of the calculated spectra to obtain the rates. At some temperatures visual comparison was found most effective in obtaining the rates. Rate constants (using the natural line shape) are shown in Table I.

**Table I**

| Temp, °C | $k$, sec$^{-1}$ | Method |
|---|---|---|
| −15.8 | 1.20 | Maximum–minimum ratios |
| −10.0 | 2.45 | Maximum–minimum ratios |
| −7.3 | 3.75 | Maximum–minimum ratios |
| −0.9 | 6.95 | Maximum–minimum ratios |
| +0.2 | 8.50 | Maximum–minimum ratios |
| 2.0 | 10 | Visual comparison |
| 5.5 | 13 | Visual comparison |
| 8.0 | 17 | Visual comparison |
| 12.3 | 34.2 | Half-height width |
| 19.5 | 54.7 | Half-height width |
| 23.0 | 79.0 | Half-height width |
| 30.0 | 132 | Half-height width |
| 49.0 | 550 | Visual comparison |
| 58.0 | 990 | Chemical shift |

A least-mean-square Arrhenius fit made by computer gave $E_A$ = 15.3 ± 0.2 kcal/mole and log $A$ = 13.2 ± 0.2,[8] where the errors quoted are standard deviations. The rate constants at 5, 13, and 55° for the $t$-amyl cation made from $t$-amyl alcohol with fluorosulfonic acid and antimony pentafluoride in sulfuryl chlorofluoride lay close to or on the best Arrhenius line through the data in Table I.

A further comment on the significance of the activation energy measured in this work is necessary. If, as has been suggested, the methide shift in step 2 is rate determining, then what has been measured is the sum of the energy difference between the secondary and tertiary ions and the activation energy for this methide shift. Since the activation energy for this methide shift, which is analogous to that in the pentamethylethyl cation, is probably less than 4 kcal, the tertiary–secondary ion enthalpy difference should then be 11–15 kcal/mole.

**Acknowledgment.** We wish to acknowledge support of this work by the National Science Foundation.

(8) D. M. Brouwer, *et al.*, report $E_A$ = 14.3 kcal/mole and log $A$ = 12.7, but gave no details: D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc.*, 147 (1964).
(9) Fellow of the Alfred P. Sloan Foundation.
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## Photosynthesis of Some Werner Complexes of Rhodium(III) and Iridium(III)

*Sir:*

Although much work has been done recently in elucidating mechanisms and products of inorganic photochemical reactions of metal complexes,[1] these reactions have not been used in the synthesis of Werner complexes. We wish to report a useful photochemical route for the preparation of mixed diacidobis(ethylene-

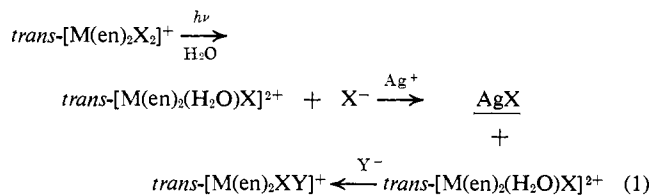(1) A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967), and references therein.

diamine) complexes of the type *trans*-[M(en)$_2$XY]$^{n+}$ (M = Rh(III), Ir(III)).

In contrast to the photochemistry of Co(III),[2] the photochemical substitutions of complexes of its congeners Rh(III) and Ir(III) are not complicated by reduction of the central metal atom, nor do *trans* → *cis* isomerizations occur in the complexes studied.

The compounds *trans*-[M(en)$_2$X$_2$]$^+$ (M = Rh(III), Ir(III); X = Cl, Br, I) in aqueous solution undergo rapid photosubstitutions to yield *trans*-[M(en)$_2$(H$_2$O)-X]$^{2+}$. The reactions are characterized by nearly quantitative yields and, where they exist during reaction, excellent isosbestic points in their ultraviolet absorption spectra are observed (Figure 1). In the presence of excess Br$^-$ and I$^-$, *trans*-[Ir(en)$_2$Cl$_2$]$^+$ reacts photochemically in aqueous solution at 25° to give *trans*-[Ir(en)$_2$Br$_2$]$^+$ and *trans*-[Ir(en)$_2$I$_2$]$^+$, respectively. *trans*-[Ir(en)$_2$Br$_2$]$^+$ and *trans*-[Ir(en)$_2$I$_2$]$^+$ with excess Cl$^-$ undergo photosubstitution reactions to yield the mixed *trans*-chlorobromo and -chloroiodo complexes, respectively. The yields in these cases are not quantitative, however, because of the formation of the corresponding aquo complexes as well.

Mixed complexes of this type are difficult to prepare by other methods because of the differing *trans*-labilizing effects for the halides (Cl < Br < I).[3] Thus the reaction of *trans*-[M(en)$_2$Cl$_2$]$^+$ with bromide or iodide yields the disubstituted complex exclusively. The complexes *trans*-[Rh(en)$_2$IX]$^+$ (X = Cl, Br) were prepared[3d] with difficulty by the thermal reaction of the diiodo complex with a large excess of X$^-$. The complexes are also very inert and, especially where M = Ir(III), require extended periods of time at high temperature to effect substitution.[4]

*trans*-[Ir(en)$_2$(H$_2$O)Cl](ClO$_4$)$_2$ was isolated in 34% yield from an irradiated (Vicor-filtered GEUA11 1200-W lamp) aqueous solution of *trans*-[Ir(en)$_2$Cl$_2$]-ClO$_4$. The aquo complex was prepared *in situ* photochemically for the preparation of other mixed chlorohalogeno complexes. The compounds prepared and their analyses appear in Table I. The general method of synthesis of *trans*-[M(en)$_2$XY]$^+$ is given by the reaction scheme

$$trans\text{-}[M(en)_2X_2]^+ \xrightarrow[H_2O]{h\nu}$$

$$trans\text{-}[M(en)_2(H_2O)X]^{2+} + X^- \xrightarrow{Ag^+} \underline{AgX}$$

$$+$$

$$trans\text{-}[M(en)_2XY]^+ \xleftarrow{Y^-} trans\text{-}[M(en)_2(H_2O)X]^{2+} \quad (1)$$

*trans*-[Ir(en)$_2$BrCl]ClO$_4$ was isolated in 60% yield by treating a solution of irradiated *trans*-[Ir(en)$_2$Cl$_2$]ClO$_4$ with 1 equiv of silver ion to remove the ionic chloride, and then by heating (100°, 30 min) with 1 equiv of bromide ion. *trans*-[Ir(en)$_2$ICl]ClO$_4$ was similarly prepared in 70% yield by the use of 1 equiv of iodide ion. *trans*-[Ir(en)$_2$IBr]ClO$_4$·H$_2$O was isolated in 75% yield from an irradiated solution of *trans*-[Ir(en)$_2$I$_2$]ClO$_4$ in a procedure similar to those above.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 664 ff.
(3) (a) H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.*, 1275 (1966); (b) H. L. Bott and A. J. Poë, *ibid.*, 205 (1967); (c) *ibid.*, 5931 (1965); (d) E. J. Bounsall and A. J. Poë, *ibid.*, 286 (1966).
(4) R. A. Bauer and F. Basolo, unpublished work.

Table I. Analyses of Compounds Prepared

| Compound | %C Calcd | %C Found | %H Calcd | %H Found | %N Calcd | %N Found |
|---|---|---|---|---|---|---|
| [Ir(en)$_2$(H$_2$O)Cl](ClO$_4$)$_2$ | 8.51 | 8.66 | 3.21 | 3.24 | 9.92 | 9.99 |
| [Ir(en)$_2$BrCl]ClO$_4$ | 9.11 | 9.12 | 3.06 | 2.89 | 10.63 | 10.70 |
| [Ir(en)$_2$ICl]ClO$_4$ | 8.36 | 8.54 | 2.81 | 2.89 | 9.76 | 9.94 |
| [Ir(en)$_2$IBr]ClO$_4$·H$_2$O | 7.55 | 7.57 | 2.85 | 2.72 | 8.80 | 8.86 |
| [Rh(en)$_2$BrCl]ClO$_4$ | 10.97 | 10.74 | 3.68 | 3.68 | 12.79 | 12.50 |
| [Rh(en)$_2$(ONO)Cl]ClO$_4$ | 11.89 | 11.64 | 3.99 | 3.96 | 17.33 | 17.21 |

trans-[Rh(en)$_2$(H$_2$O)Cl]$^{2+}$ was prepared in situ by irradiating an aqueous solution of trans-[Rh(en)$_2$Cl$_2$]-ClO$_4$. trans-[Rh(en)$_2$BrCl]ClO$_4$ was isolated in 80% yield by treatment of this solution with silver ion and bromide ion in the manner above. The ultraviolet spectra of both of these compounds agree with those published.[3b,c]
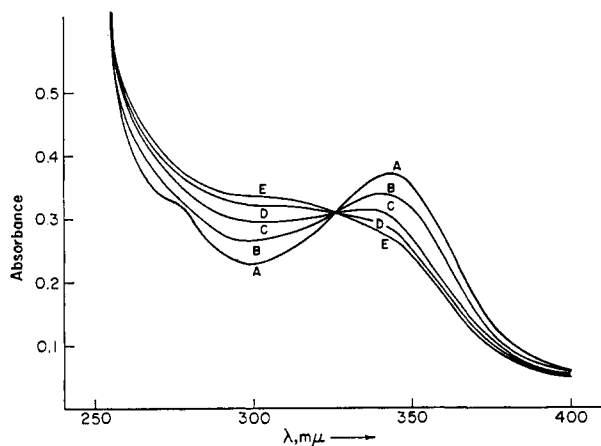


Figure 1. Spectral changes during the photoaquation of trans-[Ir(en)$_2$Cl$_2$]$^+$ in water at 25°. [Complex] = 0.0250 M. Curves A–E correspond to irradiation periods of 0, 500, 1500, 3500, and 7500 sec, respectively.

trans-[Rh(en)$_2$(ONO)Cl]ClO$_4$ was prepared from a photochemically produced solution of trans-[Rh(en)$_2$-(H$_2$O)Cl]$^{2+}$ by a method similar to that reported[5] previously for the synthesis of nitrito complexes. After irradiation of a solution of trans-[Rh(en)$_2$Cl$_2$]$^+$ and precipitation of the chloride ion as AgCl, the solution was acidified with HClO$_4$, cooled in an ice bath, and treated with excess NaNO$_2$. After 20 min the light yellow crystals were collected on a filter, washed with cold water, ethanol, and ether, and air-dried. At this low reaction temperature, the nitrito linkage isomer was isolated in 60% yield. The nitrito isomer rearranges to the more stable nitro isomer with a half-life of about 10 min at room temperature in water solution. The nitrito isomer also rearranges in the solid state with the following changes in infrared spectra (cm$^{-1}$): trans-[Rh(en)$_2$(ONO)Cl]ClO$_4$, 1435 (s), 828 (m); trans-[Rh(en)$_2$(NO$_2$)Cl]ClO$_4$ (rearranged), 1410 (s), 1415 (s), 832 (m), 812 (m); trans-[Rh(en)$_2$(NO$_2$)Cl]-ClO$_4$ (prepared by thermal replacement of Cl$^-$ in trans-[Rh(en)$_2$Cl$_2$]$^+$), 1410 (s), 1415 (s), 822 (m), 803 (m). The shifts of 10 cm$^{-1}$ in the 800-cm$^{-1}$ region of the same chloronitro compounds are apparently due to differing crystalline environments, since one was isolated from

(5) F. Basolo and G. S. Hammaker, Inorg. Chem., 1, 1 (1962).

aqueous solution and the other prepared by a solid-state reaction.

All complexes were determined to be trans isomers by their characteristic infrared spectra.[6]

Extensive application has been made of the photochemical syntheses of organometallic compounds.[7] More use should be made of this approach for the syntheses of Werner complexes, particularly complexes of the platinum metals which are often otherwise difficult to prepare.

(6) M. E. Baldwin, J. Chem. Soc., 4369 (1960).
(7) E. O. Fischer, J. P. Kögler, and P. Kuzel, Chem. Ber., 93, 3006 (1960); W. Strohmeier and K. Gerlach, Z. Naturforsch., 15b, 413 (1960); R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, J. Chem. Soc., 5916 (1963).

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## Bis(trimethylsilyldichloromethyl)mercury, a New and Useful Reagent in Synthetic Organosilicon Chemistry

Sir:

Much work has been devoted in the past 6 years to organomercury compounds of types PhHgCX$_3$, PhHg-CHX$_2$, and (XCH$_2$)$_2$Hg, which are capable of transferring CX$_2$, CHX, and CH$_2$, respectively, to olefins and other substrates.[1,2] However, thus far no functional carbene reagents of this type have been prepared. We report here the first such reagent, an organomercury compound which transfers Me$_3$SiCCl to olefins and Si–H compounds.

The recently reported trimethylsilyldichloromethyllithium[3] reacted with mercuric bromide at −135° in a solvent mixture containing tetrahydrofuran, methylal, diethyl ether, and pentane to give bis(trimethylsilyldichloromethyl)mercury, a white crystalline solid, mp 151–153°, in moderate (~35%) yield. Use of a deficiency of the lithium reagent resulted in formation of Me$_3$SiCCl$_2$HgBr, mp 132–135°.

A reaction was carried out in which a solution of 4.9 mmoles of (Me$_3$SiCCl$_2$)$_2$Hg, 5.2 mmoles of diphenylmercury,[4] and 0.1 mole of cyclohexene in 25 ml of

(1) D. Seyferth in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," Robert A. Welch Foundation, Houston, Texas, 1966, pp 89–135 (review).
(2) D. Seyferth and R. B. King, "Annual Surveys of Organometallic Chemistry," Elsevier Publishing Co., Amsterdam: Vol. 1, 1965, pp 44–45; Vol. 2, 1966, pp 55–56; Vol. 3, 1967, pp 66–69.
(3) D. Seyferth, F. M. Armbrecht, Jr., and E. M. Hanson, J. Organometal. Chem. (Amsterdam), 10, P25 (1967).