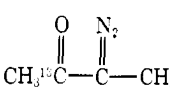
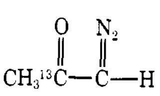
In a previous communication[7] we reported that the Wolff rearrangement extends to α-diazo esters as well, and the reaction occurs not only in solutions but also in the gas phase. The ketene formed subsequently undergoes *in situ* photolysis to yield carbon monoxide and a secondary carbene. The gas-phase reaction offers the distinct advantage that it is free from complications arising from possible solvent–carbene interaction and intervention of ionic intermediates. We therefore reexamined the reaction in the gas phase, using a symmetrical and an asymmetrical ^{13}C-labeled α-diazo ketone, both containing 55% ^{13}C.


$$CH_3{}^{13}\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle N_2}{\|}}{C}-CH_3$$

and


$$CH_3{}^{13}\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle N_2}{\|}}{C}-H$$

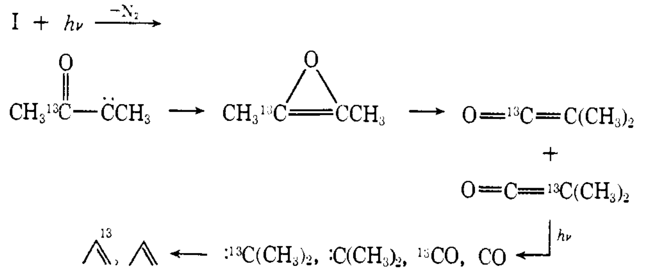
I

II

The photolysis of *ca.* 5 torr of I with 5 torr of 1-propanol (from which it could not be separated) was carried out using a 140-W lamp with a 2200 Å cutoff filter. Three major products resulted, N_2 and CO in equal yields and propylene, along with smaller amounts of ethane, ethylene, propane, and methane. The combined yield of the latter four products was about 40% of that of propylene.

High-resolution (MS-9) mass spectrometric analysis gave for the isotopic distribution of carbon monoxide, after correction for incomplete ^{13}C labeling in the starting material, 51.8% ^{13}CO and 48.2% ^{12}CO. Isotopic analysis of the propylene gave 48% ^{13}C-labeled propylene and 52% normal propylene. The ethylene product was also partially labeled, but the ethane contained no ^{13}C.

These results require the intervention of the oxiirene structure in the mechanism

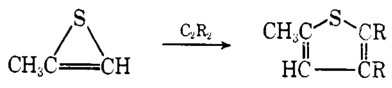


The precursor of ethane and methane is the methyl radical, and of ethylene, the vinyl radical, formed by some cracking reactions.

The photolysis of *ca.* 10 torr of II afforded N_2 and CO in not quite equal yields together with small amounts of H_2 and CH_4. The major component of the condensable fraction was ethylene, with acetylene (20%) and a few per cent each of ethane, propane, and propylene.

Isotopic analyses gave $^{13}CO = 84\%$ and $CO = 16\%$. Also 27% of the ethylene and 23% of the acetylene were ^{13}C labeled.

Thus we conclude that oxiirene is an intermediate in the gas-phase Wolff rearrangement of the α-keto carbenes from I and II. With the symmetrical dimethyloxiirene all the initially formed carbenes undergo cyclization, and ring opening is equally possible on either side. With the asymmetrical monomethyloxiirene, ring opening preferentially occurs on the hydrogen side, a trend which has been observed with thiirene.



The exact cause of the discrepancy with earlier results is not clear. It may be due to solvent effects, substituent effects, pressure effects, or to a difference in the excess energy of the initial carbene. It is hoped that further studies currently in progress will shed light on these questions.

Preparation of I. $CH_3{}^{13}COONa$ (Merck 55% ^{13}C) was treated[8] with $POCl_3$ to give $CH_3{}^{13}COCl$ which was further treated with a 1-propanol–ether solution of diazoethane.[9] The excess solvent was evaporated and the residue distilled under vacuum. Ir and mass spectrometric analyses indicated the presence of about 50% 1-propanol, which could not be removed by distillation.

Preparation of II. The $CH_3{}^{13}COCl$ was allowed to react with excess diazomethane and after the solvent was removed by evaporation II was subjected to low-temperature distillation.

Both I and II contained 55% ^{13}C.

Acknowledgment. The authors are grateful to the National Research Council of Canada for financial support.

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(9) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

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The Aquorhodium(II) Ion

Sir:

Extensive work[1] on the polarographic behavior of aquo, halo, and ammine complexes of rhodium(III) has failed to yield unequivocal proof of the existence of the corresponding rhodium(II) complexes. Several compounds containing Rh(II) have been prepared, among them $Rh(CH_3CO_2)_2$[2,3] together with related substances[4,5] and a number of compounds in which back-bonding ligands are coordinated to Rh(II).[6,7]

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(1) See, for example, P. Beran and J. Dolezal, *Collect. Czech. Chem. Commun.*, **23**, 608 (1958); D. Cozzi and F. Pantani, *J. Inorg. Nucl. Chem.*, **8**, 385 (1958); M. B. Bardin and V. I. Shapiro, *Uch. Zap. Kishinevsk. Gos. Univ.*, **68**, 64 (1963); R. J. Magee and W. H. Douglas, *J. Inorg. Nucl. Chem.*, **26**, 1707 (1964); G. Van Loon and J. A. Page, *Talanta*, **12**, 227 (1965); R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 4107 (1965).

(2) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

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The acetato complex has been shown by X-ray investigation to be dimeric,[8] and the existence of a metal–metal bond in the dimer can reasonably be inferred from the structure. The other compounds, with one exception,[9] are probably dimeric as well and may also feature metal–metal bonds. The stability of the metal–metal bond in a complex containing only saturated ligands is a matter of considerable interest. The existence of compounds such as $Rh_2(CH_3CO_2)_4$ does not detract from this interest because here the stability of the metal–metal bond is obscured by the fact that the ligand bridges the two metal centers.

The experiments which will be described indicate that the hydrated ion Rh_2^{4+} exists and that it is kinetically a rather stable species. It is generated by the reaction of $Cr^{2+}(aq)$ with $Rh(H_2O)_5Cl^{2+}$, a reaction which proceeds rapidly and essentially quantitatively according to the stoichiometry

$$2Rh(H_2O)_5Cl^{2+} + 2Cr^{2+} = Rh_2(H_2O)_{10}^{4+} + 2CrCl^{2+}$$

The reaction seems to be rather specific and is not paralleled by other chlororhodium(III) complexes with Cr^{2+} or by $RhCl^{2+}$ with V^{2+}, Eu^{2+}, or V(II) $EDTA^{2-}$, all of which produce elementary rhodium. The action of Cr^{2+} on $Rh(NH_3)_5Cl^{2+}$ was found to be very much slower than on $RhCl^{2+}$, and no interesting new species was observed.

The ion $RhCl^{2+}$ was prepared as described elsewhere[10] and was separated on a cation-exchange column from which it was eluted with 1 *M* $HClO_4$. Solutions containing Cr^{2+} were prepared by Zn reduction. For all of the air-sensitive operations, including chromatographic separations, N_2 or Ar was used as a blanketing gas. Except for the Cl^- initially bound to Rh(III), ClO_4^- was the only anion present in the reaction solutions. The experiments were done at room temperature, *ca.* 25°.

The reactant solutions were made up to contain $RhCl^{2+}$ and $HClO_4$ at the 1.5×10^{-3} and 1.0 *M* concentration levels, respectively, and in different experiments the amount of Cr^{2+} added was varied, covering for the ratio $(Cr^{2+})/(RhCl^{2+})$ the range 0.5–4.0. With this concentration ratio equal to 1.00, the solution turns green immediately, and the product solution shows absorption bands at 630, 415, and 250 mμ. The intensity of the new bands is not changed by raising the ratio $(Cr^{2+})/(RhCl^{2+})$ to 2 or to 4, except for the contribution to the absorption by Cr^{2+}, but is reduced if the ratio is less than 1.0. These observations demonstrate the 1:1 stoichiometry. It should be noted that if a large excess of Cr^{2+} is used, further reduction does proceed and rhodium metal is formed slowly.

The product solution made up with the reactants at equal concentrations was separated using a cation-exchange resin (Dowex 50W-X2). With 1 *M* $HClO_4$ as eluent, a broad band was separated which had a spectrum identical with that of $CrCl^{2+}$,[11] showing absorption bands at 610 and 427 mμ.

Taking the values of the extinction coefficients to be 16.3 and 20.6, respectively, the measurements of absorption showed that the Cr^{2+} which reacted was converted quantitatively (±10%) to $CrCl^{2+}$. With 3 *M* $HClO_4$ as eluent, a second compact green band was eluted having absorption bands at 630 mμ (ϵ 39.8), 412 (59.1), and 250 (10.6×10^3). The chromatographic behavior indicates that the charge on the second species is greater than 3+ (both $Cr(H_2O)_6^{3+}$ and $Rh(H_2O)_6^{3+}$ are eluted more readily than is the new species).

The charge carried per rhodium was determined by the method of Cady and Connick.[12] Acidified cerium(III) perchlorate was used as eluent. In one experiment the solution eluted contained Ce^{3+}, Rh(II), and H^+ at the concentrations 0.0826, 0.0057, and 0.500 *M*, respectively, and yielded 1.95 for the charge per rhodium atom. An earlier experiment, less accurate because it was a trial run, yielded the value 1.6. The concentrations of Ce^{3+} and rhodium were determined spectrophotometrically, after the solution was treated with chlorine to oxidize Rh(II) to $RhCl^{2+}$.

The magnetic susceptibility of the Rh(II) was determined by the proton nmr technique.[13] As before, the Rh(II) species was separated on a cation-exchange column. Using 1 *M* H_2SO_4 as eluent, a solution was obtained which was 0.294 *M* in Rh(II). The solution containing Rh(II) proved to be slightly paramagnetic as compared to a reference solution 1 *M* in H_2SO_4 (each solution contained 2% *t*-butyl alcohol by volume). If the paramagnetic component is assumed to have a spin of $^1/_2$ per Rh(II), the shift observed corresponds to 6% of the rhodium being present in the paramagnetic form. The Rh(II) species, it should be noted, is eluted freely by H_2SO_4, presumably because substitution is facile and the species is converted to a sulfate complex. Using a solution 0.3 *M* in $La(ClO_4)_3$ and 1.0 *M* in $HClO_4$, the eluent solution was found to contain 0.026 *M* Rh(II). Again this solution was found to be slightly paramagnetic relative to the elutrient reference solution and, on making the calculations as above, we found that 10% of the Rh(II) in this solution was present in the paramagnetic form.

The new species contained in the second fraction is fairly stable if stored under N_2. It is oxidized slowly by air, rapidly and quantitatively to $Rh(H_2O)_6^{3+}$ by Ce(IV), and also by Cl_2 and Br_2, yielding $Rh(H_2O)_5Cl^{2+}$ and $Rh(H_2O)_5Br^{2+}$. The spectrum of the latter, heretofore unreported, shows bands at 345 and 442 mμ; the reported bands for the aquo and the monochloro complexes lie at 311, 396 mμ and 335, 426 mμ, respectively.

As already suggested by the elution behavior with H_2SO_4, the new species reacts readily with ligands. If NaOAc is added to bring the pH to ~6, the color changes to a deeper green, and the bands in the visible region shift to 445 and 587 mμ; the new spectrum is similar to that reported for $(Rh(OAc)_2H_2O)_2$ (447, 587 mμ).[2] We failed in attempts to obtain a crystalline solid from this solution at room temperature, but, when the solution was heated on a steam bath for 5 min, a dark green crystalline powder precipitated. This solid could be recrystallized from acetone, and, in terms of spectrum and chemical behavior in different solvents, resembles $Rh_2(OAc)_4$,[2] except in the behavior with py

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[8] M. A. Porai-Koshitz and A. S. Antsyshkina, *Dokl. Akad. Nauk SSSR*, **146**, 1102 (1962).

[9] E. Billig, S. I. Shupack, J. H. Waters, R. W. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 926 (1964).

[10] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

[11] H. B. Johnson and W. L. Reynolds, *ibid.*, **2**, 468 (1963).

[12] H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, 80, 2646 (1958).

[13] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

added where, contrary to earlier reports, we find the product of the interaction to be quite soluble.

Taking into account the stoichiometry of the reaction producing the new species, its spectrum, its cation-exchange behavior, and the magnetic susceptibility, we conclude that the dominant form must be formulated as Rh_2^{4+}. The hydrated ion is presumably $Rh_2(H_2O)_8(H_2O')_2^{4+}$, but the supposition as to its formula awaits confirmation by isotopic studies. These are planned, and further work on the properties of the new species is in progress. Important in this program are more detailed studies of the magnetic susceptibility which indicates that the equilibrium

$$Rh^{4+} = 2Rh^{2+}$$

is a significant aspect of the behavior of the system.

In view of the existence[14] of binuclear carboxylates of Mo(II), it seems likely that an aquo ion analogous to that described for Rh(II) exists for molybdenum as well.

Acknowledgment. Financial support by the Atomic Energy Commission, Contract No. At 04 3 326, P.A. 6 Mod. 6, and by the Consiglio Nazionale Delle Ricerche Fellowship of Italy to F. M. is gratefully acknowledged.

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(15) On leave from Università di Roma.

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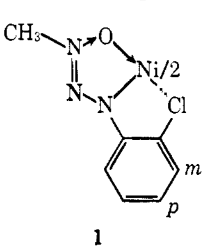
Coordination by the Chloro Group. Intramolecular Planar ⇌ Octahedral Equilibrium in a Nickel Complex

Sir:

A novel example of the intramolecular solution equilibrium[1]

$$\text{planar } (S = 0) \rightleftharpoons \text{octahedral } (S = 1) \qquad (1)$$

is provided by the substituted triazene 1-oxide[2] chelate of Ni(II), **1** (the dotted line is used to indicate that the chlorine atom may ($S = 1$) or may not ($S = 0$) be coordinated). Intramolecular equilibria of this kind are



1

known in a few cases, *e.g.*, in some salicylaldimines.[4] However, none of these involves halogen coordination. The chloro group attached to a benzene ring will normally be recognized as a very poor donor. The uniqueness of **1** lies in this group demonstrably acting as a labile coordination site for Ni(II).

The olive-green complex **1** is synthesized by reacting the ligand[5] with nickel acetate in aqueous alcoholic solution. In Nujol mull, it shows only one electronic band in the visible region at 710 mμ. It is diamagnetic and hence planar in the crystalline state. However, its greenish brown solution in chloroform is "partially" paramagnetic, the magnetic moment[6] being ~2 BM at 32°. The solution shows two electronic bands at 725 and 1095 mμ having molar extinction coefficients (ϵ) of 62 and 24 l. mole^{-1} cm^{-1}, respectively. The behavior of **1** in benzene solution is similar except that the concentration of the triplet species is appreciably less. In this solvent, the 1095-mμ band strictly follows Beer's law in the concentration range 0.005–0.05 *M*. The osmometric (37°) molecular weight of **1** in benzene is 434 (calcd 428).

These data strongly suggest the existence of equilibrium 1 in the above solutions. In chloroform solution, many planar Ni(II) chelates of triazene 1-oxides show a singlet–singlet band at ~730 mμ (ϵ ~110).[7] On this basis, the observed ϵ (725 mμ) of **1** suggests a ~57% population of the singlet state at 32°. If the reasonable[4] assumption is made that the octahedral form of **1** has a magnetic moment of ~3.2 BM, the observed moment (2 BM) agrees reasonably well[8] with the above population. The 1095-mμ band is assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) transition[9] assuming effective octahedral symmetry for the triplet species. In nickel complexes having strict O_h symmetry, ν_1 generally has[10] $\epsilon < 5$. The relatively high intensity in the present case is indicative of considerable deviation from O_h symmetry.[11] A parallel situation exists in some other hexacoordinated nickel chelates derived from tridentate ligands.[4]

An important evidence in favor of coordination by the chloro group in **1** is provided by the observation that the corresponding chelates having a chloro group in *meta* or *para* position show no spectral or magnetic evidence for any appreciable population of the triplet state, *e.g.*, the *m*-chloro complex shows only a singlet–singlet band at 730 mμ (ϵ 110) in benzene. In these cases *intramolecular* chloro coordination is not possible

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(1) The words "planar" and "octahedral" are not used in strict sense.

(2) This formulation is supported by ir data.[3]

(3) T. Mitsuhasi, Y. Osamura, and O. Simamura, *Tetrahedron Letters*, 2593 (1965); A. Chakravorty, B. Behera, and P. S. Zacharias, *Inorg. Chim. Acta*, 2, 85 (1968).

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(5) S. M. Dugar and N. C. Sogani, *J. Indian Chem. Soc.*, 43, 289 (1966).

(6) Measurements were done by an nmr method: D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(7) B. Behera and A. Chakravorty, submitted for publication.

(8) % planar species = $\{1 - (2^2/(3.2)^2)\} \times 100 \approx 61$.

(9) Of the other two crystal-field transitions, *viz.* $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), ν_3 is most probably hidden under the tail of an intense allowed transition (340 mμ ($\epsilon \sim 9000$)) centered mainly in the ligand. We did not get any direct evidence for ν_2 (expected in the 600–700-mμ region) either. However we strongly suspect that it is hidden under the envelope of the relatively intense 725-mμ band of the singlet species. Strong supporting evidence is provided by the methoxyl analog (*i.e.*, OCH_3 in place of Cl in **1**). In benzene or chloroform solution, this monomeric chelate is ~100% in the octahedral triplet state (methoxyl coordination). Two broad bands at 1180 and 690 mμ are observed. These are assignable to ν_1 and ν_2, respectively. The shape of the 1180-mμ band is very similar to that of the 1095-mμ band of **1**.

(10) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 887 (1956).

(11) We believe that the tridentate ligand in **1** is meridionally disposed in the octahedral configuration. The resulting *cis* geometry has no center of symmetry. In addition to intensification, this may cause splitting of bands. We have evidence that the 1095-mμ absorption consists of at least two overlapping components. The possibility that the high-spin chelate is five-coordinated (coordination by only one of the chloro groups) was considered. However, the balance of spectral evidence favors six-coordination.