Journal of Organometallic Chemistry, 335 (1987) 269–276
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

A kinetic investigation of reaction of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ with methyl iodide

Patricia A. Shapley* **and Zang Yuan Own**

University of Illinois at Urbana-Champaign, School of Chemical Sciences, 1209 W. California St., Urbana, Illinois 61801 (U.S.A.)

(Received April 15th, 1987)

Abstract

A high oxidation state alkylnitridoosmium complex, $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ acts as a nucleophile in reactions with alkyl halides. Alkylimido complexes, $Os(NR)(CH_2SiMe_3)_4$, are produced. The reaction between $[Os(N)(CH_2SiMe_3)_4]$-$[NBu^n_4]$ and MeI is second order with $k_2 = 9.5 \times 10^{-5}$ sec^{-1} M^{-1} at 23°C in CD_2Cl_2 under pseudo first order conditions. The entropy of activation, $\Delta S^{\neq}$, was found to be -10.6 ± 0.5 cal M^{-1} K^{-1} and the enthalpy of activation, $\Delta H^{\neq}$, was found to be 19.6 ± 0.2 kcal M^{-1}. The reaction proceeds faster in polar, non-coordinating solvents than in either non-polar solvents or in solvents which can coordinate to the osmium center.

Introduction

Electron-rich transition metal complexes are known to react with alkyl halides and other organic electrophiles to generate alkylmetals [1–3]. Typical is the reaction of the complex $(\eta^6\text{-}C_6H_6)OsL_2$ with MeI and NH_4PF_6 to give $[(\eta^6\text{-}C_6H_6)OsL_2(Me)]$-$[PF_6]$ [4]. This converts an electron rich osmium(0) species to an osmium(II) complex. In transition metal complexes that have been shown to react with alkyl halides by an S_N2 mechanism, the metal oxidation state is always low.

Nitrido ligands in transition metal complexes are relatively unreactive [5,6] but can sometimes react directly with alkyl halides by an S_N2 mechanism [7].

We have previously shown that the alkylosmium(VI) complexes, $[Os(N)R_4]$-$[NBu^n_4]$ (where R = CH_3, CH_2SiMe_3, CH_2CMe_3, CH_2Ph) [8], react with $[Me_3O][BF_4]$ to form the corresponding methylimido complexes, $Os(NMe)R_4$, in high yield [9]. The same methylimido products are obtained in the reaction of $[Os(N)R_4][NBu^n_4]$ with trimethylsilyl trifluoromethyl sulfonate or with methyl iodide, a less powerful electrophile.

0022-328X/87/$03.50

Although the osmium center in $[Os(N)R_4]^-$ is formally in the +6 oxidation state, the electron-donating ability of the alkyl groups causes the metal to be more electron rich in these complexes than would be otherwise expected. It may be possible for an electrophile, such as CH_3I, to react at the metal center forming an intermediate methylosmium complex prior to formation of the methylimidoosmium complex. Migration of an alkyl group to nitrogen in transition metal complexes and on supported metals has been proposed to occur in catalytic amination and ammoxidation of olefins [10–13]. Alkyl migrations to nitrogen in transition metal imide or nitride complexes have not yet been observed, however [14].

We have examined the reactions between the nitridoosmiumtetraalkyl anions and alkyl halides in order to determine whether the final product results from direct addition to nitrogen or whether a methylosmium complex is an intermediate. Here we report the results of our investigation into the kinetics of the reaction of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ with MeI.

Results

The kinetics of the reaction between $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and methyl iodide under various conditions were studied by ^1H NMR spectroscopy. The only product of the reaction was the methylimido complex, $Os(NMe)(CH_2SiMe_3)_4$, and conversion approached 100% at long reaction times. The percent conversion for all kinetic runs was determined from the integration of the methylene resonance of the trimethylsilylmethyl ligands of starting material at δ 1.02 ppm and product at δ 2.10 ppm.

The reaction order was determined at 23° C in methylene chloride-d_2 under pseudo first order conditions. The observed rate constants were calculated using a linear least squares program for plots of $\ln[Os(N)(CH_2SiMe_3)_4^-]$ versus time. Plots of k_{obs} versus [MeI] were linear and passed through the origin showing that the reaction is first order in $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and first order in MeI (Fig. 1). The second order rate (Fig. 2) is 9.5×10^{-5} sec^{-1} M^{-1} under these conditions. The addition of tetra-n-butylammonium chloride to the solution had no effect on the rate constant. Room light had no effect on the reaction rate.

There was a pronounced solvent effect in this reaction. The reaction proceeded more slowly in non-polar solvents, such as benzene, than in non-coordinating polar solvents, such as methylene chloride. The coordinating polar solvents, acetonitrile and tetrahydrofuran, were intermediate. The reaction was inhibited by methylisonitrile.

The relative rates of reaction of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ with primary alkyl halides were determined by monitoring the percent conversion of the alkylnitrido complex to $Os(NR)(CH_2SiMe_3)_4$ by ^1H NMR. Ethyl iodide was 20 times slower than methyl iodide in its reaction with the osmium complex. The ethylimidoosmium complex, $Os(NEt)(CH_2SiMe_3)_4$, formed with ethyl iodide was characterized by NMR, IR and elemental analysis [16*]. Ethyl bromide was even slower to react than the iodide. We found no reaction between $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and n-propyl iodide after several days at 23° C.

The reactions between $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and MeI at 283 K, 296 K and 308 K were monitored by ^1H NMR. The temperature range was limited by the low boiling point of solvent and methyl iodide and by the fact that the reaction was

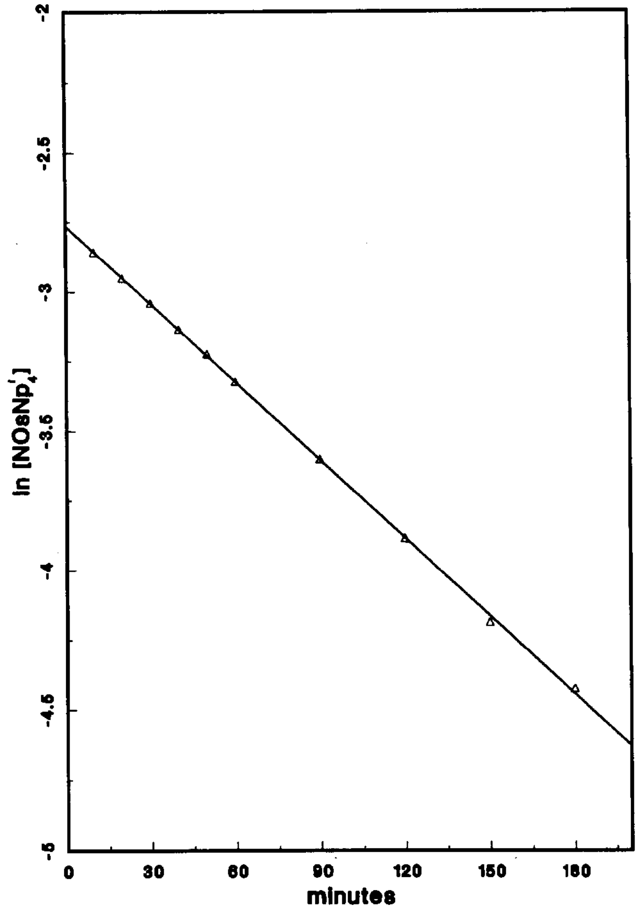

Fig. 1. Representative plot of ln[Os(N)(CH$_2$SiMe$_3$)$_4$$^-$] vs. time in minutes, pseudo first order conditions.

too slow to measure conveniently at lower temperatures. Temperature was maintained to ±0.5 °C during the course of these reactions and the ^{1}H NMR spectra were recorded automatically at regular intervals. The reactions were repeated at least 3 times at each temperature. Values for k_{obs} were consistent to within 5%. The

Table 1

Rate of reaction of [Os(N)(CH$_2$SiMe$_3$)$_4$][NBu$_4$] with MeI at 23° C

[Os(N)R$_4$]	[MeI]	k_{obs} (s^{-1})	$t_{1/2}$ (s)
1.26×10^{-2}	0.684	6.1×10^{-5}	11300
3.35×10^{-2}	0.684	6.0×10^{-5}	11500
4.19×10^{-2}	0.684	6.0×10^{-5}	11600
8.38×10^{-3}	0.163	1.9×10^{-5}	35900
9.31×10^{-3}	0.369	3.2×10^{-5}	21800
8.38×10^{-3}	1.460	1.4×10^{-4}	5070

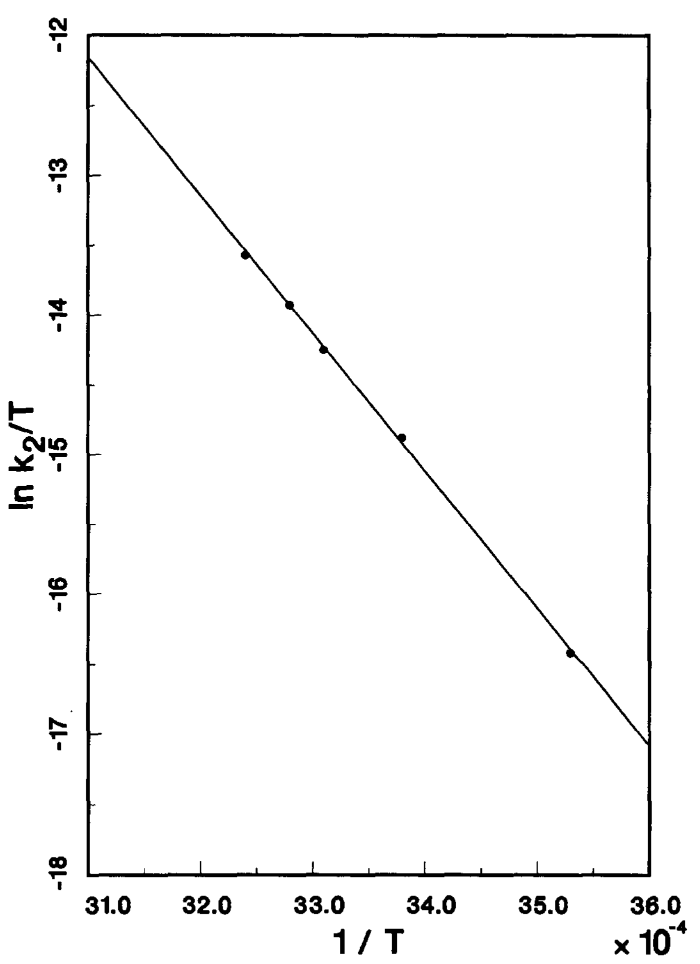

Fig. 2. Plot of $\ln(k_2/T)$ vs. $1/T$ were k_2 is the second order rate constant and T is temperature (K).

Table 2

Solvent effects on the rate of reaction [15*]

Solvent	ϵ	μ	% conversion after 4 h
C_6H_6	2.28	0	< 5
CH_3CN	36.2	3.92	11
THF	7.32	1.63	20
CH_2Cl_2	8.9	1.60	63

activation parameters were obtained from the plot of ln k/T versus T. The entropy of activation, $\Delta S^{\neq}$, was found to be -10.6 ± 0.5 cal M^{-1} K^{-1}. The enthalpy of activation, ΔH^{*}, was found to be 19.6 ± 0.2 kcal M^{-1}.

---

[*] Reference numbers with asterisks indicate notes in the list of references.

Table 3

Change in rate with temperature [17 *]

Solvent	T (K)	k_2 (s^{-1} M^{-1})
CD_2Cl_2	283	7.0×10^{-5}
CD_2Cl_2	296	9.6×10^{-5}
CD_2Cl_2	302	1.9×10^{-4}
CD_2Cl_2	305	2.7×10^{-4}
CD_2Cl_2	308	3.8×10^{-4}
CD_3CN	308	1.1×10^{-4}

Discussion

The kinetic data presented here support an S_N2 mechanism for the reaction between $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and iodides. The rate is first order with respect to the nitridoosmium complex and with respect to methyl iodide. The activation parameters are also consistent with an S_N2 mechanism. The values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ of -10.6 cal M^{-1} K^{-1} and 19.6 kcal M^{-1} are in the same range as values measured for the other transition metal nucleophiles in their reactions with methyl iodide [18]. As is the case in other nucleophilic substitution reactions, the rates decrease on going from methyl iodide to ethyl iodide to propyl iodide and alkyl iodides react faster than alkyl bromides. Consistent rates, lack of effect of light on the reaction, and quantitative conversion to product suggest that radicals are not involved in the reaction [19–23].

The rates of reaction of transition metal nucleophiles with methyl iodide vary over a wide range. The osmium complex is considerably slower than many of the others. $[CpFe(CO)_2][NBu_4]$ reacts at a rate of 2.8×10^6 while $RhCl(CO)(PPh_3)_2$ reacts at a rate (3.6×10^{-5}) comparable to the the rate observed with $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ [18]. The range of reactivity for non-transition metal nucleophiles is also large [24]. The relatively low rate of reaction of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ with methyl iodide is understandable given the high formal oxidation state of this complex, which ought to make the metal a weak nucleophile, and the strong metal–nitrogen bond, which should make the nitrogen lone pair less available.

The increase in the rate in going from C_6D_6 to CD_2Cl_2 solution can be explained by a decrease in the ion pairing of the salt in the more polar solvent. This would increase the nucleophilicity of the metal complex. Tetrahydrofuran and acetonitrile are more polar solvents than methylene chloride, but these solvents can also ligate to the coordinatively unsaturated metal. Methyl isonitrile is an even better ligand than thf or MeCN [25 *].

There are two possible explanations for the changes in the relative rates of reaction of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ with methyl iodide in different polar solvents. The presence of a donor ligand on the metal *trans* to nitrogen would weaken the osmium–nitrogen bond, increase the electron density on the nitrogen atom, and should increase the rate of reaction at nitrogen. Certain six-coordinate nitridoalkyl complexes of osmium have been isolated, including $Os(N)Me_3(thf)_2$. The metal nitrogen stretching vibration is at lower energy for six coordinate complexes than for related five coordinate osmium nitrides [8]. The observed decrease in rate of reaction in the presence of thf, MeCN and MeNC can be explained by competition between methyl iodide and these donor molecules for the open coordination site at the metal.

We see no evidence for the coordination of donor solvents at the nitrogen atom. Although the nitrotetrachloride osmium(V) anion reacts with the Lewis base triphenylphosphine to form a phosphineimidato complex, $(PPh_3)_2Cl_3Os(NPPh_3)$, this type of reaction does not occur with the nitridotetraalkylosmium(VI) complexes [26]. There is no reaction between $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and the phosphines PPh_3, PBu_3, or PMe_3 even at 90 °C. On the contrary, the nitride does interact with Lewis acids forming a 1/1 complex with BF_3 and $AlMe_3$ [8].

Steric factors may also explain the lower rate of reaction in coordinating polar solvents than in non-coordinating solvents. The six-coordinate, solvated osmium complex is more crowded than the five coordinate species. The nitrido nitrogen atom may be sterically less available for reaction with methyl iodide in acetonitrile or tetrahydrofuran than it is in methylene chloride. The differences in the rate of the reaction of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ with methyl, ethyl, and propyl iodides show that steric factors are important [27*].

Conclusion

Reaction between methyl iodide and $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ occurs by an S_N2 pathway. Although the nitrogen atom is ultimately the site of alkylation, there is some evidence of participation of the metal center in the reaction.

Experimental

Materials. A Vacuum Atmospheres dry box or Schlenk techniques were used for all sample transfers and manipulations. Deuterated benzene was distilled from sodium/benzophenone. CD_3CN was distilled from CaH_2. CD_2Cl_2 and alkyl halides were distilled prior to use. $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ was prepared as was previously reported [8]. $[NBu^n_4][Cl]$ was prepared from $[NBu^n_4][OH]$ and HCl.

Instrumentation. NMR spectra were recorded on a Bruker WP200sy FT NMR spectrometer. Chemical shifts are listed in ppm downfield from TMS.

Reaction order. A stock solution was prepared by adding 0.066 g (0.0828 mmol) of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ to CD_2Cl_2 in a 1.0 ml volumetric flask. Six NMR samples were prepared by adding different volumes of this stock solution, methyl iodide and CD_2Cl_2 to 5 mm NMR tubes. The tubes were capped, and placed in a constant temperature bath (22–23 °C). NMR spectra were obtained at regular intervals.

Activation parameters. In the dry box, 66 mg $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ and 12.5 μl CH_3I were dissolved in 1.2 ml CD_2Cl_2 in a precooled vial. The solution was added to 3 NMR tubes which were then sealed. The samples were maintained at −78 °C prior to the start of the kinetic runs. Each tube was placed in the probe of the NMR instrument. Temperature was maintained at either 283, 296 or 308 K ± 0.5 K during the course of the reaction. The ^1H NMR spectra were recorded automatically at regular intervals.

Solvent effects. To each of 4 vials was added 0.01 g $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$, 0.05 ml CH_3I, and 1.0 ml solvent. The solutions were allowed to remain at room temperature (23 °C) for 4 h. Solvent and remaining MeI were then removed under vacuum. The residue was dissolved in C_6D_6 and the percentage of conversion to $Os(NMe)(CH_2SiMe_3)_4$ was determined by integration of the ^1H NMR spectrum of each sample. Another sample containing 0.01 g $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$, 0.05 ml CH_3I, and 1.0 ml C_6D_6 was allowed to remain at room temperature for 3 days before work-up. An NMR sample was prepared with 22 mg $[Os(N)(CH_2SiMe_3)_4]$-$[NBu^n_4]$, 4.2 μl CH_3I, and 0.40 ml CD_3CN. The sample was sealed, then maintained at 308 K in the probe of the NMR instrument while ^1H NMR spectra were automatically obtained at regular intervals. The observed rate constant was determined as above.

Salt effect. An NMR sample was prepared with 22 mg $[Os(N)(CH_2SiMe_3)_4]$-$[NBu^n_4]$, 4.2 μl CH_3I, 10 mg NBu_4Cl, and 0.40 ml CD_2Cl_2. The sample was sealed, then maintained at 296 K in the probe of the NMR instruments while ^1H NMR spectra were automatically obtained at regular intervals. The observed rate constant was determined as above.

Acknowledgment

We gratefully acknowledge the financial support of the donors of the Petroleum Research Fund administered by the American Chemical Society, the Research Corporation, and the National Science Foundation (CHE 84-20768).

References

1 J.K. Stille and K.S.Y. Lau, Acc. Chem. Res., 10 (1977) 434.

2 M.D. Johnson, Acct. Chem. Res., 11 (1978) 57.

3 J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, 1980, chapter 11.

4 H. Werner and R. Werner, J. Organomet. Chem., 181 (1980) C7.

5 W.A. Nugent and B.L. Haymore, Coord. Chem. Rev., 31 (1980) 123–175.

6 W.P. Griffith, Coord. Chem. Rev., 8 (1972) 369–396.

7 M.W. Bishop, J. Chatt, J.R. Dilworth, M.B. Hursthouse, Motevalle, J. Less Common Metals, 54 (1977) 487.

8 P.A. Belmonte and Z.Y. Own, J. Am. Chem. Soc., 106 (1984) 7493.

9 P.A. (Belmonte) Shapley, Z.Y. Own and J.C. Huffman, Organometallics, 5 (1986) 1269.

10 K.B. Sharpless, A.Y. Teranishi and J.-E. Backvall, J. Am. Chem. Soc., 99 (1977) 3120.

11 A.O. Chang, K. Oshima and K.B. Sharpless, J. Am. Chem. Soc., 99 (1977) 3420.

12 A.K. Rappe and W.A. Goddard III, J. Am. Chem. Soc., 104 (1982) 3288.

13 J.D. Burrington and R.L. Grasselli, J. Catal., 59 (1979) 79.

14 W.A. Nugent and R.L. Harlow, J. Am. Chem. Soc., 102 (1980) 1759.

15 Values of dielectric constant, ϵ^0, and dipole moment, μ, were taken from: A.J. Gordon and R.A. Ford, The Chemists Companion; New York, John Wiley & Sons, 1972.

16 ^1H NMR (200 MHz, C_6D_6, 298 K): δ (ppm) 0.204, s, 36H, Me_3Si; 0.827, t, 3H, CH_3CH_2; 2.152, q, 2H, CH_3CH_2; 3.47, s, 8H, CH_2Si.

17 The concentration of $[Os(N)(CH_2SiMe_3)_4][NBu^n_4]$ was 6.91×10^{-2} *M* and the concentration of MeI was 0.314 *M* in these experiments.

18 R.G. Pearson and P.E. Figdore, J. Am. Chem. Soc., 102 (1980) 1541 and ref. therein.

19 J.S. Bradley, D.E. Connor, D. Dolphin, J.A. Labinger and J.A. Osborn, J. Am. Chem. Soc., 94 (1972) 4043.

20 J.A. Labinger, A.V. Kramer and J.A. Osborn, J. Am. Chem. Soc., 95 (1973) 7908.

21 P.J. Krusic, P.J. Fagan and J. San Fillippo, Jr., J. Am. Chem. Soc., 99 (1977) 250.

22 G.M. Williams, K.I. Gell and J. Schwartz, J. Am. Chem. Soc., 102 (1980) 3660.

23 G.M. Williams and J. Schwartz, J. Am. Chem. Soc., 104 (1982) 1122.

24 R.G. Pearson, H. Sobel and J. Songstad, J. Am. Chem. Soc., 90 (1968) 319.

25 The complexes, $[Os(N)Y_4]^-$ (where Y = Cl, $OSiMe_3$, or alkyl), are coordinatively unsaturated. Although the six coordinate species cannot be isolated, the five- and six-coordinate complexes are in rapid equilibrium in donor solvents. Two N–Os stretching vibrations are observed in THF and MeCN solutions corresponding to $Os(N)Y_4L^-$ and $Os(N)Y_4^-$. Coordination of solvent causes a decrease in the energy of the Os–N stretch. The intensity of the second band decreases with $Y = Cl > OSiMe_3 > R$.

26 D. Pawson and W.P. Griffith, J. Chem. Soc. Dalton Trans., (1975) 417.

27 We wish to thank one of the referees for pointing this out.