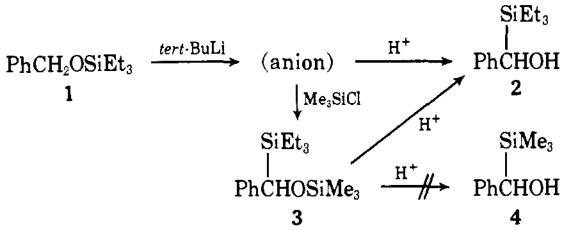


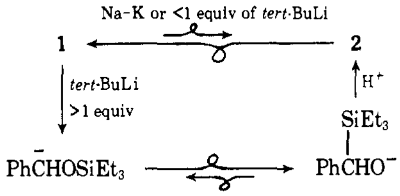
Excess *tert*-butyllithium remained after this time, as shown by a positive Gilman color test I. The solution was neutralized with dilute HCl, becoming pale yellow. The organic layer was immediately separated from the aqueous layer and the solvent evaporated. Vacuum distillation yielded 4.0 g of a clear oil which contained 75% rearranged isomer **2**, 18% **1**, and 7% benzyl alcohol and hexaethyldisiloxane, hydrolysis products of **1**. Repeating the experiment with a fivefold excess of *tert*-butyllithium, 96% **2**, 0.8% **1**, and 3% hydrolysis products were obtained after 144-hr reaction time, showing that not more than 0.8% **1** remained protonated in *tert*-butyllithium–pentane solution. Unlike the Wittig rearrangement there are no significant competing reactions apart from hydrolysis of starting material.

Elemental analysis and mass spectroscopy showed that **2** was isomeric with **1**. Structure **2** was assigned from the proton nmr which showed the characteristic triethylsilyl multiplet between τ 8.9 and 9.8, a broadened singlet at 8.2 (OH), a singlet at 5.45 (CH), and a singlet at 2.84 (C_6H_5), with relative intensities 15.8:1.0:0.92:4.9. The ir spectrum (neat) shows a broad (OH) stretch between 3200 and 3650 cm^{-1}; $n^{22}{}_D$ 1.5164.

When the rearrangement was repeated with the anionic species being trapped with trimethylchlorosilane, hydrolysis of the product **3** produced **2** in 67% yield but none of **4**, showing that **3** had the structure $PhCH(SiEt_3)OSiMe_3$. Therefore derivatization both with water and $(CH_3)_3SiCl$ suggests that the anion is in the form of **2** at the instant of reaction with the derivatizing agent.

"Anti-Wittig" rearrangement of the usual type studied by Brook also takes place for **2**. Treatment of **2** in anhydrous diethyl ether with sodium–potassium alloy gave 100% **1** after 2-min contact, without observable evolution of hydrogen or attack on the alkali metal. The reaction, repeated in pentane, required 40 min for 99.5% completion. Since this is still much faster than the silyl-Wittig rearrangement it was of interest to add sodium–potassium alloy to the completely deprotonated product of the silyl-Wittig rearrangement, known to give only **2** upon neutralization, to see if **1** would still form. No **1** was observed after 24-hr treatment of the anion solution with sodium–potassium alloy. Thus, with sodium–potassium alloy, **2** is the preferred product when anions are equilibrated, and **1** the preferred product when neutral species are equilibrated. Catalytic quantities of *tert*-butyllithium also cause rearrangement of **2** to **1**. When 1 mmol of **2**, neat, was treated with 0.50 mmol of 1.25 *M* *tert*-butyllithium in pentane, 0.53 mmol of **1** was formed at equilibrium after 24 hr.

These rearrangements can be summarized in the following cyclic reaction scheme.[11]



Rearrangements of silylcarbinols and related compounds to alkoxysilanes have been explained as proceeding in the observed direction because of the stability of the Si–O bond in the product. This explanation may be valid when neutral species are equilibrated, as with sodium–potassium alloy. In our example the anions are equilibrated and the rearrangement proceeds in the opposite direction. We believe this is because the greater stability of the oxyanion *vs.* the carbanion outweighs the energy difference between the Si–O and C–O bonds. Further experiments should establish whether this is true for silylcarbinolate anions generally.[12]

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[11] However, it is also possible that the anion of **2** has a unique bridged structure, rather than being a simple alkoxide ion as drawn.

[12] Examples of probable 1,3 and 1,4 anionic rearrangements of silyl groups from O to C have also been found. See ref 9.

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On the Stereochemical Aspects of the Photochemistry of Mixed-Ligand Chromium(III) Complex Ions

Sir:

Some discussion is being generated[1,2] about the stereochemical implications of Adamson's empirical rules[3–6] governing the photolysis of nonoctahedral chromium(III) complexes. Some of our recent results have an important bearing on this subject.

The question is the extent to which the rules as stated by Adamson in a series of papers on Cr(III) photolysis[3–6] imply stereochemical consequences with regard to the course of photoreaction and the final configuration of the products. If one reads this series of papers carefully one is left with the definite impression that the author does expect such stereochemical consequences[5,6] despite his occasional denials that they are required by the rules.[5,6] The recent paper by Balzani[2] draws attention to this apparent inconsistency and to the question of whether the rules can be considered empirical should they not imply stereochemical consequences. It seems that the stereochemical question has not, however, been clearly separated into its components.

Fundamentally there are two points at issue, both meaningful and susceptible to experimental proof, at least in principle. They are as follows.

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[1] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 101.

[2] M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).

[3] A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

[4] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

[5] A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).

[6] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).

1. Does photochemical activation of a nonoctahedral Cr(III) complex result in labilization along the weak-field axis such that the particular strong-field ligand originally located on that axis becomes the leaving group?

2. Does the entering group adopt the same coordination position as was occupied by the leaving group, giving retention of stereochemical configuration?

These are the experimentally accessible questions. Previous statements of the problem have introduced questions of the electronic nature of the excited state, the coordination number and possible geometries of hypothetical transition states, etc., and these have served in part to obscure the basic problem.

The present author shares with Balzani the opinion that Adamson's suggestion of photochemical labilization on the weak-field axis requires a yes answer to question 1 or the corresponding rules have no meaning. However, careful reading of the papers by Adamson leaves little doubt that this was in fact his intention. Rather the dispute hinges on the second question, and it is here that our recent results are helpful.

Study of the photoaquation in acidic aqueous solution of *trans*-dichlorobis(ethylenediamine)chromium(III)[7] indicated that this ion underwent exclusive chloride aquation (quantum yield 0.32–0.35 in the wavelength range 540–400 nm), but the product chloroaquobis(ethylenediamine) ion was at least 70% in the cis configuration. This result is very similar to the findings for $[CrCl(NH_3)_5]^{2+}$ [2,8] and $[CrBr(NH_3)_5]^{2+}$,[9] where the product haloaquotetraammine species are in the cis configuration, but is considerably less ambiguous in interpretation. For *trans*-$[CrCl_2(en)_2]^+$, it is clear that the reaction mode was that expected for labilization along the Cl–Cl weak-field axis, in accord with Adamson's rules. (This was possibly also true for the cis complex, which showed predominantly ethylenediamine aquation, but again this result is ambiguous even were the isomer of the product known.) Since the position of the leaving group is known, the isomeric characterization of the product ($\geqslant$70% cis) gives a clear answer also to question 2. Thus, independent of any speculation about the configuration or coordination number of the transition state, the entering water molecule in effect attacks the complex trans to the leaving group at least 70% of the time. Cr(III) photoaquations may therefore show stereomobility, in contrast to the retention observed for thermal aquations.[10]

The corollary is that one cannot obtain unambiguous information about the position of the leaving group in these photoreactions by isomer characterization of products. While this fact has been tacitly recognized by Adamson, and probably forms the basis for his claims that his rules "are not required to imply stereochemical consequences,"[5] he has used the trans configuration of the product from $[Cr(NCS)(NH_3)_5]^{2+}$ photolysis to suggest that the ammonia trans to the thiocyanate is the leaving group. This may be correct but is not required by this evidence. Balzani's conclusion[2] that the ammonia cis to the chloride ion in $[CrCl(NH_3)_5]^{2+}$ is aquated photochemically because of the cis configuration of the product $[CrCl(H_2O)(NH_3)_4]^{2+}$ is equally invalid. If analogy to our results is valid, it suggests that the ammonia trans to the chloride ion may well be the leaving group, in accord with Adamson's rules, with the entering water adopting the cis position as a result of attack trans to the leaving ammonia.

We have at present no indication of the range of systems in which stereochemical change occurs in photoaquation other than for the systems *trans*-$[CrCl_2(en)_2]^+$ [7] and $[Cr(ox)_2en]^+$.[11] It is nevertheless appropriate to point out that of all the work published to date on Cr(III) photoreactions only one study, that of $[Cr(SCN)(NH_3)_5]^{2+}$,[6] is inconsistent with the possibility of complete or partial stereochemical change consequent upon photochemical excitation. Moreover, in this particular case the authors themselves appear to leave some room for doubt about the trans configuration of the product. It is therefore interesting to examine previous work on the supposition that photoaquation would be associated with stereomobility.

Adamson studied the photolysis of *cis*- and *trans*-$[Cr(OH)_2(en)_2]^+$.[3,12] The results for the cis compound showed ethylenediamine aquation with quantum yield (about 0.2) similar to that found for *cis*-$[Cr(Cl)_2(en)_2]^+$ (ϕ = 0.13). The main difference in behavior lay in the findings for the trans complexes, where *trans*-$[Cr(OH)_2(en)_2]^+$ showed isomerization with $\phi = 0.01$ (but $\phi = 0.3$ in acid solution for $[Cr(H_2O)_2(en)_2]^{3+}$, a more comparable result, owing to similar experimental conditions), while *trans*-$[CrCl_2(en)_2]^+$ showed only chloride aquation with $\phi = 0.32$, accmpanied by stereochemical change. The comparison suggests that the isomerization of *trans*-$[Cr(H_2O)_2(en)_2]^{3+}$ may occur by a water-exchange process associated with complete or partial stereochemical change. It is suggested that a measurement of the extent of water exchange in this system would reveal it as the major mechanism of isomerization. Otherwise it remains an anomaly that, apart from systems involving bidentate ligands, isomerization seems to be an important photochemical process only for complexes specifically having water as one of the ligands.

Again, a study of the photolysis of the reineckate ion[13] yielded evidence that the products of photoaquation differed spectrally from those obtained thermally, although the process in both cases involved thiocyanate aquation. This was ascribed by the authors to the simultaneous occurrence of photoaquation and photoisomerization (presumably of the reineckate ion itself, since an analogy is drawn with $[Cr(OH)_2(en)_2]^+$). However, retention of configuration during thermal aquation, and stereochemical change during the photoaquation, might provide the explanation for these observations.

It is seen that recognition of the possibility of stereomobility in photoaquation reactions can give a fresh interpretation to existing data. It is obviously of some importance to try to determine experimentally the extent to which stereomobility does in fact occur, and fur-

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[7] A. D. Kirk, K. C. Moss, and J. G. Valentin, manuscript in preparation.

[8] H. F. Wasgestian and H. L. Schlafer, *Z. Phys. Chem. (Frankfurt am Main)*, 57, 282 (1968).

[9] P. Riccieri and H. L. Schlafer, *Inorg. Chem.*, 9, 727 (1970).

[10] R. D. Archer, *Coord. Chem. Rev.*, 4, 243 (1969).

[11] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, in press.

[12] A. W. Adamson, *Advan. Chem. Ser.*, **No. 49**, 273 (1965).

[13] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

ther work will be undertaken along these lines. A most important point to be investigated is the precise ratio of cis and trans products to be found for specific systems involving stereomobility, since its extent is not certain either from our work or the studies of $[CrCl(NH_3)_5]^{2+}$. Resolution of the question of which ammonia molecule is lost in the photoaquation of $[CrX(NH_3)_5]^{2+}$ will have to depend not on product characterization but on experiments such as the photolysis of *trans*-$[CrX(NH_3)_4(^{15}NH_3)]^{2+}$.

It is the sincere hope of the author that this note helps resolve any confusion about the stereochemical implications of Adamson's rules and will also suggest new directions for future investigations.

Acknowledgment. I wish to express my thanks to A. W. Adamson and V. Balzani for useful past discussions and for supplying preprint copies of their work, and to my coworkers, K. C. Moss and J. G. Valentin, for their contributions to the experimental work quoted in this note.

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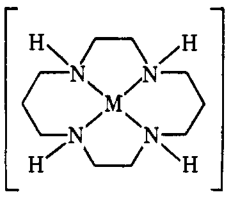
Nontemplate Synthesis of an Unsaturated Tetraaza[14]macrocycle and Its Metal(II) Complexes

Sir:

In recent years considerable effort has been directed toward development of convenient synthetic routes to macrocyclic polydentate ligands and their metal complexes.[1] The general class of compounds which has attracted the most interest is composed of 14-membered tetraaza ring systems, which are readily classified according to their degree of unsaturation: 1,4,8,11-tetraazacyclotetradecane complexes[2] (**1**) and C-methyl derivatives thereof,[3] *cis*- and *trans*- (**2**) -tetraazadiene complexes and their tetraimino oxidation products[3] (*e.g.*, **3**), substituted tetraazatetraene species[4] (**4**), and the "tetraazaannulenes" (**5**) of Jäger[5] and Hiller, *et al.*[6] The macrocycles shown in **2** and **5** are most efficiently synthesized by metal-ion-assisted reactions; but can be obtained in lower yield in the absence of metal ions.[3,6] The species **4** have thus far been obtained only by template reactions involving as the most common precursor a tetradentate ketoamine complex substituted with a carbonyl-containing group (R = alkyl, aryl, OEt) at the β positions.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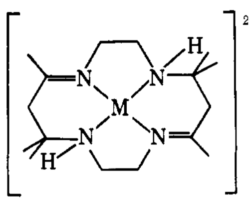
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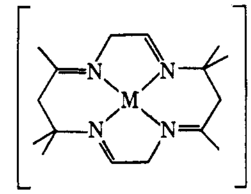
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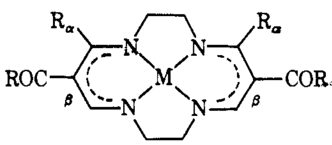
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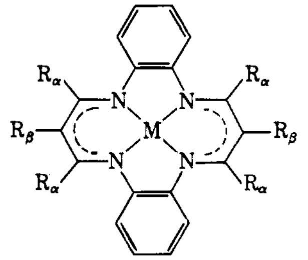
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In the course of a systematic investigation of the electronic properties and electrochemical and chemical redox reactions (including oxidative addition and reaction with molecular oxygen) of d^4–d^{10} metal ions in a planar N_4 ligand field, soluble neutral complexes with the degree of unsaturation in **4** or **5** but lacking potentially reactive functional groups were required. The low solubility of the parent complex[6] **5** ($R_\alpha = R_\beta = H$) and several substituted derivatives render them unattractive. Template reactions analogous to those[5,6] affording **5** (R_α, R_β = Me, Ph, H) have thus far not yielded the corresponding diethylene-bridged complexes lacking carbonyl-containing substituents at the β positions.[7] We report here a facile nontemplate synthesis of the basic macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13- tetraene (H_2(MeHMe-(en)$_2$, **7**) and its first row d^6–d^{10} complexes **8**.

4-Amino-3-penten-2-one (**6**, 0.30 mol) in 200 ml of dry dichloromethane was O alkylated by treatment with an equimolar amount of triethyloxonium tetrafluoroborate in 150 ml of dry dichloromethane under nitrogen for 30 min at ~25°. After dropwise addition of 0.15 mol of ethylenediamine over 30 min, the reaction was allowed to proceed at 25° for an additional 3 hr, the solvent removed (reduced pressure), and 400 ml of absolute methanol added. Sodium methoxide (0.30 mol) in 150 ml of methanol and 0.15 mol of ethylenediamine were introduced, and the reaction mixture was stirred (4 hr) as ammonia was evolved. After removal of methanol, extraction of the residue with absolute ethanol and recrystallization of the separated product from this solvent afforded pure **7**[9] (30–35%) as cream-colored platelets: mp 226–228°; pmr ($CDCl_3$, TMS reference) −1.95 (12, Me), −3.51 (8, CH_2), −4.58 (2, =CH−),

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[1] D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinatius Alfred Werner*, 174 (1967); J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," Elsevier, Amsterdam, 1968, pp 83–99.

[2] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

[3] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968), and references therein.

[4] E.-G. Jäger, *Z. Chem.*, **8**, 30, 470 (1968).

[5] E.-G. Jäger, *Z. Anorg. Allg. Chem.*, **364**, 177 (1969), and references therein.

[6] H. Hiller, P. Dimroth, and H. Pfitzner, *Justus Liebigs Ann. Chem.*, **717**, 137 (1968).

[7] For example, reactions of bis(acetylacetone)ethylenediiminemetal(II) complexes with ethylenediamine under forcing conditions (*i.e.*, refluxing in neat ethylenediamine for 2 days) did not result in cyclization. Failure to form ethylene-bridged macrocycles from these complexes has also been noted briefly by Bamfield,[8] whose work on template reactions of complexes derived from 2-hydroxymethylenecyclohexanone and 2-hydroxymethylenecyclohexa-1,3-dione further emphasizes the apparent necessity of β-carbonyl substituents for cyclization reactions involving ethylenediamine.

[8] P. Bamfield, *J. Chem. Soc. A*, 2021 (1969).

[9] *Anal.* Calcd for $C_{14}H_{24}N_4$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.83; H, 9.70; N, 22.65. All other new compounds also gave satisfactory elemental analyses.