J. Am. Chem. Soc. **1994,** *116,* 12103−12104

Spontaneous Loss of Molecular Hydrogen from Tungsten(IV) Alkyl Complexes To Give Alkylidyne Complexes

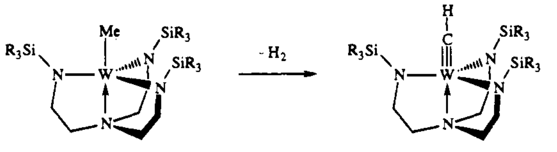
Keng-Yu Shih, Karen Totland, Scott W. Seidel, and Richard R. Schrock*

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received September 2, 1994

We have begun to explore the chemistry of Mo and W complexes that contain triamidoamine ligands, $(R'NCH_2CH_2)_3N$, where R′ is a silyl group (e.g., $SiMe_3$)[1] or C_6F_5.[2] (The only other reported W or Mo complex in this category is $[(MeNCH_2CH_2)_3N]Mo{\equiv}N$.[3]) We found that paramagnetic $[(R_3SiNCH_2CH_2)_3N]Mo(CH_3)$ and $[(R_3SiNCH_2CH_2)_3N]Mo(C{\equiv}CR'')$ (R_3Si = Me_3Si, $PhMe_2Si$, or Ph_2MeSi; R″ = Me, Ph, or $SiMe_3$) complexes could be prepared readily from $[(R_3SiNCH_2CH_2)_3N]MoCl$.[1] We have now found that attempted syntheses of $[(R'NCH_2CH_2)_3N]W(alkyl)$ complexes usually yield alkylidyne complexes, even when β protons are present in the alkyl.

The monochloride complexes $[(R_3SiNCH_2CH_2)_3N]WCl$ (R_3Si = Me_3Si, Me_2PhSi, or $MePh_2Si$) can be prepared in low yields (~20%) in THF from WCl_4(1,2-dimethoxyethane) or $WCl_4(THF)_2$ and the trilithium salts of the ligands, $(R_3SiNLiCH_2CH_2)_3N$. (See supplementary material for details.) Addition of methyllithium to $[(Me_3SiNCH_2CH_2)_3N]WCl$ in ether yields paramagnetic $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$ in high yield. By the Evan's method the magnetic moment was found to be 2.5 μ_B at 25 °C, slightly less than the expected spin-only value (2.83 μ_B) for two unpaired electrons. Two characteristic ligand methylene resonances can be observed in C_6D_6 at −31.43 (width at half-height = $w_{1/2}$ = 40 Hz) and −72.70 ppm ($w_{1/2}$ = 23 Hz) at 25 °C, while the TMS methyl resonances are observed at 9.89 ppm. The CH_3 resonance cannot be observed, although the CD_3 resonance in $[(Me_3SiNCH_2CH_2)_3N]W(CD_3)$ *is* observed at 7.5 ppm ($w_{1/2}$ = 5 Hz) in the ^2H NMR spectrum.[4−6] $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$ is converted virtually quantitatively into $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CH$ ($\delta(C_\alpha)$ = 272.6 ppm, J_{CW} = 244 Hz, $\delta(H_\alpha)$ = 7.08 ppm, J_{HW} = 81 Hz) (eq 1) between 25 and 80 °C. The reaction is first order through several half-lives and independent of concentration over a 5-fold range (Table 1) as determined by proton NMR at 500 MHz by following the decrease in the intensity of the TMS resonance. A resonance for molecular hydrogen can be observed, although dihydrogen's low solubility in toluene-d_8 does not allow the amount to be quantified by NMR. From the data presented in Table 1, values for $\Delta H^‡$ = 19.2 kcal mol^{-1} and $\Delta S^‡$ = −16 eu were calculated (Figure 1). For the analogous $[(Me_3SiNCH_2CH_2)_3N]W(CD_3)$ complex k_H/k_D was found to be 5.6 at 47 °C and 5.3 at 68 °C (Table 1). These values are approximately the same as those found for α hydrogen abstraction reactions in d^0 species.[7−9] When $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CD$ was placed in C_6D_6 under 2 atm of dihydrogen, no $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CH$ was observed after a period of 14 days. Therefore the loss of hydrogen from $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$ appears to be essentially irreversible under ambient conditions. $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$ also is converted in high yield to $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CH$ in the solid state (5 h at 90 °C under dynamic vacuum). Analogous decompositions of $[(Me_2PhSiNCH_2CH_2)_3N]W(CH_3)$ and $[(MePh_2SiNCH_2CH_2)_3N]W(CH_3)$ in solution proceed progressively more slowly (Table 1).



(1)

Table 1. Kinetic data and oxidation potentials for methyl complexes[a]

compd	T (K)	k (10^{-4} s^{-1})	$E_{1/2}$(ox) (V)[b]
$[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$	351	30.6	−0.81 (298 K)
	341	12.2, 11.8	
	330	4.35	
	320	1.56, 1.49, 1.50[c]	
	310	0.644	
	300	0.251	
$[(Me_3SiNCH_2CH_2)_3N]W(CD_3)$	341	2.30	
	320[c]	0.273	
$[(Me_2PhSiNCH_2CH_2)_3N]W(CH_3)$	341	6.32	−0.63 (298 K)
	320	0.764	
$[(MePh_2SiNCH_2CH_2)_3N]W(CH_3)$	341	1.89	−0.49 (298 K)
	320	0.219	

[a] The decrease in the intensity of the downfield-shifted MeSi resonance was followed by NMR at 500 MHz in toluene-d_8 in each case through at least two half-lives at a concentration of ~0.020 M, except where noted. [b] In dichloromethane under dinitrogen using 0.1 M $[NBu_4]^+PF_6^-$ as the electrolyte and ferrocene as the internal reference (0.47 V). Data were acquired at a 200 mV s^{-1} scan speed using a Pt bead electrode. In all cases $i_{p,a} \approx i_{p,c}$ and $E_{p,a} - E_{p,c}$ values are in the range 90−120 mV. [c] 0.0038 M.

$[(R_3SiNCH_2CH_2)_3N]WCl$ complexes react with $LiCH_2R'$ reagents (R′ = Me, Pr, $SiMe_3$, CMe_3) or KCH_2Ph in ether or THF at room temperature to give $[(R_3SiNCH_2CH_2)_3N]W{\equiv}CR'$ complexes in high yield. The alkyl complexes $[(R_3SiNCH_2CH_2)_3N]W(CH_2R')$ are not observed. Gas evolution is evident in all cases upon adding the alkylating agent. $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CCMe_3$ prepared in this manner is identical to a sample prepared from $(dme)Cl_3W{\equiv}CCMe_3$[10] and $(Me_3SiNLiCH_2CH_2)_3N$,[11] while $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CPh$ prepared in this manner is identical to a sample prepared from $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CCMe_3$ and $PhC{\equiv}CH$ by a triple bond metathesis reaction.[11]

$[(C_6F_5NCH_2CH_2)_3N]WCl$[2] also reacts with $LiCH_2R'$ reagents (R′ = Pr or $SiMe_3$) in toluene to give $[(C_6F_5NCH_2CH_2)_3N]W{\equiv}CR'$ complexes in moderate isolated yields. These results suggest that the phenomenon is not *restricted* to the silylated tren ligand system.

It should be noted that molybdenum methyl complexes that contain silylated tren ligands, e.g., $[(Me_3SiNCH_2CH_2)_3N]Mo(CH_3)$, are thermally stable.[1] The linear relationship (not shown) between the rates of decomposition of $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$, $[(Me_2PhSiNCH_2CH_2)_3N]W(CH_3)$, and $[(MePh_2SiNCH_2-$

---

(1) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994,** *116,* 8804.

(2) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994,** *116,* 4382.

(3) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992,** *114,* 2275.

(4) Often only ^2H NMR resonances are observable in a paramagnetic species as a consequence of a significantly smaller line width than in ^1H NMR spectra.[5] The advantages of ^2H NMR in transition metal chemistry have been demonstrated recently.[6]

(5) *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic: New York, 1973.

(6) Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994,** *13,* 2907.

(7) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979,** *101,* 3210.

(8) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.

(9) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991,** *39,* 1.

(10) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982,** *1,* 1645.

(11) Joel S. Freundlich, unpublished observations.

0002-7863/94/1516-12103$04.50/0 © 1994 American Chemical Society

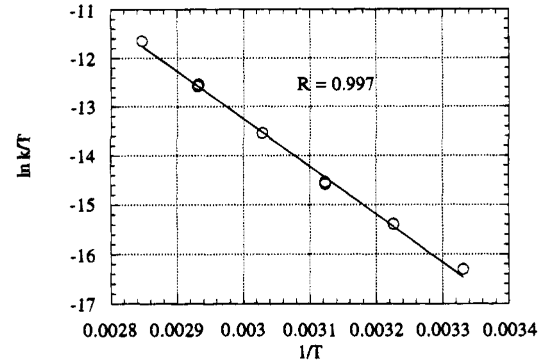
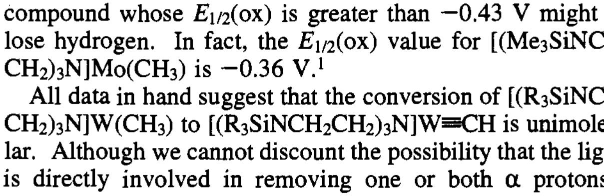


Figure 1. Plot of ln(k/T) versus $1/T$ for $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$ employing data in Table 1.

$CH_2)_3N]W(CH_3)$ and the potentials at which they each undergo a reversible oxidation (Table 1) suggests that any methyl compound whose $E_{1/2}(ox)$ is greater than -0.43 V might not lose hydrogen. In fact, the $E_{1/2}(ox)$ value for $[(Me_3SiNCH_2CH_2)_3N]Mo(CH_3)$ is -0.36 V.[1]

All data in hand suggest that the conversion of $[(R_3SiNCH_2CH_2)_3N]W(CH_3)$ to $[(R_3SiNCH_2CH_2)_3N]W{\equiv}CH$ is unimolecular. Although we cannot discount the possibility that the ligand is directly involved in removing one or both α protons, a plausible explanation would consist of "α elimination" to give a W(VI) methylene hydride complex, perhaps with concomitant dissociation of the apical nitrogen donor (eq 2), followed by "α abstraction" of the alkylidene H_α by the hydride to give molecular hydrogen. When no β protons are present in the alkyl (alkyl = CH_2Ph, CH_2SiMe_3, or CH_2CMe_3), we propose that the mechanism is most likely to be analogous to that for the methyl complex, even though the alkyl intermediates have not yet been observed. However, when β protons are present (as in the butyl complex), we cannot exclude the possibility that β hydride elimination and other, more unusual proton migration reactions are part of a series of rapid steps that lead to the stable alkylidyne complexes.[12] Almost certainly, the *steric protection against intermolecular reactions* provided by the substituted triamidoamine ligand *combined with the low probability of dissociation* of the triamidoamine ligand are important features of the chemistry observed here.



(2)

Several reactions in the literature that involve monomeric species[13] may be related, at least distantly, to the conversions observed here. One concerns a reaction between $W(PMe_3)_4Cl_2$ and 2 equiv of $AlMe_3$ to give *trans*-$Cl(PMe_3)_4W{\equiv}CH$ in ~65% yield and 0.9–1.2 equiv of a gas that consists of 70–85% methane and 30–15% hydrogen[14,15a] (see also ref 15b). Another is a reaction in which a rhenium polyhydride complex is transformed in the presence of acid and an alkyne into a rhenium hydrido–alkylidyne complex.[16] A third is the reaction between $MoH(\eta^3\text{-allyl})(dppe)_2$ and a large excess of anhydrous HCl in THF to give (at high concentrations of HCl) $MoH_2Cl_2(dppe)_2$, molecular hydrogen, and propyne.[17] It is clear from the results reported here that an alkylidyne complex can be sufficiently favorable thermodynamically that "α,α-dehydrogenation" of the metal–alkyl bond becomes possible.

The findings reported here raise many interesting questions concerning the possibly multifaceted role that a substituted triamidoamine ligand[18] might play in the chemistry of high oxidation state species. It remains to be seen the extent to which dehydrogenation of alkyl ligands is possible in other ligand environments, or the extent to which "oxidation" of the metal under typical reducing conditions in classical olefin and acetylene metathesis systems[19] can be attributed to dehydrogenation of alkyl ligands.

Acknowledgment. R.R.S. thanks the National Science Foundation (CHE 91 22827) for research support, and K.T. thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship.

Supplementary Material Available: Experimental details for the syntheses of $[(R_3SiNCH_2CH_2)_3N]WCl$ (R_3Si = Me_3Si, Me_2PhSi, or $MePh_2Si$), $[(R_3SiNCH_2CH_2)_3N]W(CH_3)$, $[(Me_3SiNCH_2CH_2)_3N]W(CD_3)$, $[(R_3SiNCH_2CH_2)_3N]W{\equiv}CH$, $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CD$, $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CCH_3$, $[(PhMe_2SiNCH_2CH_2)_3N]W{\equiv}CCH_3$, $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}C$-*n*-Pr, $[(PhMe_2SiNCH_2CH_2)_3N]W{\equiv}C$-*n*-Pr, $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}C$-*t*-Bu, $[(PhMe_2SiNCH_2CH_2)_3N]W{\equiv}C$-*t*-Bu, $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CSiMe_3$, $[(PhMe_2SiNCH_2CH_2)_3N]W{\equiv}CSiMe_3$, $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CPh$, $[(C_6F_5NCH_2CH_2)_3N]W{\equiv}CSiMe_3$, and $[(C_6F_5NCH_2CH_2)_3N]W{\equiv}CPr$ (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(12) Interestingly, preliminary investigations (^{13}C, ^2H, and ^1H NMR) of the butylidyne products of the reactions between $LiCD_2CH_2CH_2CH_3$ and $[(Me_3SiNCH_2CH_2)_3N]WCl$ or $[(C_6F_5NCH_2CH_2)_3N]WCl$ suggest that the deuterons are *not* present in the butylidyne ligand in $[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CCH_2CH_2CH_3$, but they *are scrambled throughout the butylidyne chain* in the C_6F_5 tren derivative. Additional studies are under way.

(13) Reactions in which a methylidyne is formed from a methyl complex are known in multimetallic chemistry; see, for example, the low-yield conversion of $[Ru_2(CH_3)(CO)(dppm)Cp_2]^+$ into $[Ru_2(CH)(CO)(dppm)Cp_2]^+$ reported by Davies et al.: Davies, D. L.; Gracey, B. P.; Guerchais, V.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.*, **1984**, 481.

(14) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.

(15) (a) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322. (b) Atagi, L. M.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483.

(16) Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 1890.

(17) Oglieve, K. E.; Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1994**, 474.

(18) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

(19) Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983.