

Communications

Catalytic C-H Activation in Early Transition-Metal Dialkylamides and Alkoxides[†]

William A. Nugent,* Derick W. Ovenall, and Steven J. Holmes¹

Central Research and Development Department
E. I. du Pont de Nemours and Company
Experimental Station, Wilmington, Delaware 19898

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Summary: Labeling studies provide evidence for reversible cyclometalation in d⁰ dialkylamido complexes (140–180 °C) and in d⁰ alkoxo complexes (180–220 °C). In contrast to the facile α -metalation of dimethylamine, catalytic metalation occurs exclusively at the β -position of ethanol. Such a cyclometalation process serves as the basis for the catalytic aminomethylation of terminal olefins and may also be involved in the stereoselective isomerization of 3-buten-1-ol to *cis*-crotyl alcohol.

Cyclometalation of coordinated ligands is a common feature in low-valent transition-metal complexes² but has rarely been observed in d⁰ early transition-metal compounds.^{3,4} However, we wish to report evidence that, at elevated temperatures, facile reversible cyclometalation occurs in both d⁰ dialkylamido⁵ and alkoxo⁶ complexes.

Treatment of dimethylamine-*N-d* with early transition-metal dimethylamides at 140–180 °C caused rapid incorporation of deuterium into the methyl group (Table I).



The Ta and Zr catalysts could be recovered unchanged after the reaction. The Nb and W amides were reduced to as yet unidentified active catalyst species.⁷ The reaction could be conveniently monitored by gas-phase IR spectroscopy by following the disappearance of the N-D bending mode at 1243 cm⁻¹ and the concomitant increase in the C-D band at 2085 cm⁻¹. For selected runs, the results were confirmed by ²H NMR spectroscopy. Using the isotopic shift, we found that exclusive monodeuteration of the methyl group occurs at low conversions. Equation

Table I. Catalysts for H-D Exchange in Me₂ND and for Addition of Me₂NH to 1-Pentene^a

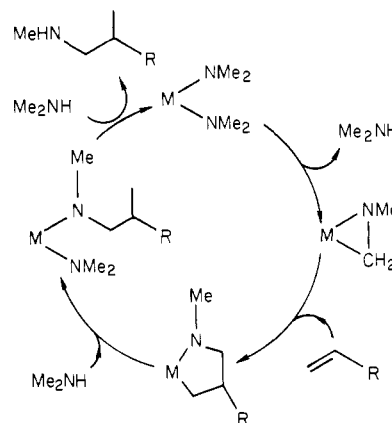
catalyst	% H-D exchange ^c	insertn (turnovers) ^d
Ti(NMe ₂) ₄	0 ^e	0.0
Zr(NMe ₂) ₄	37	0.0
Hf(NMe ₂) ₄	0 ^e	
Nb(NMe ₂) ₅	67	4.5
Ta(NMe ₂) ₅	26	0.3
W(NMe ₂) _n ^b	57	7.0
Sn(NMe ₂) ₄	0 ^e	0.0

^a All runs in evacuated sealed tubes 14 h at 160 °C.

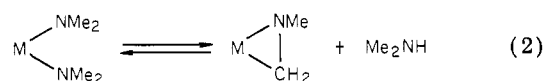
^b Catalyst was 2:1 adduct of W₂(NMe₂)₆/W(NMe₂)₆ prepared by method of Chisholm.¹⁷ ^c Percent decrease in 1243-cm⁻¹ band. All runs contained 0.25 mmol of catalyst and 12.5 mmol of Me₂ND in 5 mL of decalin.

^d Yield of hexylmethylenamines in mol/mol of catalyst. All runs contained 0.25 mmol of catalyst, 12.5 mmol of 1-pentene, and 12.5 mmol of dimethylamine in 5 mL of decalin. ^e None detected under conditions where as little as 3% exchange could be observed.

Scheme I

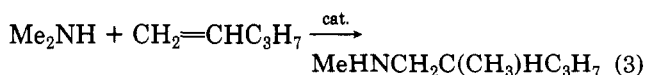


1 is presumed to involve the reversible metalation of the dimethylamide ligand as shown in eq 2. Azametalla-



cyclopropanes related to those in eq 2 are reported to be formed during thermolysis of diethylamido complexes.⁸

The intermediate azametallacyclopropanes in eq 2 can apparently be trapped by terminal olefins. Thus, heating an equimolar mixture of 1-pentene and dimethylamine with 2 mol % of metal dimethylamide resulted in the catalytic aminomethylation⁹ of the pentene (eq 3). The



(8) (a) Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett.* 1978, 525–528. Airoldi, C.; Bradley, D. C.; Vuru, G. *Transition Met. Chem. (Weinheim, Ger.)* 1979, 4, 64. (b) The X-ray crystal structure of a d⁰ azametallacyclopropane derivative prepared in a different manner has been reported: Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1981, 2088–2097. See also: Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* 1979, 101, 6450–6452.

[†] Contribution No. 3079.

(1) Du Pont student summer employee.

(2) Parshall, G. W. *Acc. Chem. Res.* 1975, 8, 113–117. Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 73–86.

(3) Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* 1974, 29–30. Sharp, P. R.; Astruc, D.; Schrock, R. R. *J. Organomet. Chem.* 1979, 182, 477–488. Rausch, M. D.; Mintz, E. A. *Ibid.* 1980, 190, 65–72. Gal, A. W.; van der Heijden, H. *Angew. Chem., Int. Ed. Engl.* 1981, 21, 978–980.

(4) For a related metalation in an f⁰ organoactinide system see: Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* 1979, 101, 7728–7729.

(5) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Wiley: New York, 1980.

(6) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: London, 1978.

(7) This initial stoichiometric reduction proceeded with formation of methane (0.15 mol/mol of Nb). The catalyst could be isolated at the completion of the run and was fully active in a subsequent run.

Table II. H-D Exchange in CH₃CH₂OD Catalyzed by Transition-Metal Ethoxides^a

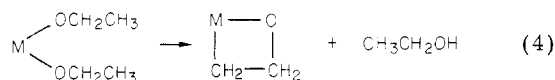
catalyst	temp, °C	% H-D exchange ^c	distribution of ² H label, ^b %		
			CH ₃ D	CD ₂ H	CD ₃
Ti(OEt) ₄	180	0 ^e			
Zr(OEt) ₄	200	14	5	25	70
Nb ₂ (OEt) ₁₀	200	18	27	41	32
Ta ₂ (OEt) ₁₀	180	9			
Ta ₂ (OEt) ₁₀	200	23	28	39	33
Ta ₂ (OEt) ₁₀	220	47			
Ta ₂ (OEt) ₁₀ + C ₆ H ₅ N ^d	200	55	38	39	23
Ta ₂ (OEt) ₁₀ + Et ₃ N ^d	200	50			
W(OEt) ₆	200	0 ^{e,f}			

^a All runs involved 0.5 mmol of catalyst in 50 mmol of ethanol-*d* for 14 h in evacuated glass tubes. ^b Relative areas of d¹, d², d³ resonances (at δ 0.98, 0.96, and 0.94, respectively) in the 61.4-MHz ¹H-decoupled ²H NMR. ^c Percent of starting OD incorporated into methyl group determined by area of OH resonance in 90-MHz ¹H NMR. ^d Run additionally contains 2.0 mmol of amine additive. ^e Catalyst decomposed to white insolubles; no exchange detected under conditions where 1% exchange could be observed. ^f Ethanol was disproportionated to diethyl ether and H₂O.

activity of the various metal amides for the reaction shown in eq 3 (Table I) roughly parallels their efficacy for H-D exchange. The regiochemistry of 1-pentene insertion varied somewhat with reaction conditions, but the product always consisted of >90% *N*-methyl-*N*-(2-methylpentyl)amine, the remainder being *N*-methyl-*N*-hexylamine. We propose that the mechanism of this reaction is that shown in the Scheme I. The proposed insertion of the olefin into the strained azametallacyclopropane intermediate has precedent in the analogous reaction of an oxametallacyclopropane recently reported by Erker.¹⁰

H-D exchange in ethanol-*d* was catalyzed by metal ethoxides at somewhat higher temperatures (180–220 °C). ²H NMR studies indicate that deuterium is incorporated exclusively into the methyl group of ethanol.¹¹ Even at low conversions, much of the product consists of di- and trideuterated ethanol (Table II). The reaction with Zr(OEt)₄ is first-order in catalyst at 185 °C, while that with Ta₂(OEt)₁₀ at 180 °C appears half-order in catalyst.¹² The rate of the H-D exchange in ethanol is enhanced by addition of triethylamine or pyridine.

Incorporation of deuterium exclusively into the β-position of ethanol can be rationalized in terms of the preferential formation of an oxametallacyclobutane intermediate¹³ (eq 4). The predominance of multiply deuterated



products, especially from the Zr catalyst, suggests that further metalation of the intermediate metallacycle is fast compared with the reverse of eq 4.¹⁴ It is noteworthy in this regard that Andersen has recently observed such an effect in the stoichiometric cyclometalation of Zr and Hf

amides. Thermal elimination of alkane from the complexes R₂M[N(SiMe₃)₂]₂ proceeded with loss of two hydrogens from the same methyl group to afford bridging carbene derivatives, e.g., {ZrCHSiMe₂NSiMe₃[N(SiMe₃)₂]₂}.¹⁵ Elimination of two hydrogens from the same methyl group has also been observed in metal alkyl chemistry.¹⁶

We have not to date demonstrated the intermolecular insertion of olefins into the C-H bond of ethanol. We have, however, observed that isomerization of 3-butenol is catalyzed by Ta₂(OEt)₁₀ at 200 °C. At 5% conversion, the product crotyl alcohol consisted >99% of the *cis* isomer. This stereospecificity suggests the possibility that the isomerization involves a cyclometalation of the type shown in eq 4, followed by ring enlargement to a oxametallacyclohexene intermediate.

Acknowledgment. The skilled technical assistance of D. M. Lattomus and J. C. Center are gratefully acknowledged. We also thank Professor Andersen for a preprint of ref 15.

Registry No. Me₂ND, 917-72-6; Me₂NH, 124-40-3; Zr(NMe₂)₄, 19756-04-8; Nb(NMe₂)₅, 19824-58-9; Ta(NMe₂)₅, 19824-59-0; W₂(NMe₂)₆, 54935-70-5; W(NMe₂)₆, 68941-84-4; CH₃CH₂OD, 925-93-9; Zr(OEt)₄, 18267-08-8; Nb₂(OEt)₁₀, 3236-82-6; Ta₂(OEt)₁₀, 6074-84-6; 1-pentene, 109-67-1.

(15) Planalp, R. P.; Andersen, R. A.; Zalkin, A., submitted for publication.

(16) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* 1980, 102, 6608-6609. Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Ibid.* 1981, 103, 965-966. Wengrovits, J. H.; Sancho, J.; Schrock, R. R. *Ibid.* 1981, 103, 3932-3934.

(17) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* 1976, 98, 4477-4485.

(9) Noteworthy in this regard is a claim in the patent literature that insertion of olefins into the α C-H bonds of dialkylamines is promoted by a variety of transition-metal species including NbCl₅. German Patent 2748293 (to ANIC S.p.A.)

(10) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* 1982, 224, 29-42.

(11) In contrast, exclusive deuteration of the methylene carbon of ethanol by low-valent group 8 catalysts has been reported: Regan, S. L. *J. Org. Chem.* 1974, 39, 260-261. Sasson, Y.; Blum, J. *J. Chem. Soc., Chem. Commun.* 1974, 309-310.

(12) The degree of aggregation of tantalum ethoxide in refluxing ethanol has been determined as 1.78 (vs. 1.98 in refluxing benzene). Bradley, D. C.; Chakravarti, B. N.; Wardlaw, W. *J. Chem. Soc.* 1956, 2381-2384.

(13) Given eq 4, it is intriguing that in no case have we observed the formation of ethylene, which would be the expected product of Wittig-type cleavage of the cyclometalated intermediate.

(14) An alternative explanation which we cannot exclude is that deuterium incorporation occurs in a reactive intermediate in which both cyclometalation and its reverse reaction are fast relative to alkoxide exchange with solvent. However, it is known that alkoxide exchange with free alcohol is very rapid in the homoleptic transition-metal alkoxides (see ref 6).

Synthesis of a Binuclear Hafnium Hydride Complex Which Incorporates Hybrid Multidentate Ligands

Michael D. Fryzuk* and Hugh David Williams

Department of Chemistry, University of British Columbia
Vancouver, British Columbia, Canada V6T 1Y6

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Summary: Disproportionation of HfCl[N(SiMe₂CH₂PMo₂)₂]₂ by excess HfCl₄ results in the formation of the "mono" amide complex HfCl₃[N(SiMe₂CH₂PMo₂)₂]HfCl₄ which can be converted to Hf(BH₄)₃[N(SiMe₂CH₂PMo₂)₂] and Hf(BH₄)₄ by reaction with excess LiBH₄. The reaction of Lewis bases with Hf(BH₄)₃[N(SiMe₂CH₂PMo₂)₂] generates the new binuclear