**Spectral Data.** $^1$H NMR ($CDCl_3$): $\delta$ 2.92 (d, $J = 10$ Hz).[12] Uv–vis ($CH_3NO_2$): $\lambda_{max}$ 372 nm (log $\epsilon$ 3.05). Ir ($CHCl_3$, NaCl cells): 2935 (m), 2850 (m), 2810 (w), 1485 (m), 1460 (m), 1305 (m), 1235 (w), 1194 (m), 1128 (s), 1070 (m), 1045 (m), 998 (vs), 970 (sh), 759 (m), 732 (m), 700 (w), 652 (vw) $cm^{-1}$. Ir (Nujol, polyethylene cells): 530 (m), 483 (s), 380 (sh), 365 (s), 340 (s), 300 (m), 225 (w) $cm^{-1}$. Raman: 1480 (w), 1445 (w), 1420 (w), 1310 (vw), 1155 (m), 1090 (vw), 1070 (vw), 990 (sh), 970 (vs), 760 (w), 653 (s), 520 (m), 480 (vw), 360 (m), 307 (s), 220 (w, sh) $cm^{-1}$. Mass spectrum, *m/e* (relative abundance, assignment): 332[13] (4.0, $TiCl_3 \cdot HMPA$), 297[13] (2.5, $TiCl_2 \cdot HMPA$), 188[13] (22, $TiCl_4$), 179 (100, HMPA), 153[13] (37, $TiCl_3$), 135 (95, $O{=}P[N(CH_3)_2]_2$), 92 (63, $O{=}PN(CH_3)_2$), 44 (61, $N(CH_3)_2$).

**Acknowledgment.** We are grateful to PHS–NIH for generous financial support of this work (Grant 5-RO1-AI-11690-02 MCHB). We appreciate discussions with Professor E. A. Deutsch and R. C. Elder and the technical assistance of Mr. Rodney Erkes, all of this department.

**Registry No.** I, 59219-54-4.

## References and Notes

(1) J. E. Mc Murry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974), and other papers in the series.
(2) (a) R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963); (b) G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *ibid.*, 5873 (1963).
(3) *Chem. Abstr.*, **71**, 39 789, 49 231 (1969). It is likely that, in THF, the sixth coordination site in $TiCl_3 \cdot 2HMPA$ is occupied by a solvent molecule, which is readily displaced by oxygen.
(4) Similar behavior was observed in toluene, the solvent previously used to prepare $TiCl_3 \cdot 2HMPA$.[3]
(5) The uptake rate was initially rapid, with approximately half of the theoretical amount absorbed after 1.5 h.
(6) T. P. Freedman, C. M. Yoshida, and T. M. Leohr, *J. Chem. Soc., Chem. Commun.*, 1016 (1974); A. J. Meleuger, L. R. Anderson, and C. T. Ratcliffe, *Appl. Spectrosc.*, **26**, 381 (1972).
(7) (a) R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organomet. Chem.*, **50**, 145 (1973); (b) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).
(8) H. Schafer, F. Wartenpfuhl, and W. Weise, *Z. Anorg. Allg. Chem.*, **295**, 268 (1958); N. V. Ageer, *Chem. Abstr.*, **79**, 147 791 (1973).
(9) (a) B. N. Chakravarte, *Naturwissenschaften*, **45**, 286 (1958). (b) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2840 (1965). (c) B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, **8**, 498 (1969). Cryoscopic molecular weights were somewhat ambiguous. Structure assignment was based on the absence of Ti=O stretch and mass spectral data.
(10) W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
(11) J. J. Salzman, *Helv. Chim. Acta*, **51**, 903 (1968).
(12) The methyl doublet of HMPA occurs at $\delta$ 2.66; that of $TlCl_3 \cdot 2HMPA$, at $\delta$ 2.83.
(13) Lowest *m/e* peak of chlorine isotope cluster.
(14) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

---

Contribution from the Research School of Chemistry,
The Australian National University,
Canberra, A.C.T. 2600, Australia

# Stereochemistry of Chlorine Oxidation of Some Dimethyl Sulfoxide–Cobalt(III) Complexes

W. G. Jackson and A. M. Sargeson*

*Received November 18, 1975* AIC50838P

The evidence for intermediates of reduced coordination numbers arising from rapid induced aquation of coordinated ligands in cobalt(III) amine complexes comes from two sources. First, the competition ratios for nucleophiles relative to water (both anions and neutral nucleophiles) were essentially independent of the leaving group.[1] Second, the stereochemistry of the reaction products was also independent of the leaving group.[1]

The induced aquation reactions suitable for yielding the second set of data were limited: namely, the nitrosation of coordinated azide ion,[2] e.g.

$$\begin{array}{l}(en)_2CoClN_3{}^+ + NO^+ \rightarrow (en)_2CoCl(NNNNO)^{2+} \\ \quad \rightarrow (en)_2CoCl^{2+} + N_2 + N_2O \\ \qquad \downarrow H_2O \\ \quad (en)_2CoClOH_2{}^{2+}\end{array}$$

and the $Hg^{2+}$-catalyzed aquation of halide ion,[2] e.g.

$$(en)_2CoCl_2{}^+ + Hg^{2+} \rightarrow (en)_2CoCl^{2+} + HgCl^+ \xrightarrow{H_2O} (en)_2CoClOH_2{}^{2+}$$

A portion of the data suffers from the problem that two such examples could coincidentally agree and there is an obvious need to generate the intermediate by some other route. This aspect of substitution chemistry is complementary of course to a need for finding more methods of accelerating what are usually relatively slow reactions and to putting the intermediates to use for synthetic purposes.[1]

We report here additional evidence for the five-coordinate $[Co(en)_2X]^{2+}$ intermediates generated by $Cl_2$ oxidation of dimethyl sulfoxide (DMSO) in *cis*-$[Co(en)_2(DMSO)X]^{n+}$ ions (X = Cl, $OH_2$, DMSO).

## Results and Discussion

Only one isomer of $Co(en)_2(DMSO)Cl^{2+}$ is known[3] and this has been assigned as the cis configuration with DMSO oxygen bonded[3,4] from the amine proton signal pattern in the $^1$H NMR and from the similarity of its visible spectrum to that of *cis*-$Co(en)_2(OH_2)Cl^{2+}$. This cis configuration is now confirmed, both by the observation of the small (~1 Hz at 100 MHz) diastereotopic splitting in the DMSO methyl resonances in the $^1$H NMR ($10^{-3}$ M DCl) and by its resolution into catoptric forms (vide infra). The cis assignment for the other DMSO (and TMSO)[5] complexes reported herein follows similarly.

*cis*-$[Co(en)_2(DMSO)Cl](ClO_4)_2$ or $[Co(en)_2(DMSO)Cl]NO_3ClO_4$ ($\epsilon_{519}$ 96.8, $H_2O$; $\epsilon_{521}$ 112.0, DMSO) reacts rapidly (seconds, 20 °C) with excess $Cl_2$ (0.02–0.08 M) in dilute solution ($3 \times 10^{-4}$ to $10^{-2}$ M) in aqueous $HClO_4$ (0.01–0.1 M). The visible spectrum after 5 min ($\epsilon_{510}$ 70.5 ± 0.8 (5))[6] corresponds to 74 ± 1% *cis*- and 26 ± 1% *trans*-$Co(en)_2(OH_2)Cl^{2+}$. Similar experiments in which excess (200-fold) $NaHCO_3$ was added following oxidation showed $\epsilon_{510}$ 107 ± 2 (3) after 5–10 min. Analysis in terms of $Co(en)_2CO_3{}^+$ ($\epsilon_{510}$ 133.8) and *trans*-$Co(en)_2ClOCO_2(H)^{n+}$ ($\epsilon_{510}$ 21.2)[7] revealed an identical isomer composition, 76 ± 2% cis.

(−)-*cis*-$[Co(en)_2(DMSO)Cl](ClO_4)_2$ ($[\alpha]_{589}$ −247°, $[\alpha]_{578}$ −308°, $[\alpha]_{560}$ −324°, $[\alpha]_{480}$ +439°, $[\alpha]_{350}$ +782°, 20 °C, 0.01 M $HClO_4$, *c* $1.69 \times 10^{-3}$ g/ml; $[\alpha]_{589}$ −197°, $[\alpha]_{578}$ −191°, $[\alpha]_{510}$ +384°, $[\alpha]_{350}$ +745°, 20 °C, DMSO, *c* $1.75 \times 10^{-3}$ g/ml) and (−)-$[Co(en)_2(DMSO)Cl]NO_3ClO_4$ were prepared by allowing (−)-*cis*-$[Co(en)_2Cl_2]ClO_4$ ($[\alpha]_{589}$ −575°)[8] to react with $AgClO_4$ (1.05 equiv) in DMSO (1 h, 20 °C). Work-up by the usual procedure[3] yielded crystals of the diperchlorate which were recrystallized from water to constant rotation. After reaction with $Cl_2$ in $HClO_4$ (0.01 M) as above the visible and rotary dispersion spectra were recorded ($\epsilon_{510}$ 70.5 ± 0.5 (2), $[M]^{20}{}_{589}$ −715 ± 20 (2)° $M^{-1}$ $m^{-1}$, $[M]^{20}{}_{578}$ −935 ± 20 (2)° $M^{-1}$ $m^{-1}$).[9] The properties recorded[8] for (−)-*cis*-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ ($\epsilon_{510}$ 91.2, $[M]^{20}{}_{589}$ −903°, $[M]^{20}{}_{578}$ −1272°) and *trans*-$[Co(en)_2(OH_2)Cl]SO_4$ ($\epsilon_{510}$ 11.0) show that the spectrophotometric data correspond to 74 ± 1% cis, and the polarimetric data, to 76 ± 3% (−)-cis product. The fraction of optically pure cis product was fixed more precisely by quenching with $HCO_3{}^-$, as earlier ($\epsilon_{510}$ 106.5 ± 1.0 (2), $[M]^{20}{}_{589}$ −3480 ± 20°, $[M]^{20}{}_{578}$ −4100 ± 20°, $[M]^{20}{}_{490}$ +6550 ± 20°). Optically pure (−)-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$ in this medium shows $[M]^{20}{}_{589}$ −4590°, $[M]^{20}{}_{578}$ −5430°,

$[M]^{20}_{490}$ +8540°, and $\epsilon_{510}$ 134.2. These numbers correspond to 75.5 ± 1.5% cis and 76 ± 1% (−)-cis, indicating full activity in the cis product.

*cis*-$[Co(en)_2(TMSO)Cl](ClO_4)_2$ and $[Co(en)_2(TMSO)Cl]NO_3ClO_4$ ($\epsilon_{519}$ 109.2, $H_2O$) were prepared in a manner similar to the preparation of DMSO analogues. Chlorine oxidation (0.08 M, in 0.1 M $HClO_4$), complete inside 3 min at 20 °C, yielded $\epsilon_{510}$ 71.0 ± 0.3 (2), and again this corresponds to 75 ± 0.5% *cis*-$Co(en)_2(OH_2)Cl^{2+}$.

The common stereochemical result (76 ± 1% (−)-cis, 24 ± 1% trans) for $Cl_2$ oxidation of *cis*-$Co(en)_2(R_2SO)Cl^{2+}$ agrees closely with the results of studies on (−)-*cis*-$Co(en)_2Cl_2^+$ + $Hg^{2+}$ (77 ± 2% (−)-cis) and (−)-*cis*-$Co(en)_2ClN_3^+$ + $NO^+$ (79 ± 2% (−)-cis).[2] The same result in four cases, where the variation in the leaving group now surely provides sufficient opportunity for differing product distributions, seems clear-cut evidence for the common dissymmetric five-coordinate species proposed previously.[2]

Recently the induced aquations *cis*-$Co(en)_2(OH_2)N_3^{2+}$ + $NO^+$ and *cis*-$Co(en)_2(OH_2)X^{2+}$ (X = Cl, Br) + $Hg^{2+}$ were shown to give 95.0 ± 0.5% cis product.[10] Although the product ratio is less well defined here, we examined the $Cl_2$ oxidation of *cis*-$Co(en)_2(OH_2)(DMSO)^{3+}$ to see if this also fitted the pattern. *cis*-$[Co(en)_2(OH_2)(DMSO)](NO_3)_2ClO_4$ ($\epsilon_{500}$ 92.9, 0.01 M $HClO_4$), from *cis*-$[Co(en)_2(DMSO)Br](ClO_4)_2$ and excess $AgClO_4$ in 0.01 M $HClO_4$, was crystallized from water by the addition of $LiNO_3$, $LiClO_4$, and ethanol. Chlorination through to the diaquo species gave $\epsilon_{492}$ 78.0 ± 0.5 (2) which indeed corresponds to 95.5 ± 0.5% cis product ($Co(en)_2(OH_2)_2^{3+}$: $\epsilon_{492}$(cis) 80.9, $\epsilon_{492}$(trans) 17.6).[10] The four common results now strengthen the case for a $Co(en)_2(OH_2)^{3+}$ pentacoordinate intermediate, although the cis:trans ratio here is less accurate than that arising from $[Co(en)_2Cl]^+$.

*cis*-$[Co(en)_2(DMSO)_2](ClO_4)_3$[4] or $[Co(en)_2(DMSO)_2](ClO_4)_2NO_3$ ($\epsilon_{510}$ 112.0, $H_2O$) was also oxidized rapidly by $Cl_2$ in $HClO_4$ in two steps through to $Co(en)_2(OH_2)_2^{3+}$ ($\epsilon_{492}$ 74.8 ± 0.8 (2)). If it is assumed that *trans*-$Co(en)_2(OH_2)(DMSO)^{3+}$ gives the established[10] stereochemistry for induced aquation (62 ± 0.5% trans), as the cis isomer does (vide supra), then the steric course for the first step is calculated as 92 ± 1.5% *cis*-$Co(en)_2(OH_2)(DMSO)^{3+}$. *cis*-$Co(en)_2(DMSO)Cl^{2+}$ + $Hg^{2+}$ (0.5 M in 0.5 M $HClO_4$) ($\epsilon_{500}$ 87.5 ± 0.8 (2)) and *cis*-$Co(en)_2(DMSO)Br^{2+}$ + $Hg^{2+}$ (0.2–1.0 M in 0.2–1.0 M $HClO_4$) ($\epsilon_{500}$ 88.6 ± 0.5 (2)) clearly indicate a common product and the formation of $Co(en)_2(DMSO)^{3+}$ which captures water with predominant but not complete retention ($\epsilon_{500}$ 92.9 for pure *cis*-$Co(en)_2(OH_2)(DMSO)^{3+}$). Treatment of the $Co(en)_2(OH_2)(DMSO)^{3+}$ products in each case with $Cl_2$ caused the slow formation of $Co(en)_2(OH_2)_2^{3+}$. $Hg^{2+}$ in excess shifts the very rapid $Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$ equilibrium to the right through $Cl^-$ complexation, and our observations confirm that HOCl oxidation of coordinated DMSO is at least 2 orders of magnitude slower than that of $Cl_2$.[11] Readjusting the stoichiometry (0.02 M $Hg^{2+}$, 10 min, followed by 0.08 M $Cl_2$, 3 min) enabled the rapid stepwise generation of $Co(en)_2(OH_2)_2^{3+}$ from *cis*-$Co(en)_2(DMSO)X^{2+}$ (X = Cl, $\epsilon_{492}$ 75.5 ± 0.5 (2); X = Br, $\epsilon_{492}$ 75.7 ± 0.5 (2)) and the final extinction coefficients matched that observed for *cis*-$Co(en)_2(DMSO)_2^{3+}$ + $Cl_2$ ($\epsilon_{492}$ 74.8 ± 0.8). *cis*-$[Co(en)_2(DMSO)N_3]NO_3ClO_4$ ($\epsilon_{505}$ 326, $H_2O$), prepared from *cis*-$[Co(en)_2(DMSO)_2](ClO_4)_3$ + $NaN_3$ (1.0 equiv) in DMSO (1.5 h, 20 °C), reacted rapidly with excess $NO^+$ to yield $\epsilon_{500}$ 88.0 ± 0.5 (2), providing a fourth example of these common product distribution reactions; subsequent treatment of the $Co(en)_2(OH_2)(DMSO)^{3+}$ products with $Cl_2$ yielded $\epsilon_{492}$ 76.0 ± 0.8 (2), as confirmation. Since all of these reactions are largely although not wholly retentive and $\epsilon$(cis) >> $\epsilon$(trans) at these wavelengths,[12] the calculated steric course for the directly observed first step is not especially sensitive to $\epsilon$(trans), and the result (93 ± 1% cis) is in close accord with that determined above (92 ± 1.5% cis), indicating that the $OH_2$ group (95.0 ± 0.5% cis) has a directing capacity similar to that of DMSO for water entry into the $Co(en)_2X^{3+}$ intermediate.

$Cl_2$ (0.08 M) oxidation of *cis*-$[Co(en)_2(DMSO)Br](ClO_4)_2$ or *cis*-$[Co(en)_2(DMSO)Br]NO_3ClO_4$ ($\epsilon_{529}$ 102.8, $H_2O$) in 0.1 M $HClO_4$ yielded largely *cis*- and *trans*-$Co(en)_2(OH)Cl^{2+}$ ($\epsilon_{510}$ 64.3 ± 0.5 (3), 66% cis). The $HCO_3^-$ quenched product mixture had $\epsilon_{510}$ 103.1 ± 0.5 (2) which corresponds to the different composition, 73 ± 0.5% cis. Appreciable amounts of HOCl (~15%) exist in 0.1 M $HClO_4$,[11,13] and since HOCl oxidation of coordinated bromide leads to aquo product and $Cl_2$ and HOCl oxidation rates are similar,[13] formation of some $Co(en)_2(OH_2)_2^{3+}$ renders spectrophotometric analysis in terms of $Co(en)_2(OH_2)Cl^{2+}$ inaccurate (66% cis). Both *cis*-$Co(en)_2(OH_2)Cl^{2+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$ give the common product $Co(en)_2CO_3^+$,[8] and hence the $HCO_3^-$ result is probably more accurate (73% cis).

*cis*-$Co(en)_2(DMSO)Br^{2+}$ can react by first oxidation of DMSO to give *cis*- and *trans*-$Co(en)_2(OH_2)Br^{2+}$ followed by $Cl_2$ oxidation with retention[13,14] to give *cis*- and *trans*-$Co(en)_2(OH_2)Cl^{2+}$. Alternatively, bromide oxidation may occur first or competitively. The first possibility is expected to give 73% cis,[10] and the second, up to 76% cis[2] product. Clearly the observed result cannot distinguish the alternatives and provides no definitive information about the existence of either $Co(en)_2Cl^{2+}$ or $Co(en)_2Br^{2+}$. Evidence for $Co(en)_2Br^{2+}$ rests with results for the spontaneous aquation of (−)-*cis*-$Co(en)_2Br_2^+$[4] and the reactions (−)-*cis*-$Co(en)_2Br_2^+$ + $Hg^{2+}$, (−)-*cis*-$Co(en)_2BrN_3^+$ + $NO^+$, and (−)-*cis*-$Co(en)_2(DMSO)Br^{2+}$ + $Cl_2$–0.1 M HCl (to suppress HOCl formation) all of which will be considered in detail elsewhere.

Chlorine oxidation of *cis*-$[Co(en)_2(DMSO)N_3]NO_3ClO_4$ also entails a double oxidation removing both DMSO and $N_3^-$ and we cannot as yet confirm the existence of $Co(en)_2N_3^{2+}$ (84 ± 2% (−)-*cis*-, 26 ± 2% *trans*-$Co(en)_2(OH_2)N_3^{2+}$)[2] by this route. A following paper considers the prospects of steric change and anion competition in $Cl_2$ (and HOCl) oxidation of several azidoaminecobalt(III) complexes.

A recent note described the synthesis of the labile $Co(NH_3)_5OClO_3^+$ species, prepared in strong $ClO_4^-$ media by capture of $Co(NH_3)_5^{3+}$ generated by usual routes.[11] This complex was first observed in the reaction of $Co(NH_3)_5(DMSO)^{3+}$ with $Cl_2$ in $HClO_4$. Anion competition ($Y^-$), especially high in this system, is believed to proceed by two routes, one via $Co(NH_3)_5^{3+}$ and the other via $Co(NH_3)_5OS(Cl)(CH_3)_2^{4+},Y^-$ which because of increased ion association leads to enhanced anion entry. However, the prospect of significant amounts of six-coordinate perchlorato intermediates in the present study can be eliminated. Substantial incorporation of $ClO_4^-$ into this type of complex by the induced aquation reactions requires a high concentration of $ClO_4^-$ ion (≥1 M).[11] This condition is not met under the present circumstances where $[ClO_4^-] \leq 0.1$ M and, moreover, the results were constant in the $[ClO_4^-]$ range 0.01–0.1 M.

The nature of the leaving group in these reactions is not yet established, but whether it be $SO(Cl)(CH_3)_2^+$, or $O_2S(CH_3)_2$ which is the ultimate product, its loss is exceedingly rapid and conducive to pentacoordinate intermediate formation. The present work supplies additional evidence for the existence of such intermediates arising from the redox reaction at the coordinated ligand.

**Registry No.** *cis*-$[Co(en)_2(DMSO)Cl](ClO_4)_2$, 15618-10-7; *cis*-$[Co(en)_2(DMSO)Cl]NO_3ClO_4$, 59301-94-9; (−)-*cis*-$[Co(en)_2(DMSO)Cl](ClO_4)_2$, 59366-39-1; (−)-*cis*-$[Co(en)_2(DMSO)Cl]NO_3ClO_4$, 59366-40-4; (−)-*cis*-$[Co(en)_2Cl_2]ClO_4$, 23791-82-4; *cis*-$[Co(en)_2(TMSO)Cl](ClO_4)_2$, 59301-96-1; *cis*-$[Co(en)_2$-

(TMSO)Cl]$NO_3ClO_4$, 59301-97-2; *cis*-[Co(en)$_2$($OH_2$)(DMSO)]($NO_3$)$_2ClO_4$, 59301-99-4; *cis*-[Co(en)$_2$(DMSO)$_2$]($ClO_4$)$_3$, 14781-36-3; *cis*-[Co(en)$_2$(DMSO)$_2$]($ClO_4$)$_2NO_3$, 59302-00-0; *cis*-[Co(en)$_2$(DMSO)$N_3$]$NO_3ClO_4$, 59302-02-2; *cis*-[Co(en)$_2$(DMSO)Br]($ClO_4$)$_2$, 15818-85-6; *cis*-[Co(en)$_2$(DMSO)Br]$NO_3ClO_4$, 59302-03-3; *cis*-Co(en)$_2$($OH_2$)$Cl^{2+}$, 15693-74-0; (–)-*cis*-[Co(en)$_2$($OH_2$)Cl]$^{2+}$, 45837-48-7; *trans*-Co(en)$_2$($OH_2$)$Cl^{2+}$, 14403-92-0; (–)-*cis*-[Co(en)$_2CO_3$]$ClO_4$, 38673-77-7; *cis*-Co(en)$_2$($OH_2$)(DMSO)$^{3+}$, 59301-98-3.

## References and Notes

(1) A. M. Sargeson, *Pure Appl. Chem.*, **33**, 527 (1973).
(2) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1807 (1967).
(3) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2291 (1964).
(4) I. R. Lantzke and D. W. Watts, *Aust. J. Chem.*, **20**, 35 (1967).
(5) TMSO = tetramethylene sulfoxide, $(CH_2)_4SO$.
(6) The number of determinations is given in parentheses.
(7) *trans*-Co(en)$_2$($OH_2$)$Cl^{2+}$ reacts rapidly (seconds, 20 °C) with excess $HCO_3^-$ to yield *trans*-Co(en)$_2ClOCO_2(H)^{n+}$; the visible spectrum which is pH dependent does not change rapidly with time (W. G. Jackson and A. M. Sargeson, unpublished data). *cis*-Co(en)$_2$($OH_2$)$Cl^{2+}$ with $HCO_3^-$ goes rapidly (minutes, 20 °C) through to the chelate Co(en)$_2CO_3^+$ with complete retention of geometric and optical configuration.[8]
(8) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).
(9) If the units deg $M^{-1}$ $m^{-1}$ (≡deg $mol^{-1}$ $dm^2$) are used for molar rotation, the customary values from [M] = (mol wt)$\alpha/cd$ (where $\alpha$ is rotation observed, $c$ is concentration in % w/v, and $d$ = is path length in dm) are retained.
(10) W. G. Jackson, *Inorg. Chim. Acta*, **10**, 51 (1974).
(11) J. N. MacB. Harrowfield, A. M. Sargeson, B. Singh, and J. Sullivan, *Inorg. Chem.*, **14**, 2864 (1975).
(12) DMSO is spectrochemically very similar to $Cl^-$; $\epsilon_{500}$ ~15 for *trans*-Co(en)$_2$($OH_2$)$Cl^{2+}$ was used for the calculation.
(13) J. F. Remar, D. E. Pennington, and A. Haim, *Inorg. Chem.*, **4**, 1832 (1965).
(14) Cf. (–)-*cis*-Co(en)$_2Br_2^+$ and (–)-*cis*-Co(en)$_2$($OH_2$)$Br^{2+}$ which are oxidized in $Cl_2$ (0.08 M)–HCl (0.1 M) with 100 ± 2% retention of geometric and optical configuration (W. G. Jackson and A. M. Sargeson, unpublished data).

---

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida

## Reaction of the Simmons–Smith Reagent with Trimethylamine–Borane

B. R. Gragg* and G. E. Ryschkewitsch

*Received December 17, 1975* AIC50908S

In the course of seeking alternate syntheses for 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane[1] the reaction of the Simmons–Smith reagent with several boron compounds was investigated.

A methylene-transfer reaction to a boron–nitrogen bond of the four-membered ring system of dimeric $(CH_3)_2NBH_2$ using the Simmons–Smith reagent, an organometallic complex formed between Zn and $CH_2I_2$ known to be an active methylene-transfer agent to carbon–carbon double bonds,[2-4] was attempted. The carbon atom of the active methylene in the Simmons–Smith reagent exhibits electrophilic character[4] and could compete for the electrons shared between boron and nitrogen in forming the four-membered ring system of dimeric $(CH_3)_2NBH_2$. Although the desired reaction did not occur, it was found that the Simmons–Smith reagent will transfer a methylene group to a boron–hydrogen bond.

### Discussion

The Simmons–Smith reagent reacts with $(CH_3)_3N\cdot BH_3$ transferring methylene groups to B–H bonds to produce, as the simplest moiety, a B–$CH_3$ unit.

The production of ethane during aqueous hydrolysis of the nonvolatile portion of the reaction mixtures with 0.1 M HCl confirms the presence of $C_2H_5$ units in the reaction mixture. The isolation of what is thought to be a high molecular weight alkane or mixture of alkanes suggests the presence of alkyl species containing an unknown number of methylene groups.

If the methylene groups transfer nonselectively to a B–H or a B–$CH_3$ bond, then on a purely statistical basis the probability of obtaining three methylene transfers to a $BH_3$ unit before obtaining a methylene group transfer to a resulting B–$CH_3$ bond is 22.2%. The yield of $B(CH_3)_3$ obtained when the Simmons–Smith reagent was prepared in the presence of $(CH_3)_3N\cdot BH_3$ (3 mol:1 mol, respectively) is close to this value (25%). Large excesses of the Simmons–Smith reagent did not increase the yield of $B(CH_3)_3$. Thus, the transfer appears to be essentially nonselective in nature when the Simmons–Smith reagent is prepared in the presence of $(CH_3)_3N\cdot BH_3$.

In the reaction of the Simmons–Smith reagent with $(CH_3)_3N\cdot BH_3$ in a 1:1 ratio $B(CH_3)_3$ was not produced. Over 68% of the $(CH_3)_3N$ put into the system as $(CH_3)_3N\cdot BH_3$ was recovered as a $ZnI_2$ complex of $(CH_3)_3N$. Thus, the B–N bond is destroyed during the initial stages of the reaction of the Simmons–Smith reagent with $(CH_3)_3N\cdot BH_3$.

If the Simmons–Smith reagent was formed in the absence of $(CH_3)_3N\cdot BH_3$ and then reacted with $(CH_3)_3N\cdot BH_3$, the maximum yield of $B(CH_3)_3$ obtained was 6.9%.

This difference in yields of $B(CH_3)_3$ is thought to be due to a change in nature of the Simmons–Smith reagent with time. This possibility has been mentioned previously[3] but was not seriously considered.

In order to obtain additional information about the reagent the present authors reacted the Simmons–Smith reagent with $(CH_3)_3N$ in hope of isolating an organometallic species. The product obtained was shown to be $[(CH_3)_2NCH_2]ZnI_2[N(CH_3)_3]$ in 7.1% yield. A similar compound has been previously prepared by allowing a $ZnCl_2$ solution in diethyl ether, treated with diazomethane, to react with $(CH_3)_3N$. The product reported was $[(CH_3)_3NCH_2ZnCH_2N(CH_3)_3]^{2+}Cl^-{}_2$.[5]

The new compound prepared here demonstrates that only 7.1% of the active methylene present in the Simmons–Smith reagent after 4 h in refluxing diethyl ether is in a position such that a $CH_2ZnI_2$ moiety can be trapped by $(CH_3)_3N$.

In the reaction of $(CH_3)_3N\cdot BH_3$ with the Simmons–Smith reagent, formed over a 4-h period, it is interesting to observe that the yield of $B(CH_3)_3$ is very close to the amount of Zn–$CH_2$ trapped by $(CH_3)_3N$ under similar conditions.

It appears that the Simmons–Smith reagent is a methylene-transfer reagent that has a high percentage of a reactive intermediate present upon initial formation that either decomposes or rearranges to a less reactive or more selective species with time. The present authors contend that this feature of the Simmons–Smith reagent should be reconsidered.

### Experimental Section

**Preparation of the Simmons–Smith Reagent.** In a typical synthesis of the Simmons–Smith reagent a sample (3.85 g, 52.7 mmol) of Zn/Cu couple [commercially available from Ventron or prepared by reacting 40-mesh Zn in glacial acetic acid with copper acetate] and $CH_2I_2$ (13.61 g, 48.2 mmol) were added to a 250-ml one-necked flask, equipped for magnetic stirring and reflux, containing 100 ml of diethyl ether. The mixture was brought to gentle reflux under a nitrogen atmosphere and maintained at reflux for 4 h or until the $^1H$ NMR spectrum showed that all of the $CH_2I_2$ had been consumed.

**Reaction of Trimethylamine–Borane with the Simmons–Smith Reagent—I.** A sample of $(CH_3)_3N\cdot BH_3$ (1.79 g, 24.5 mmol) was added to $CH_2I_2$ (19.92 g, 70.6 mmol) and the Zn/Cu couple (5.23 g, 71.6 mmol) in 100 ml of diethyl ether in a 250-ml one-necked flask equipped with a magnetic stirring bar.

This mixture was connected to a large cold finger filled with a dry ice–acetone mixture. The upper outlet was connected to a series of three liquid $N_2$ traps on the vacuum line to trap any –78 °C non-

---

* To whom correspondence should be addressed at the Department of Chemistry, University of Kentucky, Lexington, Ky. 40506.