub> ; 1.84, s, H <sub>2</sub> C=CH <sub>2</sub> ; 4.12, m, NCH <sub>2</sub> CH <sub>2</sub>	29.92	23.24	27.25, $(CH_2)_2$ ; 54.26, $H_2C=CH_2$ , $J_{CH} = 147$ ; 55.68, $N(CH_2)_2$	
$({}^{t}Bu_{3}SiO)_{2}Ta(\eta^{2}-C_{2}H_{4})(NC_{5}H_{10}) \ ^{b}$ (7-pip)	1.15	1.53, m, (CH <sub>2</sub> ) <sub>2</sub> ; 1.80, s, H <sub>2</sub> C=CH <sub>2</sub> ; 4.03, m, N(CH <sub>2</sub> ) <sub>2</sub>	29.99	23.32	25.77, CH <sub>2</sub> ; 29.02, (CH <sub>2</sub> ) <sub>2</sub> ; 55.08, H <sub>2</sub> C = CH <sub>2</sub> , J <sub>CH</sub> = 147; 56.07, N(CH <sub>2</sub> ) <sub>2</sub>	
( <sup>t</sup> Bu <sub>3</sub> SiO) <sub>2</sub> (H <sub>8</sub> C <sub>4</sub> N) <sup>T</sup> aCH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> <sup>'</sup> CH <sub>2</sub> <sup>c</sup> (8-pyrr)	1.21	1.56, m (CH <sub>2</sub> ) <sub>2</sub> ; 2.26, m, TaCH <sub>2</sub> ; 2.89, m, TaCH <sub>2</sub> CH <sub>2</sub> ; 3.90, m, N(CH <sub>2</sub> ) <sub>2</sub>	30.92	23.64	26.93, NCH <sub>2</sub> CH <sub>2</sub> ; 35.41, TaCH <sub>2</sub> CH <sub>2</sub> , J <sub>CH</sub> = 126; 53.27, N(CH <sub>2</sub> ) <sub>2</sub> ; 76.99, TaCH <sub>2</sub> , J <sub>CH</sub> = 116	
$({}^{t}Bu_{3}SiO)_{2}(CH(CH_{2})_{3}N)Ta(\eta^{2}-NC_{5}H_{5})$ (9-pyrr)	1.15, 1.19	1.55, m, NCH <sub>2</sub> CH <sub>2</sub> ; 3.69, d, TaCH, ${}^{3}J = 1.3$ ; 4.08, m, N(CH <sub>2</sub> ) <sub>2</sub> ; 5.36, t, TaNCHCH, $J = 6$ ; 5.83, ddt, TaNCHCHCH, $J = 6$ , 9, 1; 6.41, dm, TaCHCH, $J = 9$ ; 7.55 dm TaNCH $J = 6$	29.92, 30.02	23.18, 23.39	27.07, (CH <sub>2</sub> ) <sub>2</sub> ; 54.66, N(CH <sub>2</sub> ) <sub>2</sub> ; 76.03, TaCH; 109.01, TaNCHCH; 120.51, TaCHCHCH; 128.29, TaCHCH; 144.75, TaNCH	
$({}^{t}Bu_{3}SiO)_{2}(CH_{2}(CH_{2})_{4}N)Ta(\eta^{2}-NC_{5}H_{5})$ (9-pip)	1.17, 1.24	1.35–1.60, m, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ; 3.74, m, N(CH <sub>2</sub> ) <sub>2</sub> ; 3.90, d, TaCH, ${}^{3}J$ = 1.3; 5.43, t, TaNCHCH, J = 6; 5.87, ddt, TaNCHCHCH, J = 6, 9, 1; 6.39, dm, TaCHCH, J = 9; 7.54, dm, TaNCH, J = 6	29.98, 30.18	23.07, 23.53	25.01, CH <sub>2</sub> ; 28.59, (CH <sub>2</sub> ) <sub>2</sub> ; 54.03, N(CH <sub>2</sub> ) <sub>2</sub> ; 77.21, TaCH; 109.16, TaNCHCH; 121.46, TaCHCHCH; 126.94, TaCHCH; 145.19, TaNCH	
$(^{t}Bu_{3}SiO)_{2}(\overline{CH_{2}(CH_{2})_{3}}N)Ta=NMe$ (10-pyrr) $(^{t}Bu_{3}SiO)_{2}(\overline{CH_{2}(CH_{2})_{3}}N)Ta=NMe^{b}$ (10-pin)	1.25 1.28	1.49, m, (CH <sub>2</sub> ) <sub>2</sub> ; 3.85, m, N(CH <sub>2</sub> ) <sub>2</sub> ; 3.94, s, NCH <sub>3</sub> 1.48, m, (CH <sub>2</sub> ) <sub>2</sub> ; 3.75, m, N(CH) <sub>2</sub> ) <sub>2</sub> ; 3.88, s, NCH <sub>3</sub>	29.94	23.20	26.35, (CH <sub>2</sub> ) <sub>2</sub> ; 30.49, NCH <sub>3</sub> ; 48.49, N(CH <sub>2</sub> ) <sub>2</sub>	
$({}^{t}Bu_{3}SiO)_{2}Cen_{2}(cen_{2/4}, c)na$ (if pip) $({}^{t}Bu_{3}SiO)_{2}Ta(NMe)(NC_{5}H_{4})$ (11)	1.41	3.93, s, NCH <sub>3</sub> ; 6.48, ddd, TaNCHCH, $J = 7.6$ , 5.1, 1.1; 7.01, td, TaCCHCH, $J = 7.5$ , 1.2; 7.74, dt, TaCCH, J = 7.4, 1.3; 8.32, dt, TaNCH, $J = 5.1$ , 1.3	30.67	23.75	48.12, NCH <sub>3</sub> , $J_{CH} = 134$ ; 122.33, =CH-, $J_{CH} = 162$ ; 130.22, =CH-, $J_{CH} = 165$ ; 136.67, =CH-, $J_{CH} = 158$ ; 144.33, =CH-, $J_{CH} = 178$ ; 238.87, TaC	
$(^{t}Bu_{3}SiO)_{2}Ta=NMe(NHMe)$ (12)	1.27	3.47, d, HNC <i>H</i> <sub>3</sub> , <i>J</i> = 7; 3.98, s, =NCH <sub>3</sub> ; 4.58, br q, NH				
$(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$ ( <b>2</b> -3,5-Lut)	1.23	1.84, s, $(CH_3)_2$ ; 5.02, s, CH; 5.54, bs, $N(CH)_2$	31.45	24.35	20.86, CH <sub>3</sub> ; 120.71, N(CH) <sub>2</sub> , <i>v</i> <sub>1/2</sub> = 142 Hz; 126.78 NCHCMe: 127.19 NCHCMeCH	
(silox) <sub>2</sub> NbNCH=CMeCH=CHCMe <sub>2</sub> Si <sup>t</sup> Bu <sub>2</sub> O (14)	1.27	1.24, s, <sup>t</sup> Bu; 1.43, s, C(CH <sub>3</sub> ) <sub>2</sub> ; 1.66, s, C(CH <sub>3</sub> ); 2.01, s, C(CH <sub>3</sub> ); 5.54, s, CH; 6.12, d, <sup>t</sup> CH, $J = 16$ ; 6.86, d, <sup>t</sup> CH, $J = 16$ ; 7.03, s, NCH	30.94, 31.58	23.62, 24.12	21.10, CH <sub>3</sub> ; 21.95, CH <sub>3</sub> ; 26.73, (CH <sub>3</sub> ) <sub>2</sub> ; 32.96, $C(CH_3)_2$ ; 121.64, $C(CH_3)$ ; 127.09, CH; 130.63, CH; 134.32, $C(CH_3)$ ; 139.64, CH; 141.84, b, NC	

<sup>a</sup> (H<sub>2</sub>)<sub>2</sub> in <sup>1</sup>H NMR spectrum. <sup>b</sup> CH<sub>2</sub> obscured in <sup>1</sup>H NMR spectrum. <sup>c</sup> Assigned via homonuclear <sup>1</sup>H NMR decoupling, selective <sup>13</sup>C{<sup>1</sup>H} decoupling experiments, and comparison to related compounds.



115 °C), and afforded the ethylene adduct.  $(silox)_2(C_4H_8N)Ta(\eta^2-C_2H_4)$  (7-pyrr,  $\sim 80\%$ ) and  $C_2H_6$  (Eq. (4)) as the major products. A  ${}^{13}C{}^{1}H{}$ NMR spectrum of 7-pyrr revealed normal resonances for the siloxide and amide and a broad resonance assigned to the  $\eta^2$ -ethylene carbons at  $\delta$  54.26  $(^{1}J_{CH} = 147 \text{ Hz})$ . Related spectral features have been observed for  $(silox)_3Ta(\eta^2-C_2H_4)$  (e.g.  ${}^1J_{CH} = 143$  Hz) [31], which is considered to possess metallacyclopropane character. Perhaps 7-pyrr is generated via a β-abstraction path similar to that of the pyrrolidide dimethyl derivative of Eq. (3).

## 2.1.3. Reductions of $(silox)_2 TaCl_2 NR_2$

In an attempt to generate Ta(III) centers [12,15,32] capable of oxidatively adding a C-N bond, the chlorides were subjected to reductions. When treated with sodium amalgam in various solvents (THF, DME, toluene), or with cesium in benzene, the amides  $(silox)_2 Ta\underline{Cl_2NR_2}$   $(NR_2 = NMe_2, 4-Me_2; N(CH_2)_3CH_2,$ 4-pyrr;  $N(CH_2)_4CH_2$ , 4-pip) generated complex mixtures, and all attempts at purification and isolation were unsuccessful. Reductions with Na/Hg in the presence of H<sub>2</sub>, PMe<sub>3</sub>, or CO as trapping agents were similarly abortive. Treatment of (silox)<sub>2</sub>TaCl<sub>2</sub>(N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>) (4pyrr) and (silox)<sub>2</sub>TaCl<sub>2</sub>(N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>) (4-pip) with excess Na/Hg in the presence of 1 equiv. of ethylene generated 7-pyrr and  $({}^{t}Bu_{3}SiO)_{2}(C_{5}H_{10}N)Ta(\eta^{2}-C_{2}H_{4})$ (7-pip), respectively (Eq. (5)). NMR spectra of 7-pip showed characteristic signals for the siloxide and piperidide ligands in addition to the resonance of the coordinated ethylene at  $\delta$  1.80. Carbons signals at  $\delta$ 55.08 ( ${}^{1}J_{CH} = 147$  Hz) and  $\delta$  56.06 ( ${}^{1}J_{CH} = 135$  Hz) were assigned to the ethylene ligand and the amido  $\alpha$ methylene, respectively,

$$\begin{array}{ccccc} & xs \ Na/Hg \\ -2 \ NaCl \\ & -2 \$$

based on selective heteronuclear  ${}^{13}C{}^{1}H$  decoupling experiments. Thermolysis studies suggested that the ethylene ligands of these compounds are tightly bound. For example, thermolysis of a sample of 7-pyrr at 80 °C for 2 days and 115 °C for 17 h showed little change; free  $C_2H_4$  was not observed (<sup>1</sup>H NMR).

Reduction of  $(silox)_2 TaCl_2(\dot{N}(CH_2)_3\dot{C}H_2)$  (4-pyrr) under excess  $C_2H_4$  or exposure of  $(silox)_2$ - $(C_4H_8N)Ta(\eta^2-C_2H_4)$  (7-pyrr) to excess  $C_2H_4$  resulted in the formation of tantallacyclopentane (silox)<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>N) $TaCH_2(CH_2)_2CH_2$  (8-pyrr, Eq. (6)). Only a minor quantity of the analogous product was observed in the piperidide system. A combination of homonuclear



<sup>1</sup>H NMR decoupling experiments, selective  ${}^{13}C{}^{1}H$ heteronuclear decoupling experiments, and comparisons with related compounds permitted the spectral assignments for **8**-pyrr shown in Table 1. Note that **8**-pyrr is also likely to be fluxional since the metallacycle exhibits only two types of methylene resonances.

Thermolysis of  $(silox)_2(C_4H_8N)$ TaCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> (**8**pyrr) in sealed NMR tubes led to elimination of ethylene, yielding 7-pyrr (115 °C, 1 h, ~40% complete). These reactions were reversible and reverted to the coupled product upon standing at room temperature. Heating **8**-pyrr in refluxing toluene with flowing nitrogen atmosphere allowed isolation of 7-pyrr, although the product contained a substantial amount of unidentified impurities.

With 1 equiv. or excess pyridine, Na/Hg reduction of  $(silox)_2TaCl_2(N(CH_2)_3CH_2)$  (4-pyrr) and  $(silox)_2TaCl_2$ ( $N(CH_2)_4CH_2$ ) (4-pip) generated  $\eta^2$ -pyridine complexes  $(silox)_2(C_4H_8N)Ta(\eta^2-(N,C)-NC_5H_5)$  (9-pyrr, 81%) and  $(silox)_2(C_5H_{10}N)Ta(\eta^2-(N,C)-NC_5H_5)$  (9-pip, 82%; Eq. (7)). The NMR spectra of these compounds bear striking resemblance to the static, crystallographically characterized  $(silox)_3Ta(\eta^2-(N,C)-NC_5H_5)$  complex [31]. Thermolysis



of **9**-pyrr and **9**-pip in  $C_6D_6$  (130 °C, weeks) proceeded with loss of pyridine (<sup>1</sup>H NMR) and generation of intractable mixtures of unidentified siloxide containing species.

2.1.4. Degradation of  $\eta^2$ -py complexes with methylamine In HDN, nucleophilic attack has been proposed as one path toward C–N bond cleavage [1–8], hence degradation in the presence of a reasonably relevant nucleophile, MeNH<sub>2</sub>, was undertaken. Treatment of (silox)<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>N)Ta( $\eta^2$ -(N,C)–NC<sub>5</sub>H<sub>5</sub>) (**9**-pyrr) and (silox)<sub>2</sub>(C<sub>5</sub>H<sub>10</sub>N)Ta( $\eta^2$ -(N,C)–NC<sub>5</sub>H<sub>5</sub>) (**9**-pip)



with 1 equiv.  $CH_3NH_2$  in  $C_6D_6$  revealed the formation of tantalum imido derivatives  $(silox)_2(C_4H_8N)Ta=NMe$ (10-pyrr) and  $(silox)_2(C_5H_{10}N)Ta=NMe$  (10-pip, Eq. (8)), respectively. <sup>1</sup>H NMR spectra of these compounds revealed standard shifts for all the ligands, and a <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 10-pyrr corroborated its formulation.

The reactions with methyl amine proceeded with an initial release of secondary amine (piperidine or pyrrolidine) and H<sub>2</sub>, as shown in Scheme 1. One intermediate was cleanly observed during the course of the transformation, and <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra permitted its tentative identification as the  $\alpha$ -pyridyl-methylimido complex, (silox)<sub>2</sub>Ta(NMe)(NC<sub>5</sub>H<sub>4</sub>) (11), based in part on comparison with other  $\alpha$ -pyridyl compounds [33]. The relative rates of 9-pyrr and 9-pip were slightly different; 95% of the pyrrolidide is consumed after 1 week (23  $^{\circ}$ C) while only 66% of the piperidide is converted during the same time span, and a greater amount of 11 is detected in the former, presumably due to its greater rate of formation. Anoher product detected (<sup>1</sup>H NMR) in the 9-pip reaction was tentatively assigned as  $(silox)_2Ta =$ NMe(NHMe) (12), which may result from reaction of residual MeNH<sub>2</sub> with product 10-pip.

Treatment of  $(silox)_2(C_4H_8N)Ta(\eta^2-(N,C)-NC_5D_5)$ (9-pyrr-d<sub>5</sub>), generated by Na/Hg reduction of  $(si-lox)_2TaCl_2(N(CH_2)_3CH_2)$  (4-pyrr) under pyridine-d<sub>5</sub>, with methylamine yielded  $(silox)_2(C_4H_8N)Ta=NMe$ (10-pyrr), H<sub>2</sub> (δ 4.46), HD (δ 4.42, t, J<sub>HD</sub> = 43 Hz), and partially α-protio pyridine. Integration of the <sup>1</sup>H NMR showed a total of 38% H (50% for complete exchange in one site) in the α-positions of the free pyridine (0.76 H in one α-position). As shown in Scheme 1, several paths may account for this phenomenon. Initial transamination leads to a methylamidopyridine species that can undergo  $\alpha$ -activation of the py. Proton incorporation can be subsequently effected via 1,2-elimination to give an imido-hydride or the product via an intermediate that has reincorporated pyrrolidine. Since (silox)<sub>2</sub>Ta(NMe)(NC<sub>5</sub>D<sub>4</sub>) (11-d<sub>4</sub>) is observed, its formation via H<sub>2</sub> loss from the amidohydride  $\alpha$ -pyridyl species provides yet another means of H/D exchange. <sup>1</sup>H NMR spectral analysis of 11-d<sub>4</sub> shows little H incorporation into the TaNCH position ( $\delta$  8.32,  $\sim$  3% H). It is perhaps more puzzling that deuterium remains in  $\alpha$ -positions of the product, perhaps suggesting that there exists a more direct path from 9-pyrr to 10-pyrr that does not involve  $\alpha$ -pyridine activation.

## 2.2. A 3,5-lutidine adduct

2.2.1. Synthesis of  $(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$  (2-3,5-Lut)

While the above derivatives were prepared in the hope of observing model denitrogenation steps, no discrete C–N bond cleavage events could be identified. In contrast, the pyridine ring opening of  $(silox)_3Nb(\eta^2$ py) (**2**-py) and various related picoline derivatives has been observed [13,18,19], and it was noted that increasing steric bulk on the heterocycle apparently hampers a critical bimolecular step in the overall process. Seeking a labile source of  $(silox)_3Nb(2)$ , 3,5-lutidine was

$$({}^{\mathsf{YBu}_{3}\mathsf{SiO}})_{3}\mathsf{NbCI}_{2} \xrightarrow{\mathsf{xs Na/Hg}} {}^{\mathsf{ts Na/Hg}} \xrightarrow{\mathsf{-2 NaCl}} {}^{\mathsf{ts Na/Hg}} ({}^{\mathsf{tBu}_{3}\mathsf{SiO}})_{3}\mathsf{Nb} \xrightarrow{\mathsf{N}} {}^{\mathsf{Nb}} ({}^{\mathsf{tB}})_{3}\mathsf{SiO})_{3}\mathsf{Nb} \xrightarrow{\mathsf{N}} {}^{\mathsf{Nb}} ({}^{\mathsf{tB}})_{3}\mathsf{SiO})_{3}\mathsf{Nb} \xrightarrow{\mathsf{Nb}} {}^{\mathsf{Nb}} ({}^{\mathsf{Nb}})_{3}\mathsf{Nb} \xrightarrow{\mathsf{Nb}} ({}^{\mathsf{Nb}})_{3} ({$$

explored as a 'masking ligand' [19]. Treatment of  $(silox)_3NbCl_2$  (13) with sodium amalgam in the presence of excess 3,5-lutidine afforded  $(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$  (2-3,5-Lut) in 57% yield (Eq. (9)). A singlet was observed for the 3,5-dimethyl substituents, and a



Scheme 1.

broad singlet was attributed to the  $\alpha$ -hydrogens, signifying rapid shuttling between both N,C-bound forms, as was observed for the (silox)<sub>3</sub>Nb( $\eta^2$ -N,C-NC<sub>5</sub>H<sub>5</sub>) and various picoline derivatives [13,18].

## 2.2.2. Thermolysis of $(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$ (2-3,5-Lut)

Thermolysis of  $(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$  (2-3,5-Lut) for 4 days at 120 °C led to an unusual C–N bond activation product,  $(silox)_2NbN-cis$ -CH=CMe*cis*-CH=CMe-*trans*-CH=CHCMe\_2Si<sup>t</sup>Bu<sub>2</sub>O (14), involving CH-bond activation of the <sup>t</sup>Bu<sub>3</sub>SiO ligand, as shown in Eq. (10). Dihydrogen is a



presumed byproduct in the reaction, although Toepler pump measurements detected only 0.20 equiv. H<sub>2</sub> per mol of **14** formed. The reaction is remarkably clean (> 90%) according to monitoring by <sup>1</sup>H NMR spectroscopy, but **14** could only be isolated in 27% yield from hexanes due to its extreme solubility.

A mechanism for the complicated conversion of 2-3,5-Lut to 14 is given in Scheme 2, and some of its features show a commonality to aforementioned results.  $\alpha$ -Pyridyl formation [33] precedes cyclometallation [31,34] concomitant with loss of H<sub>2</sub>. A migratory insertion of the 'tucked-in' cyclometallated <sup>t</sup>Bu group leads to a substituted metallaziridine [15] that can  $\beta$ -H- eliminate, reinsert and undergo a retro 2+2 reaction to afford the imido cyclometallated product.

2.2.3. X-ray crystal structure of  $(silox)_2$ NbN-cis-CH=CMe-cis-CH=CMe-trans-CH=CHCMe\_2Si'Bu\_2O (14) Table 2 provides the crystallographic data for  $(silox)_2$ 

NbN-cis-CH=CMe-cis-CH=CMe-trans-CH=CHCMe<sub>2</sub>

Si<sup>t</sup>Bu<sub>2</sub>O (14), while Table 3 lists pertinent bond distances and angles. Fig. 1. shows that 3,5-lutidine ringopened product 14 is pseudo-tetrahedral, with O-Nb-O and N-Nb-O angles that average 110.7 (18) and 108.2  $(11)^{\circ}$ , respectively. The nearly linear ( $\angle Nb-N1-C1 =$ 171.6 (4)°) niobium imido functionality possesses a typical distance of 1.773 (5) Å [35], the niobium siloxide bond lengths (1.903 (10) Å (ave)) are normal, and the alternating single (d(N1-C1) = 1.396 (7) Å, d(C2-C1) = 1.396 (7) ÅC4 = 1.458 (9) Å, d(C5-C6) = 1.453 (13) Å, d(C9-C6)C8 = 1.532 (8) Å) and double (d(cis-C1-C2) = 1.359(7) Å, d(cis-C4-C5) = 1.303 (11) Å, d(trans-C6-C9) =1.269 (10) Å) bonds of the metallacycle are readily discerned. The siloxide containing the metallacycle (  $\angle$ Nb–O1–Si1 = 167.5 (2)°) cannot be distinguished from the remaining silox ligands (  $\angle Nb-O2-Si2 = 166.1 (2)^\circ$ ,  $\angle$  Nb-O3-Si3 = 167.1 (2)°) aside from its periphery.

## 3. Conclusions

Efforts to demonstrate carbon-nitrogen bond activation via the thermolysis of Ta(V) amidoalkyl derivatives failed, as did attempts to observe oxidative addition of amide C-N bonds via putative Ta(III) species. Instead,



Scheme 2.

Table 2

Crystal data	and s	structure	refinement	for	(silox) <sub>2</sub>
NbNCH=CMeC	CH=CMeCH	-CHCM	$e_2 Si^t Bu_2 O(14)$		
Empirical formu	ula		C43H88NO3Si3N	b	
Formula weight			844.32		
Temperature (K	L)		173(2)		
λ (Å)			0.71073		
Crystal system			monoclinic		
Space group			$P2_1/c$		
a (Å)			18.8098 (15)		
b (Å)			11.7518 (10)		
c (Å)			22.7705 (19)		
β (°)			100.672 (4)		
V (Å <sup>3</sup> )			4946.3 (7)		
Ζ			4		
Density (calc) (l	Mg m <sup><math>-3</math></sup> )		1.134		
Absorption coef	fficient (mm	<sup>-1</sup> )	0.350		
Crystal size (mr	n <sup>3</sup> )		$0.40 \times 0.20 \times 0.1$	.0	
Indices			$-18 \leq h \leq 18,$ –	$-11 \le k$	$\leq 10,$
			$-22 \le l \le 22$		
$\theta$ Range (°)			1.10 - 20.89		
Reflections			23 649		
Independent ref	lections		5185 ( $R_{\rm int} = 0.07$	(25)	
Data/restraints/	parameters		5185/0/488		
GOF <sup>a</sup>			1.009		
$R [I > 2\sigma(I)]^{b}$			$R_1 = 0.0484, wR$	$_2 = 0.10$	)30
R (all indices) <sup>b</sup>	,		$R_1 = 0.0830, wR$	$_2 = 0.11$	.69
Largest differen (e $Å^{-3}$ )	ce peak and	hole	0.348 and -0.27	78	

<sup>a</sup> GOF =  $[\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$ ; *n*, number of independent reflections; *p*, number of parameters.

evidence of  $\beta$ -H-abstractions in the former, and the preparation of olefin, metallacyclic and  $\eta^2$ -*N*-heterocyclic compounds in the latter instances proved to be the rule. An *N*-heterocyclic ring opening was again observed for Nb, but in this instance the C–N bond scission in 3,5-lutidine involved a cyclometallation of a silox ligand [31,34], rather than the dinuclear path evident in the ring openings of less hindered pyridine and picolines. The involvement of the silox ligand in the bond cleavage process sets a precedent for its involvement in (silox)<sub>3</sub>M(olefin)  $\rightarrow$ (silox)<sub>3</sub>M(alkylidene) rearrangements [36].

### 4. Experimental

## 4.1. General considerations

All manipulations were performed using either glovebox or high vacuum line techniques. All glassware was oven dried. THF and ether were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from the same prior to use. Hydrocarbon solvents were treated in the same manner with the addition of  $1-2 \text{ ml } 1^{-1}$  tetraglyme. Benzene-d<sub>6</sub> was dried over sodium and activated 4 Å molecular sieves, vacuum transferred, and stored under nitrogen. Pyridine and pyridine-d<sub>5</sub> were dried over activated 4 Å molecular sieves and vacuum transferred before use. THF-d<sub>8</sub> was dried over sodium and vacuum transferred from sodium benzophenone ketyl prior to use. Ethylene (Matheson) was passed through a trap at -78 °C before use. Primary and secondary amines were purchased from Aldrich and dried over activated 4 Å sieves. Lithium amides were generated from the amine and "BuLi (Aldrich) and crystallized prior to use. Grignard solutions were purchased from Aldrich. (silox)<sub>2</sub>TaCl<sub>3</sub> (3)

Table 3

Selected interatomic distances (Å) and angles (°) for (silox)<sub>2</sub>NbNCH=CMeCH=CMeCH=CHCMe<sub>2</sub>Si<sup>1</sup>Bu<sub>2</sub>O (14) <sup>a</sup>

Bond lengths					
Nb-N	1.773 (5)	N-C1	1.396 (7)	C5-C6	1.453 (13)
Nb-O1	1.912 (3)	C1-C2	1.359 (8)	C6-C9	1.269 (10)
Nb-O2	1.892 (3)	C2-C3	1.501 (8)	C5A-C6A	1.51 (2)
Nb-O3	1.906 (4)	C2-C4	1.458 (9)	C5A-C7A	1.55 (2)
Si1-O1	1.665 (4)	C4-C5	1.303 (11)	C6A-C33	1.640 (18)
Si2-O2	1.658 (3)	C4-C5A	1.26 (2)	C9-C8	1.532 (8)
Si3-O3	1.653 (4)	C5-C7	1.523 (13)	Si-C(ave)	1.915 (10)
C-C(ave)	1.540 (12)				
Bond angles					
N-Nb-O1	109.14 (18)	O1-Nb-O2	109.52 (14)	Nb-O1-Si1	167.5 (2)
N-Nb-O2	106.96 (17)	O1-Nb-O3	112.73 (15)	Nb-O2-Si2	166.1 (2)
N-Nb-O3	108.48 (19)	O2-Nb-O3	109.84 (14)	Nb-O3-Si3	167.1 (2)
Nb-N-C1	171.6 (4)	C1-C2-C4	127.0 (10)	C4-C5-C6	122.6 (9)
N-C1-C2	128.6 (6)	C3-C2-C4	115.6 (6)	C4-C5-C7	120.1 (9)
C1-C2-C3	117.5 (6)	C2-C4-C5	128.6 (7)	C6-C5-C7	117.2 (10)
C5-C6-C9	133.4 (9)	C6-C9-C8	128.2 (7)	C4-C5A-C6A	121.3 (15)
C4-C5A-C7A	122.1 (16)	C6A-C5A-C7A	116.0 (18)	C5A-C6A-C33	116.2 (14)
O-Si-C(ave)	106.3 (11)	C-Si-C(ave)	112.4 (9)	Si-C-C(ave)	111.3 (16)
C-C-C(ave)	107.5 (12)				

<sup>a</sup> Disorder as described in experimental; both models included.



Fig. 1. Molecular view of (silox)<sub>2</sub>NbNCH=CMeCH=CMeCH=CHCMe<sub>2</sub>Si<sup>t</sup>Bu<sub>2</sub>O (14).

and  $(silox)_3NbCl_2$  (13) were prepared following published procedures [26].

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained on Varian XL-200 and XL-400 spectrometers. Chemical shifts are reported relative to benzene-d<sub>6</sub> (<sup>1</sup>H,  $\delta$  7.15; <sup>13</sup>C{<sup>1</sup>H},  $\delta$  128.00. IR spectra were recorded on a Mattson FT IR, Perkin–Elmer 299B grating IR, or PE 377 grating IR. Combustion analyses were performed by Oneida Research Services (Whitesboro, NY), Robertson Microlit Laboratories (Madison, NJ), or Texas Analytical (Houston, TX).

## 4.2. Synthesis

## 4.2.1. $(silox)_2 TaCl_2 NMe_2$ (4-Me<sub>2</sub>)

A 100 ml flask was charged with  $(silox)_2 TaCl_3$  (3, 0.500 g, 0.696 mmol) and fitted with a sidearm containing lithium dimethylamide (0.035 g, 0.686 mmol). THF (60 ml) and a catalytic amount of dimethylamine (~0.05 equiv.) were added to the flask in vacuo at -78 °C. The solution was warmed to 23 °C and stirred. Slow addition of the lithium amide generated a yellow color in the solution. After stirring for 24 h, the volatiles were removed and the solid residue was extracted with

hexane. The solution was filtered, concentrated, and cooled causing a white solid to precipitate. Recrystallization from hexane netted 241 mg **4**-Me<sub>2</sub> (48%). IR (Nujol, cm<sup>-1</sup>) 1465 (s), 1375 (s), 1265 (m), 1180 (w), 1135 (m), 1050 (m), 1010 (m), 930 (s), 860 (br, s), 815 (s), 625 (s). *Anal.* Calc. for TaSi<sub>2</sub>NCl<sub>2</sub>O<sub>2</sub>C<sub>26</sub>H<sub>60</sub>: C, 42.97; H, 8.32; N, 1.93. Found: C, 42.97; H, 8.12; N, 1.91%.

## 4.2.2. $(silox)_2 TaCl_2(\dot{N}(CH_2)_3\dot{C}H_2)$ (4-pyrr)

A 250 ml flask was charged with **3** (1.705 g, 2.374 mmol) and fitted with a solid addition tube containing lithium pyrrolidide (0.185 g, 2.401 mmol). The flask was attached to a 180° needle valve and evacuated. A catalytic quantity of pyrrolidine (~0.1 equiv.) was condensed into the flask at -78 °C followed by THF (70 ml). Warming to 23 °C resulted in an orange/yellow solution. The lithium pyrrolidide was added slowly to the stirred solution, which became bright yellow. After stirring for 4 h, the volatiles were removed and the solids were extracted with hexane, the solution was filtered and the salts were washed repeatedly until the washings were colorless. The hexane solution was concentrated to 5 ml and cooled to -78 °C, yielding 1.556 g of **4**-pyrr (87%)

as pale yellow crystals. IR (Nujol, cm<sup>-1</sup>) 1475 (s), 1375 (m), 1340 (m), 1180 (w), 1045 (m), 1010 (w), 940 (s), 865 (br, s), 820 (s), 625 (s). *Anal.* Calc. for TaCl<sub>2</sub>Si<sub>2</sub>-NO<sub>2</sub>C<sub>28</sub>H<sub>62</sub>: C, 44.67; H, 8.30; N, 1.86. Found: C, 44.85; H, 8.48; N, 1.67%.

## 4.2.3. $(silox)_2 TaCl_2(\dot{N}(CH_2)_4 CH_2)$ (4-pip)

Into a 250 ml flask was placed 3 (1.968 g, 2.740 mmol). A solid addition tube containing lithium piperidide (0.250 g, 2.745 mmol) was attached to the flask. THF (90 ml) and a small amount of piperidine ( $\sim 0.1$ equiv.) were added via vacuum transfer at -78 °C. The flask was warmed to 23 °C and the lithium amide was added to the solution over 30 min generating a bright yellow color. After stirring for 6 h the volatiles were removed. Hexane was added and the solid residue was extracted repeatedly until no yellow color remained in the salts. The hexane solution was concentrated to 8 ml and cooled to -78 °C, yielding a copious mass of pale yellow crystals that were collected by filtration and washed once with cold hexane (1.694 g). A second crop of 4-pip was obtained (0.215 g, 91% total). IR (Nujol, cm<sup>-1</sup>) 1475 (s), 1375 (m), 1270 (w), 1190 (m), 1145 (m), 1085 (m), 1050 (m), 1035 (w), 1010 (m), 955 (s), 920-800 (br, s), 625 (s). Anal. Calc. for TaSi2NCl2O2C29H64: C, 45.42; H, 8.41; N, 1.83. Found: C, 45.40; H, 8.44; N, 1.53%.

## 4.2.4. $(silox)_2(C_4H_8N)TaEt_2$ (5-pyrr-Et<sub>2</sub>)

A 100 ml flask was charged with 4-pyrr (0.813 g, 1.080 mmol) and attached to a  $180^{\circ}$  needle valve. The flask was evacuated and Et<sub>2</sub>O (50 ml) was added at -78 °C in vacuo. Against a counterflow of argon, EtMgCl (1.18 ml, 2.0 M in Et<sub>2</sub>O, 2.36 mmol, 2.2 equiv.) was added via syringe to the cold solution. The solution was degassed, warmed, and stirred. The initial pale vellow color faded over 1 h as the solution became turbid, and stirring was maintained for an additional 15 h. The volatiles were removed and the resulting white solid was extracted into hexane and filtered. The salts were washed several times with hexane. The hexane solution was concentrated and cooled to -78 °C, affording 0.637 g (80%) colorless microcrystals of 5-pyrr-Et<sub>2</sub>. IR (Nujol,  $cm^{-1}$ ) 1470 (s), 1375 (s), 1335 (m), 1290 (w), 1250 (br, w), 1200 (br, w), 1180 (br, w), 1165 (br, w), 1105 (w), 1070 (m), 1045 (m), 1010 (w), 990 (m), 920 (br, s), 860 (br, s), 820 (s), 620 (s). Anal. Calc. for TaSi<sub>2</sub>NO<sub>2</sub>C<sub>32</sub>H<sub>72</sub>: C, 51.94; H, 9.81; N, 1.89. Found: C, 52.31; H, 10.38; N, 1.82%.

## 4.2.5. $(silox)_2(C_5H_{10}N)TaMe_2(5-pip-Me_2)$

A 250 ml flask was charged with 4-pip (0.808 g, 1.054 mmol) and fitted with a septum. The flask was evacuated and Et<sub>2</sub>O (100 ml) was added at -78 °C. The solution was warmed to 23 °C while stirred. Argon was admitted to the assembly and MeMgBr (0.77 ml, 3.0 M in Et<sub>2</sub>O, 2.31 mmol, 2.2 equiv.) was added via

syringe. A white precipitate was observed after 1 h and stirring continued for 24 h. The volatiles were removed in vacuo and the solid residue was triturated with hexane. Extraction of the residue with hexane and filtration gave a solution which was cooled to -78 °C to afford 0.584 g colorless microcrystals of 5-pip-Me<sub>2</sub>. A second crop was obtained (0.092 g, 88% total). IR (Nujol, cm<sup>-1</sup>) 1465 (s), 1375 (s), 1315 (w), 1280 (w), 1190 (w), 1150 (m), 1090 (m), 1050 (w), 1040 (m), 1025 (w), 1010 (w), 955 (w), 920 (s), 930-800 (br, s), 720 (m), 620 (s). *Anal.* Calc. for TaSi<sub>2</sub>NO<sub>2</sub>C<sub>31</sub>H<sub>70</sub>: C, 51.29; H, 9.72; N, 1.93. Found: C, 50.90; H, 10.10; N, 1.78%.

## 4.2.6. $(silox)_2(C_4H_8N)Ta(\eta^2-C_2H_4)$ (7-pyrr)

4.2.6.1. From 4-pyrr. Into a 100 ml flask were placed 4pyrr (1.589 g, 2.111 mmol) and Na/Hg (0.194 g Na, 21.36 g Hg, 8.438 mmol, 4 equiv.). The flask was attached to a gas bulb and evacuated. DME (50 ml) was added at -78 °C. The solution was warmed and exposed to ethylene (137 Torr in 287.8 ml, 2.151 mmol, 1.02 equiv.). The purple color that formed initially faded to brown then yellow over 5 h, and the solution was stirred for an additional 2 h. The volatiles were removed, and the amalgam was decanted from the solid. The solids were extracted with hexane and filtered. Removal of the hexane in vacuo gave a yellow crystalline material that was >95% pure by <sup>1</sup>H NMR spectral assay.

4.2.6.2. Synthesis from 5-pyrr-Et<sub>2</sub>. A 100 ml flask was charged with 5-pyrr-Et<sub>2</sub> (0.501 g, 0.677 mmol) and attached to a reflux condenser on a 180° needle valve. The apparatus was evacuated and toluene (30 ml) was added via vacuum transfer. Argon was admitted and the solution was refluxed for a total of 15 h. The solution was cooled and the volatiles were removed. The solid was extracted into hexane, and the solution was filtered and concentrated to 5 ml, affording 246 mg of yellow microcrystalline 5-pyrr-Et<sub>2</sub> (51%, >95% pure by  $^{1}$ H NMR assay) upon cooling to -78 °C. Analytically pure samples were obtained upon recrystallization. IR (Nujol, cm<sup>-1</sup>) 1475 (m), 1375 (m), 1345 (w), 1115 (w), 1065 (w), 1035 (w), 990 (m), 955 (m), 915 (br, s), 820 (s), 670 (w), 625 (s). Anal. Calc. for TaSi<sub>2</sub>NO<sub>2</sub>C<sub>30</sub>H<sub>66</sub>: C, 50.75; H, 9.37; N, 1.97. Found: C, 50.69; H, 9.48; N, 1.67%.

## 4.2.7. $(silox)_2(C_5H_{10}N)Ta(\eta^2-C_2H_4)$ (7-pip)

A 50 ml flask was charged with 4-pip (1.028 g, 1.341 mmol) and Na/Hg (0.125 g Na, 13.52 g Hg, 5.437 mmol, 4 equiv.). DME (20 ml) was added at -78 °C followed by an excess of ethylene (~700 Torr). The solution was warmed to 23 °C and stirred. The initial purple color faded to yellow within 1 h and the solution was stirred for an additional 1.5 h. The volatiles were removed, and the solid was extracted into hexane and filtered. The

hexane was removed and Et<sub>2</sub>O was added. Concentration and cooling of the solution produced yellow crystals of 7-pip, which were isolated by filtration (0.422 g, 44%). IR (Nujol, cm<sup>-1</sup>) 1475 (m), 1375 (m), 1305 (w), 1270 (w), 1255 (w), 1205 (m), 1150 (m), 1110 (m), 1060 (m), 1030 (m), 1010 (w), 975 (s), 910 (br, s), 875 (m), 855 (m), 820 (s), 670 (w), 630 (s). *Anal.* Calc. for TaSi<sub>2</sub>NO<sub>2</sub>C<sub>31</sub>H<sub>68</sub>: C, 51.43; H, 9.47; N, 1.93. Found: C, 51.24; H, 9.57; N, 1.65%.

4.2.8.  $(silox)_2(C_4H_8N)$ <sup> $TaCH_2(CH_2)_2$ <sup> $CH_2$ </sup> (8-pyrr)</sup>

A 100 ml flask was charged with 4-pyrr (0.498 g, 0.661 mmol) and Na/Hg (0.061 g Na, 9.69 g Hg, 2.653 mmol, 4 equiv.). DME (50 ml) was added at -78 °C and 570 Torr of ethylene was admitted. The solution turned deep purple as it was warmed to 23 °C over 5 min. The purple faded and was replaced by a bright yellow color within 1 h. After the solution was stirred for a total of 24 h, the volatiles were removed and the residue was triturated once with hexane. The solid was extracted into hexane and filtered. The salts were washed twice and the hexane solution was concentrated to 3 ml. Cooling to -78 °C and filtration yielded an off white powder (0.303 g). <sup>1</sup>H NMR showed the solid consisted of ~15% (silox)<sub>2</sub>Ta( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(NC<sub>4</sub>H<sub>8</sub>). Prolonged exposure of this material to an atmosphere of C<sub>2</sub>H<sub>4</sub> in hexane solution followed by recrystallization gave 8pyrr in >95% purity according to <sup>1</sup>H NMR spectroscopy. IR (Nujol, cm<sup>-1</sup>) 1465 (s), 1375 (s), 1330 (m), 1310 (w), 1285 (w), 1240 (w), 1185 (br, w), 1105 (m), 1080 (w), 1065 (w), 1030 (m), 1010 (m), 980-850 (br, s), 815 (s), 720 (m), 620 (s). Anal. Calc. for TaSi<sub>2</sub>-NO<sub>2</sub>C<sub>32</sub>H<sub>70</sub>: C, 52.08; H, 9.56; N, 1.90. Found: C, 52.66; H, 9.76; N, 1.64%.

4.2.9.  $(silox)_2(C_4H_8N)Ta(\eta^2-(N,C)-NC_5H_5)$  (9pyrr)

A 100 ml flask was charged with 4-pyrr (0.945 g, 1.255 mmol) and Na/Hg (0.125 g Na, 14.33 g Hg, 5.437 mmol, 4.3 equiv.). The flask was evacuated and DME (50 ml) was added via vacuum transfer at -78 °C. An argon atmosphere was admitted to the apparatus and pyridine (1.01 ml, 12.54 mmol, 10 equiv.) was syringed into the cold solution. As the solution was warmed a dark green color was observed. This color faded over 5 h as the solution took on a yellow/orange hue. The volatiles were then removed, the amalgam was decanted from the flask and the remaining solids were slurried with hexane. The solution was filtered and the salts were washed with hexane until the washings were colorless. The amber hexane solution was concentrated and cooled to -78 °C, and yellow crystals were collected by filtration (0.770 g, 81%). IR (Nujol, cm<sup>-1</sup>) 1590 (w), 1510 (w), 1475 (s), 1420 (w), 1375 (m), 1330 (m), 1290 (w), 1240 (s), 1135 (m), 1105 (w), 1080 (w), 1035 (m), 1000 (w), 985 (s), 960-880 (br, s),820 (s), 710 (s), 625 (s). Anal. Calc. for  $TaSi_2N_2O_2C_{33}H_{67}$ : C, 52.08; H, 8.87; N, 3.68. Found: C, 51.87; H, 8.96; N, 3.63%.

## 4.2.10. $(silox)_2(C_5H_{10}N)Ta(\eta^2-(N,C)-NC_5H_5)$ (9pip)

Into a 25 ml flask were placed 4-pip (0.611 g, 0.797 mmol) and a portion of Na/Hg (0.077 g Na, 8.05 g Hg, 3.349 mmol, 4.2 equiv.). DME (15 ml) and excess pyridine were added via vacuum transfer at -78 °C. The solution was warmed and stirred for 18 h. After removal of the volatiles, the solids were triturated twice with hexane. Extraction of the solid residue and filtration gave an amber solution that was concentrated and cooled  $(-78 \ ^{\circ}C)$  to afford yellow crystals (0.192 g). Two additional crops were acquired in the same manner (0.316 g, 82% total). IR (Nujol, cm<sup>-1</sup>) 1500 (w), 1475 (s), 1375 (m), 1310 (w), 1235 (s), 1195 (w), 1150 (w), 1130 (w), 1095 (w), 1030 (w), 1025 (m), 1005 (m), 970-860 (br, s), 855 (w), 820 (s), 715 (s), 625 (s). Anal. Calc. for TaSi<sub>2</sub>N<sub>2</sub>O<sub>2</sub>C<sub>34</sub>H<sub>69</sub>: C, 52.69; H, 8.97; N, 3.61. Found: C, 51.80; H, 9.01; N, 3.31%.

4.2.11.  $(silox)_3Nb(\eta^2-3,5-Me_2-NC_5H_3)$  (2-3,5-Lut)

A 50 ml flask charged with (silox)<sub>3</sub>NbCl<sub>2</sub> (**13**, 500 mg, 0.617 mmol) and 2.5 equiv. Na/Hg (3.74 g, 0.95% Na). The system was evacuated and 3,5-lutidene (3 ml) was condensed from a measuring finger, followed by 30 ml of THF. Upon warming, the solution turned purple, and after stirring for 12 h it became brown. The volatiles were stripped and the residue was triturated with hexanes (3 × 10 ml). The residue was taken up in hexanes and filtered. The hexanes were removed and the solid was dissolved in ether and cooled to -78 °C, affording 290 mg (57%) of **2**-3,5-Lut as burgundy microcrystals. *Anal.* Calc. for NbSi<sub>3</sub>O<sub>3</sub>NC<sub>43</sub>H<sub>90</sub>: C, 61.02; H, 10.72; N, 1.65. Found: C, 60.70; H, 10.57; N, 1.38%.

4.2.12.  $(silox)_2$ 

## $\dot{N}bNCH=CMeCH=CMeCH=CHCMe_2Si^{t}Bu_2O^{\prime}$ (14)

A 50 ml bomb reactor was charged with 2-3,5-Lut (272 mg, 0.321 mmol) and 10 ml cyclohexane, then evacuated. The vessel was heated at 120 °C for 2.5 days. Toepler pump analysis of the system revealed 0.057 mmol of a combustible gas, presumed to be H<sub>2</sub>. This was 20% of the expected amount based on a 72% conversion to 14 according to <sup>1</sup>H NMR analysis. The bomb reactor was again charged with cyclohexane and the reaction mixture was heated at 120 °C for an additional 1.5 days. All volatiles were removed, leaving a brown oil that was triturated with pentane (3 × 5 ml). The residue was then taken up in hexanes (2 ml) and after slow evaporation in a small vial, 75 mg of yellow, microcrystalline 14 was obtained (27%). *Anal.* Calc. for

NbSi<sub>3</sub>O<sub>3</sub>NC<sub>43</sub>H<sub>88</sub>: C, 59.75; H, 10.51. Found: C, 59.77; H, 10.76%.

## 4.3. NMR tube reactions

#### 4.3.1. 9-Pyrr and MeNH<sub>2</sub>

A sample of **9**-pyrr (0.014 g, 0.018 mmol) was placed in an NMR tube sealed to a 14/20 joint. The tube was attached to a gas bulb and evacuated.  $C_6D_6$  (0.6 ml) was added in vacuo at 77 K followed by MeNH<sub>2</sub> (27.5 Torr in 12.3 ml, 0.018 mmol). The tube was flame sealed under dynamic vacuum and warmed to 25 °C. After ~12 h the <sup>1</sup>H NMR of the solution revealed pyridine ( $\delta$ 6.65, 6.97, 8.52), pyrrolidine ( $\delta$  2.64, NCH<sub>2</sub>;  $\delta$  1.38, NCH<sub>2</sub>CH<sub>2</sub>), H<sub>2</sub> ( $\delta$  4.46), **9**-pyrr (~30%), intermediate  $\alpha$ -pyridyl (silox)<sub>2</sub>Ta(NMe)(NC<sub>5</sub>H<sub>4</sub>) (**11**) (~48%), and methyl imido pyrrolidide **10**-pyrr (22%). By 1 week, the starting material was almost completely consumed (~5% remaining). The conversion to **10**-pyrr was ~90% complete after 16 days.

#### 4.4. 9-Pip and $MeNH_2$

An NMR tube attached to a 14/20 joint was charged with 9-pip (0.014 g, 0.018 mmol) and attached to a gas bulb. The tube was evacuated and  $C_6D_6$  (0.6 ml) followed by MeNH<sub>2</sub> (27.0 Torr in 12.3 ml, 0.018 mmol) were added in vacuo at 77 K. The tube was flame sealed and warmed to 25 °C. After 5 days, the reaction mixture was comprised of pyridine, piperidine, H<sub>2</sub>, starting material (~41%), intermediate **11** (~9%), product **10**-pip (~34%), and a product tentatively assigned as methyl imido methyl amido (silox)<sub>2</sub>Ta= NMe(NH(Me) (**12**, 16%).

## 4.4.1. 9-Pyrr- $d_5$ and MeNH<sub>2</sub>

A 10 ml flask was charged with 4-pyrr (0.035 g, 0.046 mmol) and sodium amalgam (0.005 g Na, 0.217 mmol, 5 equiv.). DME was added at -78 °C followed by excess pyridine-d<sub>5</sub>. The solution was warmed and stirred for 6 h. After removal of the volatiles, the residue was triturated three times with hexane and filtered. Removal of the volatiles yielded a yellow crystalline material (> 95% pure by <sup>1</sup>H NMR). This material (0.016 g, 0.021 mmol) was taken up in C<sub>6</sub>D<sub>6</sub> (0.6 ml) and transferred to an NMR tube attached to a 14/20 joint. The tube was attached to a gas bulb and the solution was freeze/pump/ thaw degassed three times. MeNH<sub>2</sub> (31.1 Torr in 12.3 ml, 0.021 mmol) was added at 77 K and the tube was sealed with a torch. The solution was warmed and allowed to stand for ~3 weeks.

## 4.5. Physical studies

## 4.5.1. X-ray crystal structure determination of (silox)<sub>2</sub> NbN-CH=CMeCH=CMeCH=CHCMe<sub>2</sub>Si<sup>t</sup>Bu<sub>2</sub>O (14)

Yellow crystals of 14 were grown from a slow evaporation of a concentrated solution in pentane. The crystals were isolated and covered in iso butylene. A suitable crystal was placed under a 173 °C N<sub>2</sub> stream on the goniometer head of a Siemens SMART CCD Area Detector system equipped with fine-focus molybdenum X-ray tube (Table 2). The crystal system was monoclinic and the space group was  $P2_1/c$ . An empirical correction for absorption (SADABS) was applied to the data. The structure was solved by direct methods (SHELXS), and the refinement was by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were anisotropically refined and hydrogen atoms were treated as idealized contributions. Atoms C5, C6 and C7 are disordered. Switching to space group  $P2_1$  did not relieve the disorder hence it was presumed to be intrinsic to the compound. The arm of the N-containing fragment can be attached between C4 and C9 (C5, C6 and C7) or between C4 and C33 (C5A, C6A and C7A). The occupancies are 60% for the former and 40% for the latter.

#### Acknowledgements

The National Science Foundation (CHE-9816134) and Cornell University are gratefully acknowledged.

#### References

- [1] R. Prins, Adv. Catalysis 46 (2002) 399.
- [2] (a) T.C. Ho, Catal. Rev. Sci. Eng. 30 (1988) 117;
  (b) C.N. Satterfield, Heterogenous Catalysis in Industrial Practice, McGraw-Hill, New York, 1991;
  (c) J.R. Katzer, R. Sivasubramanian, Catal. Rev. Sci. Eng. 20 (1979) 155.
- [3] C. Bianchini, A. Meli, F. Vizza, Eur. J. Inorg. Chem. 1 (2001) 43.
- [4] R. Prins, M. Jian, M. Flechsenhar, Polyhedron 16 (1997) 3235.
- [5] K.J. Weller, P.A. Fox, S.D. Gray, D.E. Wigley, Polyhedron 16 (1997) 3139.
- [6] R.J. Angelici, Polyhedron 16 (1997) 3073.
- [7] R.M. Laine, Catal. Rev. Sci. Eng. 25 (1983) 459.
- [8] (a) V. Schwartz, V.T. da Silva, S.T. Oyama, J. Mol. Catal., A Chem. 163 (2000) 251;
  (b) J.A. Marzari, S. Rajagopal, R. Miranda, J. Catal. 156 (1995) 255.
- [9] For η<sup>2</sup>-pyridines, see: (a) K.J. Covert, D.R. Neithamer, M. Zonnevylle, R.E. LaPointe, C.P. Schaller, P.T. Wolczanski, Inorg. Chem. 30 (1991) 2494;
  (b) D.P. Smith, J.R. Strickler, S.D. Gray, M.A. Bruck, R.S. Holmes, D.E. Wigley, Organometallics 11 (1992) 1275;
  (c) J.R. Strickler, M.A. Bruck, D.E. Wigley, J. Am. Chem. Soc. 112 (1990) 2814.
- [10] For η<sup>6</sup>-pyridines, see: (a) S.G. Davies, M.R. Shipton, J. Chem. Soc., Chem. Commun. (1989) 995;
  (b) B. Chaudret, F.A. Jalon, J. Chem. Soc., Chem. Commun.

(1988) 711;

- (c) E.J. Wucherer, E.L. Muetterties, Organometallics 6 (1987) 1691;
- (d) K. Dimroth, R. Thamm, H. Kaletsch, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 207;
- (e) R.E. Schmidt, W. Massa, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 39B (1984) 213.
- [11] K.D. Allen, M.A. Bruck, S.D. Gray, R.P. Kingsborough, D.P. Smith, K.J. Weller, D.E. Wigley, Polyhedron 14 (1995) 3315.
- [12] J.B. Bonanno, T.P. Henry, D.R. Neithamer, P.T. Wolczanski, E.B. Lobkovsky, J. Am. Chem. Soc. 118 (1996) 5132.
- [13] T.S. Kleckley, J.L. Bennett, P.T. Wolczanski, E.B. Lobkovsky, J. Am. Chem. Soc. 119 (1997) 247.
- [14] (a) M.H. Chisholm, K. Folting, J.C. Huffman, J. Leonelli, N.S. Marchant, C.A. Smith, L.C.E. Taylor, J. Am. Chem. Soc. 107 (1985) 3722;
  (b) K.J. Ahmed, M.H. Chisholm, K. Folting, J.C. Huffman, J.

Chem. Soc., Chem. Commun. (1985) 152.

- [15] (a) S.D. Gray, K.J. Weller, M.A. Bruck, P.M. Briggs, D.E. Wigley, J. Am. Chem. Soc. 117 (1995) 10678;
  (b) K.J. Weller, S.D. Gray, P.M. Briggs, D.E. Wigley, Organometallics 14 (1995) 5588;
  (c) K.J. Weller, I. Filippov, P.M. Briggs, D.E. Wigley, J. Organomet. Chem. 528 (1997) 225.
- [16] (a) M. Tayebani, S. Gambarotta, G.P.A. Yap, Ang. Chem., Int. Ed. Engl. 37 (1998) 3002;
  (b) M. Tayebani, H. Feghali, S. Gambarotta, C. Bensimon,
  - Organometallics 16 (1997) 5084.
- [17] M. Gandelman, D. Milstein, J. Chem. Soc., Chem. Commun. (2000) 1603.
- [18] T.S. Kleckley, Ph.D. thesis, Cornell University, 1998.
- [19] A.S. Veige, T.S. Kleckley, R.L.M. Chamberlin, D.R. Neithamer, C.E. Lee, P.T. Wolczanski, E.B. Lobkovsky, W.V. Glassey, J. Organomet. Chem. 591 (1999) 194.
- [20] S.W. Schweiger, D.L. Tillison, M.G. Thorn, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2001) 2401.
- [21] (a) P.A. Fox, S.D. Gray, M.A. Bruck, D.E. Wigley, Inorg. Chem. 35 (1996) 6027;

(b) P.A. Fox, M.A. Bruck, S.D. Gray, N.E. Gruhn, C. Grittini, D.E. Wigley, Organometallics 17 (1998) 2720.

- [22] (a) M. Egorova, Y. Zhao, P. Kukula, R. Prins, J. Catal. 206 (2002) 263;
- (b) F. Rota, V.S. Ranade, R. Prins, J. Catal. 200 (2001) 389.
- [23] D.A. Vicic, W.D. Jones, Organometallics 18 (1999) 134.
- [24] S.E. Kabir, D.S. Kolwaite, E. Rosenberg, Organometallics 15 (1996) 1979.

- [25] E. Rosenberg, S.E. Kabir, K.I. Hardcastle, M. Day, E. Wolf, Organometallics 9 (1990) 2214 (and references therein).
- [26] R.E. LaPointe, P.T. Wolczanski, G.E. Van Duyne, Organometallics 4 (1985) 1810.
- [27] Caution: related procedures (cf. Ta(NMe<sub>2</sub>)<sub>5</sub>; D.C. Bradley, I.M. Thomas, Can. J. Chem. 40 (1962) 1355) without amine present have resulted in a highly explosive powder (presumably unreacted LiNR<sub>2</sub>) upon work-up.
- [28] S.A. Strazisar, P.T. Wolczanski, J. Am. Chem. Soc. 124 (2001) 4728.
- [29] S.W. Schweiger, M.M. Salberg, A.L. Pulvirenti, E.E. Freeman, P.E. Fanwick, I.P. Rothwell, J. Chem. Soc., Dalton Trans. (2001) 2020.
- [30] M. Brookhart, M.L.H. Green, L. Wong, Prog. Inorg. Chem. 36 (1988) 1.
- [31] (a) K.J. Covert, D.R. Neithamer, M.C. Zonnevylle, R.E. La-Pointe, C.P. Schaller, P.T. Wolczanski, Inorg. Chem. 30 (1991) 2494;
  (b) D.R. Neithamer, L. Párkányi, J.F. Mitchell, P.T. Wolczanski,

J. Am. Chem. Soc. 110 (1988) 4421.

- [32] D.S.J. Arney, P.A. Fox, M.A. Bruck, D.E. Wigley, Organometallics 16 (1997) 3421.
- [33] For examples of  $\alpha$ -pyridyl complexes, see: (a) S. Dagorne, S. Rodewald, R.F. Jordan, Organometallics 16 (1997) 5541; (b) R. Duchateau, E.A.C. Brussee, A. Meetsma, J.H. Teuben, Organometallics 16 (1997) 5506; (c) B.-J. Deelman, W.M. Stevels, M.T. Lakin, A.L. Spek, J.H. Teuben, Organometallics 13 (1994) 3881; (d) A.S. Guram, R.F. Jordan, Organometallics 10 (1991) 3470; (e) R.F. Jordan, A.S. Guram, Organometallics 9 (1990) 2116; (f) R.F. Jordan, D.F. Taylor, N.C. Baenziger, Organometallics 9 (1990) 1546; (g) W.J. Evans, L.R. Chamberlain, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 110 (1988) 6423; (h) K.H. den Haan, Y. Wielstra, J.H. Teuben, Organometallics 6 (1987) 2053; (i) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schafer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203; (j) P.L. Watson, J. Chem. Soc., Chem. Commun. (1983) 276; (k) E. Klei, J.H. Reuben, J. Organomet. Chem. 214 (1981) 53.
- [34] R.L. Miller, R. Toreki, R.E. LaPointe, P.T. Wolczanski, G.D. Van Duyne, D.C. Roe, J. Am. Chem. Soc. 115 (1993) 5570.
- [35] W.A. Nugent, J.M. Mayer, Metal-Ligand Multiple Bonds, Wiley, New York, 1988.
- [36] A.S. Veige, P.T. Wolczanski, E.B. Lobkovsky, Angew. Chem. Int. Ed. 40 (2001) 3629.