Reactions of Coordinated Ligands. II. Azide and Dinitrogen Complexes of Ruthenium[1]

P. G. Douglas and R. D. Feltham*

Contribution from the Department of Chemistry,
The University of Arizona, Tucson, Arizona 85721. *Received November 29, 1971*

Abstract: The reactions of coordinated nitrosyl, azide, and dinitrogen ligands with Lewis acids and bases have been investigated. The coordinated nitrosyl group of *trans*-[RuClNO(das)$_2$]Cl$_2$ (das is *o*-phenylenebis(dimethylarsine)) reacts with azide, and the coordinated azide group of *trans*-[RuN$_3$Cl(das)$_2$] reacts with NO$^+$ *via* a cyclic species, N$_4$O. The course of these reactions was followed by isotopic substitution, ir, and nmr spectroscopy. Improved methods of preparation of *trans*-[RuClN$_2$(das)$_2$]$^+$ are discussed. The dinitrogen complex was found to be inert to reduction and oxidation. The photochemical and acid reactions of *cis*-[Ru(N$_3$)$_2$(das)$_2$] have also been studied.

We have shown[1] that coordinated nitrosyl and azide ligands will react with a variety of reagents to form new ligands including N$_2$, NO$_2^-$, and PhNHN$_2$O. The present work was undertaken to determine the scope of these reactions, to elucidate the reaction paths for the interconversion of these nitrogen-containing ligands, and to devise improved preparations for the compounds, *trans*-[RuN$_3$Cl(das)$_2$] and *trans*-[RuClN$_2$(das)$_2$]$^+$ (das is *o*-phenylenebis(dimethylarsine)).

Experimental Section

RuCl$_3\cdot$H$_2$O was purchased from the Bishop Chemical Co. [Ru(^{15}NN$_2$)Cl(das)$_2$] and *trans*-[RuClNO(das)$_2$]Cl$_2$ were prepared as previously described.[1] Azido complexes were protected from light to prevent photochemical decomposition. Infrared spectra were recorded on a Perkin-Elmer 337 or Beckman IR 12 spectrometer. The conductivity measurements were made using an Industrial Instruments Inc. conductivity bridge, Model RC-16B2. Proton nmr spectra were obtained from a Varian A-60, T-60, or HA-100 spectrometer. Mass spectra were recorded on an Hitachi-Perkin-Elmer Model RMU-6e double-focusing mass spectrometer. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz., and by Huffman Laboratories, Wheatridge, Colo.

***trans*-Azidochlorobis[*o*-phenylenebis(dimethylarsine)]ruthenium(II).** A total of 3.07 g of *trans*-[RuClNO(das)$_2$]Cl$_2$ was dissolved in water (450 ml) and sodium azide (8 g) was added. The resultant solution was heated to its boiling point and cooled, and the yellow precipitate filtered, washed with water, and dried over P$_4$O$_{10}$; yield 2.26 g or 79% based on the nitrosyl complex. The product was shown to be identical with an authentic sample of *trans*-[RuN$_3$Cl(das)$_2$] by its infrared spectrum, nmr spectrum, and by its chemical reactions. The gases evolved during the reaction were collected (1.85 mol per g-atom of Ru) and shown to consist of N$_2$ and N$_2$O in a ratio of 1.00/1.00.

***trans*-Chlorodinitrogenbis[*o*-phenylenebis(dimethylarsine)]ruthenium(II) Hexafluoroantimonate.** Nitronium hexafluoroantimonate (9 g) was added in portions to a stirred suspension of *trans*-[RuN$_3$Cl(das)$_2$] (2.26 g) in methanol (180 ml). The precipitate was filtered and recrystallized from acetone–water (with charcoal) to give the desired product as a white powder, yield 1.89 g or 64% based on the azide complex.

Anal. Calcd for C$_{20}$H$_{32}$As$_4$ClF$_6$N$_2$RuSb: C, 24.7, H, 3.4; Cl, 3.7; N, 2.9. Found: C, 25.5; H, 3.4; Cl, 3.9; N, 2.6.

trans-[RuCl(^{15}NN)(das)$_2$][SbF$_6$] was similarly prepared from *trans*-[Ru[^{15}NN$_2$)Cl(das)$_2$]. The isotopic purity of this sample was determined from its ir and mass spectra.

Action of Hydroxylamine on *trans*-[RuClNO(das)$_2$]Cl$_2$. (1) *trans*-[RuClNO(das)$_2$]Cl$_2$ (0.22 g) was dissolved in water (50 ml). To this solution was added a solution of NH$_2$OH$\cdot$HCl (0.15 g) and KOH (0.095 g) in water (10 ml). To the resultant solution, aqueous KOH (0.30 g in 20 ml) was added dropwise. The yellow-orange precipitate which formed was removed by filtration and washed with water, yield 0.075 g. This material showed weak absorption bands in the ir spectrum at 2130.5 and 2222 cm^{-1}. (2) A suspension of NH$_2$OH$\cdot$HCl (0.165 g) and NaOCH$_3$ (0.065 g) in methanol (10 ml) was stirred for 10 min. The filtered solution was added to a solution of *trans*-[RuClNO(das)$_2$]Cl$_2$ (0.215 g) in methanol (20 ml). After 20 hr a yellow precipitate had formed. This solid was separated by filtration, washed with methanol, and dried, yield 0.150 g. The ir spectrum was identical with that of authentic *trans*-[RuCl$_2$(das)$_2$].

Anal. Calcd for C$_{20}$H$_{32}$As$_4$Cl$_2$Ru: C, 32.3; H, 4.3; Cl, 9.5. Found: C, 32.4; H, 4.5; Cl, 9.9; N, 0.1.

Action of HCl on *trans*-[RuN$_3$Cl(das)$_2$]. Dry HCl gas was passed through a suspension of *trans*-[RuN$_3$Cl(das)$_2$] (0.9 g) in methanol (200 ml) for 30 min. The filtered pale green solution was evaporated to dryness. To the residue were added methanol (28 ml), water (16 ml), and activated charcoal. After 5 min, the suspension was filtered and a solution of NaBPh$_4$ (1 g) in methanol (5 ml) was added to the filtrate. The resultant cream precipitate was separated and dried. Careful recrystallization from acetone–water gave two crops of crystals.

The first crop consisted of pale cream plates (0.30 g) of *trans*-[RuClN$_2$(das)$_2$][BPh$_4$]. The diamagnetic complex was dried at 100° over KOH for 2 days.

Anal. Calcd for C$_{44}$H$_{52}$As$_4$BClN$_2$Ru: C, 50.1; H, 5.0; Cl, 3.4; N, 2.7. Found: C, 50.8; H, 5.1; Cl, 3.4; N, 2.3.

The second crop consisted of pale cream needles of *trans*-[RuClNH$_3$(das)$_2$][BPh$_4$] which were dried at 100° over KOH for 2 days. The compound is diamagnetic.

Anal. Calcd for C$_{44}$H$_{55}$As$_4$BClNRu: C, 50.6; H, 5.4; Cl, 3.4; N, 1.1; O, 0.0. Found: C, 50.7; H, 5.2; Cl, 3.4; N, 1.4; O, 0.0. In some preparations the separation of the two products was not complete after one recrystallization and a second recrystallization was required.

***cis*-Diazidobis[*o*-phenylenebis(dimethylarsine)]ruthenium(II).** A mixture of *cis*-[RuCl$_2$(das)$_2$] (1.4 g) and NaN$_3$ (7 g) in 2-methoxyethanol (150 ml) was refluxed for 4.5 hr in a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue extracted with water, leaving the desired product as a yellow powder (1.15 g).

Anal. Calcd for C$_{20}$H$_{32}$As$_4$N$_6$Ru: C, 31.7; H, 4.3; N, 11.1. Found: C, 31.5; H, 4.4; N, 10.9.

***trans*-Dichlorobis[*o*-phenylenebis(dimethylarsine)]ruthenium(II).** A mixture of RuCl$_3\cdot$H$_2$O (0.6 g), *o*-phenylenebis(dimethylarsine) (1.3 g), water (15 ml), and ethanol was heated under reflux for 5 min. The yellow-green precipitate was removed by filtration and washed with ethanol, yield, 0.58 g.

Anal. Calcd for C$_{20}$H$_{32}$As$_4$Cl$_2$Ru: C, 32.3; H, 4.3; Cl, 9.5. Found: C, 32.0; H, 4.5; Cl, 10.1. This reaction was reported in the literature[2] to yield a compound which was identified from its solubility as the cis isomer.

Results and Discussion

Preparation of *trans*-[RuN$_3$Cl(das)$_2$]. Previously, we have prepared [RuClN$_2$(das)$_2$]$^+$ by the action of NO$^+$ on the coordinated azide group in *trans*-[RuN$_3$Cl(das)$_2$].

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(1) For part I, see P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

(2) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 567 (1958).

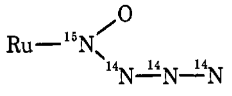
In order to explore possible effects of coordination on the reactions of the NO and azide groups, the reaction of the coordinated nitrosyl group with the azide ion was explored. Reaction of *trans*-$[RuClNO(das)_2]Cl_2$ with an excess of sodium azide produced *trans*-$[RuN_3Cl(das)_2]$ in high yield according to eq 1. The gases pro-

$$[RuClNO(das)_2]^{2+} + 2N_3^- \longrightarrow [RuN_3Cl(das)_2] + N_2 + N_2O \quad (1)$$

duced in this reaction (1.85 mol/g-atom of Ru) were collected and separated by standard vacuum line techniques. The gas consisted of equal amounts of N_2 and N_2O, and their identity was established by mass spectroscopy. When *trans*-$[RuCl(^{15}NO)(das)_2]Cl_2$ was allowed to react with NaN_3, the azido complex which was produced contained no ^{15}N. An examination of the infrared spectrum of the N_2O obtained from this reaction showed it to consist of approximately equal amounts of $^{14}N^{14}NO$ and $^{14}N^{15}NO$. No evidence was found for the presence of either $^{15}N^{14}NO$ or $^{15}N^{15}NO$. Other nitrosyl complexes of ruthenium[3] and iron[4] also react with N_3^- with the consequent formation of N_2 and N_2O.

In the absence of a coordinated metal ion, NO^+ and azide will react producing equal amounts of N_2 and N_2O. This reaction has been utilized for the quantitative determination of azide ion. The intermediate N_4O has been proposed for this reaction,[5] and in fact a yellow nitrosyl azide has been reported isolated from the reaction between $NOHSO_4$ and NaN_3.[6]

Attack on the coordinated ^{15}NO could reasonably lead to two types of intermediates and/or transition states A and B. Decomposition of species A leads to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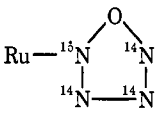
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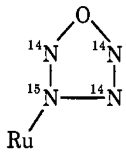
equal amounts of N_2 and of N_2O isotopically substituted exclusively at the central position, $^{14}N^{15}NO$. The cyclic species can decompose while attached to the ruthenium or be lost into solution with subsequent decomposition. In either case, both isotopically substituted and unsubstituted nitrous oxide would be obtained ($^{14}N^{14}NO$ and $^{14}N^{15}NO$). The fact that both of these nitrous oxide species were obtained from this reaction indicates that the N_4O species formed in this reaction is cyclic at some stage of its existence. The fact that the two nitrous oxide species were formed in approximately equal amounts favors a reaction sequence in which a cyclic intermediate is lost into the bulk of the solution followed by decomposition into N_2 and N_2O, since the presence of a coordinated ruthenium atom should produce unequal amounts of these two nitrous oxide species. The presence of unequal amounts of $^{14}N^{15}NO$ and $^{14}N^{14}NO$ would prove that decomposition of the N_4O species was taking place while still coordinated to the ruthenium. However, the experimental uncertainties are too large (± 10%) to allow a final conclusion to be drawn regarding the stage at which N_4O decomposes.

The related reaction between coordinated azide and uncoordinated NO^+ has also been studied. When the reaction is carried out between terminally labeled[7] *trans*-$[Ru(^{15}NN_2)Cl(das)_2]$ and NO^+, the dinitrogen complex, *trans*-$[RuCl(N_2)(das)_2]^+$, is formed which contains both $^{15}N^{14}N$ (80%) and $^{14}N^{14}N$ (20%). The fact that different products are obtained from this reaction than from the reaction described above clearly shows that an identical intermediate is not formed. These differences are also not due to subsequent reactions with NO^+ since we have found that one possible common intermediate, $[RuClN_2(das)_2]^+$, will not react with either NO^+ or N_3^- under the experimental conditions used for these reactions. However, a closely related cyclic mechanism can also be invoked in this case. Attack on the coordinated azide group could lead to cyclic species C. Decomposition could then lead to


C

the dinitrogen complex in which the ^{15}N is still bound to the metal. Unfortunately, it was not possible to analyze the gases from this reaction due to extensive decomposition of $NOPF_6$ under the conditions used.

Preparations of *trans*-$[RuClN_2(das)_2]^+$. The preparation of this compound which we have previously described involves separation of the desired product from two other compounds. A better method of preparation has now been developed. The azide complex, *trans*-$[RuN_3Cl(das)_2]$, undergoes reaction with NO_2SbF_6 to produce the dinitrogen complex. This material is formed with few impurities and is readily purified by recrystallization. The proton nmr spectrum of this product shows that the complex still has the trans configuration (Table I). Two chemical routes for this reaction suggest themselves

$$[RuN_3Cl(das)_2] + NO_2^+ \longrightarrow [RuCl(N_2O)(das)_2]^+ + N_2O \quad (2)$$

followed by $[RuCl(N_2O)(das)_2]^+ \rightarrow [RuClN_2(das)_2]^+$ and

$$[RuN_3Cl(das)_2] + NO_2^+ \longrightarrow [RuClN_2(das)_2]^+ + 2NO \quad (3)$$

Table I. CH_3^- Nmr Data for Some Ruthenium Complexes of *o*-Phenylenebis(dimethylarsine)

Compound		Solvent
trans-$[RuClN_2(das)_2]PF_6$	1.84,[a] 1.88	DMSO-d_6[b]
trans-$[RuClN_2(das)_2]SbF_6$	2.26, 2.30	DMSO-d_6[b]
trans-$[RuClN_2(das)_2]BPh_4$	1.73, 1.76	CH_2Cl_2[c]
trans-$[RuClNH_3(das)_2]BPh_4$	1.49, 1.66	CH_2Cl_2[c]
trans-$[RuCl_2(das)_2]$	1.35	$CDCl_3$[c]
cis-$[RuCl_2(das)_2]$	1.07, 1.55, 1.78, 1.82	CH_2Cl_2[c]
cis-$[Ru(N_3)_2(das)_2]$	0.99, 1.49, 1.80, 1.93	CH_2Cl_2[c]

[a] All peaks are singlets. [b] External tetramethylsilane. [c] Internal tetramethylsilane.

In order to gain further information about this reaction, the reaction between NO_2SbF_6 and *trans*-$[Ru(^{15}NN_2)(das)_2]$ was investigated. The dinitrogen complex obtained from this reaction consisted of *trans*-

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(3) F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971).

(4) R. D. Feltham and E. Leicht, unpublished results.

(5) G. Stedman, *J. Chem. Soc.*, 1702 (1960).

(6) H. W. Lucien, *J. Amer. Chem. Soc.*, 80, 4458 (1958).

(7) See ref 1. Since this and all the following reactions lead to retention of most or all the ^{15}N in the complex and to retention of the Ru–^{15}N bond, it has been concluded that ^{15}N is bound to ruthenium in the azide complex, even though direct evidence regarding this point is lacking.

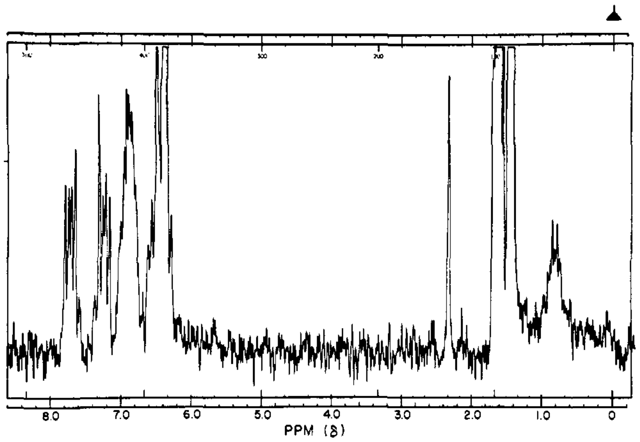

Figure 1. The proton nmr spectrum (60 MHz) of compound II.

$[RuCl(^{15}N^{14}N)(das)_2]^+$. Moreover, infrared studies of this material show that when first obtained, the ^{15}N is still bound to the ruthenium.[8] Several examples are now known in which N_2O reacts with a complex producing a coordinated dinitrogen ligand.[9-12] Such reactions presumably proceed through an intervening complex of nitrous oxide, and in fact a stable nitrous oxide complex of ruthenium has recently been isolated.[12,13] Attempts were made to verify the formation of the dinitrogen complex *via* the N_2O complex (eq 2), by preparing the N_2O complex, $[RuCl(N_2O)(das)_2]^+$, or the dinitrogen complex directly. None of the ruthenium(II) complexes of *o*-phenylenebis(dimethylarsine) were found to undergo reaction with N_2O. However, the reaction of the nitrosyl complex with hydroxylamine could conceivably lead to an N_2O complex. By allowing *trans*-$[RuClNO(das)_2]Cl_2$ to react with NH_2OH in water, a mixture of products was obtained which exhibited weak bands at 2131 and 2222 cm^{-1} in the ir spectrum. The band at 2131 cm^{-1} is characteristic of the dinitrogen complex, while the band at 2222 cm^{-1} is similar to that found at 2275 cm^{-1} in the known complex of nitrous oxide, $[Ru(NH_3)_5(N_2O)]^{2+}$. Although the ir spectrum was carefully examined, no additional bands can be identified. It has recently been shown that ruthenium nitrosyl species will form complexes of N_2O upon treatment with NH_2OH.[14] Nevertheless, we have been unable to show conclusively that an N_2O complex of ruthenium(II) with *o*-phenylenebis(dimethylarsine) exists or is formed as an intermediate (eq 2).

The azide complex, *trans*-$[RuN_3Cl(das)_2]$, can also be converted to the dinitrogen complex by treatment with HCl. While it is well known that ruthenium(III) azide complexes can be converted to dinitrogen complexes by the action of heat or acid, their preparation from ruthenium(II) azides has not heretofore been demonstrated.[15] The complex, *trans*-$[RuN_3Cl(das)_2]$, was found to be thermally stable to 300°. However, treatment of this complex with dry HCl in methanol at room temperature led to the rapid formation of two complexes in nearly equal amounts (estimated from the nmr spectrum of the crude product). These two compounds can readily be separated as tetraphenylborate salts. One of the products was readily identified as the dinitrogen complex, *trans*-$[RuClN_2(das)_2]^+$ (I), by its elemental analysis, ir spectrum (ν_{N_2} 2130 cm^{-1}), and nmr spectrum.

The second compound (II) formed in the reaction has a composition which corresponds to a complex containing one ruthenium, one chloride, one nitrogen, two *o*-phenylenebis(dimethylarsine) ligands, and one tetraphenylborate anion. The charge on this complex was established by its stoichiometry and by its conductance. The conductivity of both *trans*-$[RuClN_2(das)_2][BPh_4]$ and this material were determined as a function of concentration in acetone. The molar conductance and the dependence of the molar conductance on concentration were virtually identical and typical of 1:1 electrolytes.[16] The proton nmr spectrum of II was obtained in several solvents including deuteriochloroform, acetone-d_6, and DMSO-d_6. This compound is rather insoluble in chloroform, but the full spectrum was obtained by use of the Varian C-1024 CAT. This spectrum consisted of peaks between δ 6.5 and 8, due to the aromatic protons of *o*-phenylenebis(dimethylarsine) and tetraphenylborate, and a doublet at δ 1.2 which is typical of CH_3 groups for this series of trans complexes[1] (also see Table I). In addition, there is broad peak centered near δ 2.2 (H_2O) and a sharp peak at δ 1.5 which is due to acetone. Since the complex was recrystallized from acetone–water, the presence of these peaks in the nmr spectrum was not unexpected, and elemental analysis of the undried complex shows that there is 2% oxygen present in this sample from which the nmr spectrum was obtained. In addition to these identifiable peaks, there also was an additional broad band at δ 0.6 which could not be attributed to water, acetone, tetraphenylborate, or *o*-phenylenebis(dimethylarsine). Since the solubility in chloroform was insufficient for obtaining further information, the nmr spectrum of II was also obtained in DMSO-d_6 and acetone-d_6. The nmr spectrum of II was essentially the same in these two solvents as in deuteriochloroform, except that the water and acetone rapidly exchanged with acetone-d_6, and consequently were not observable. The nmr spectrum of the complex in acetone-d_6 is shown in Figure 1. The quintet at δ 1.7 is due to the residual CD_3COCD_2H in the deuterioacetone, and the sharp singlet at δ 2.4 is an unidentified impurity in the deuterioacetone solvent. The only remaining resonance is the broad singlet at δ 0.8. This is very near the broad singlet which was also observed in deuteriochloroform. Integration of this spectrum gives a ratio of aromatic protons of *o*-phenylenebis(dimethylarsine) to this broad singlet of 8.0:2.9. A spin-decoupling experiment was carried out by irradiating this sample at the ^{14}N nitrogen frequency, 7.223115 (1) MHz. This irradiation resulted in a much narrower line and apparently enhanced intensity (Figure 2). This result unequivocally demonstrates the presence of NH protons in this compound.

The infrared spectra of compounds I and II were compared. There are several infrared bands observed

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[8] M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, in press.

[9] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970).

[10] A. A. Diamantis and G. J. Sparrow, *Chem. Commun.*, 469 (1969).

[11] L. S. Pu, A. Yamamoto and S. Ikeda, *ibid.*, 189 (1969).

[12] A. A. Diamantis and G. J. Sparrow, *ibid.*, 819 (1970).

[13] J. N. Armor and H. Taube, *ibid.*, 287 (1971).

[14] F. Bottomley and J. R. Crawford, *ibid.*, 200 (1971).

[15] L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5565 (1970).

[16] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

in compound II which are absent in compound I. There are two weak but sharp bands in II at 3255 and 3310 cm^{-1} which are characteristic of NH_3, NH_2, and NH_2OH groups (but *not* NH groups). Two fundamental vibrations, ν_1 and ν_3, are observed in this region of the infrared spectrum of NH_3,[13] but only a single band was observed[17b] in the monoamine complex, $K_2Os(NH_3)Cl_5$. Other weak bands were found in II at 1700, 1350, 1245, 1220, and 750 cm^{-1} in the undried material, but upon drying, only the two bands at 3255 and 3310 cm^{-1} and perhaps the band at 750 cm^{-1} remained.

Since only the two bands at 3255 and 3310 cm^{-1} were positively identified, it was not possible to distinguish between the NH_3 and NH_2OH group by use of their infrared spectra. However, the formulation of II as an imido complex (NH) can be eliminated since there are *two* NH bands in the infrared spectrum of II and the integrated ratio of NH protons to ring protons is much greater than 1:8. The possibility of the complex being an amido complex (NH_2) is eliminated since such a compound would necessarily be paramagnetic, while all dimeric species are eliminated from consideration by the conductance experiments (the compound is a 1:1 electrolyte). This leaves as the only remaining possibilities: *trans*-$[RuCl(NH_2OH)(das)_2]^+$, *trans*-$[RuClNH_2OCH_3(das)_2]^+$, and *trans*-$[RuCl(NH_3)(das)_2]^+$. Several attempts were made to independently prepare each of these compounds by different routes, but these attempts were unsuccessful. The elemental analysis of the *undried* material shows the presence of oxygen which is attributed to water and acetone which were independently identified in the nmr spectrum. Elemental analysis of the sample after drying at 100° over KOH showed the absence of oxygen and a carbon analysis consistent only for the ammonia complex. Thus on the basis of the elemental analysis, the nmr spectrum, the ir spectrum, and the conductivity measurements, this compound has been identified as *trans*-$[RuCl(NH_3)(das)_2][BPh_4]$.

There are two possible reaction routes which could explain the products and their distribution from the reaction of the ruthenium(II) azide complex with HCl. First, protonation of either the coordinated or terminal nitrogen of the azide group would lead to a coordinated hydrazoic acid residue which decomposes into dinitrogen and the imido radical

$$(Ru{-}N{-}N{-}N)^+ + H^+ \longrightarrow (Ru{-}N{-}N{-}N{-}H)^{2+} \longrightarrow (Ru{-}N{-}N)^{2+} + NH \quad (4)$$

and

$$(Ru{-}N{-}N{-}N)^+ + H^+ \longrightarrow (Ru{-}\overset{\displaystyle H}{\overset{|}{N}}{-}N{-}N)^{2+} \longrightarrow (Ru{-}NH)^{2+} + N_2 \quad (5)$$

In the absence of the metal, protonation of either terminal nitrogen would be equally probable. The presence of ruthenium(II) may change the relative ease of protonation of the exo and endo nitrogens of the azide moiety. However, since the two ruthenium complexes are obtained in approximately equal amounts, the metal has had a relatively minor effect on this protonation reaction. The NH radical of course would decompose when not attached to the metal. The reactive amido complex, *trans*-$[RuClNH(das)_2]^+$, can be considered to be a complex of Ru(IV) and as such would be readily reducible by alcohol–HCl to the observed ruthenium(II)–ammonia complex.

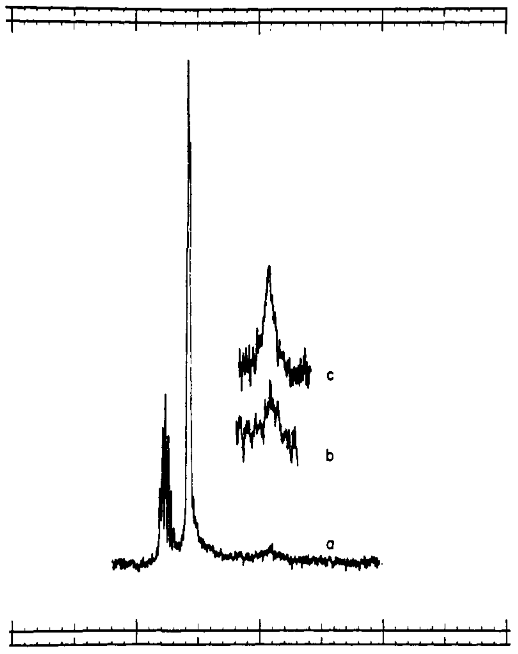

Figure 2. The spin-decoupled proton nmr spectrum of compound II in acetone-d_6 (100 MHz): (a) in the δ 0–2 region; (b) the same as a, but at higher gain; (c) the same as b, except the sample was irradiated at the ^{14}N frequency (7.223115 (1) MHz).

In order to further investigate the course of the reaction between HCl and $(RuN_3)^+$, the complex, *trans*-$[Ru(^{15}NN_2)Cl(das)_2]^+$, was allowed to react with HCl, and the products from this reaction were examined. The two ruthenium species were again formed in equal amounts. The dinitrogen complex obtained from this reaction consisted exclusively of *trans*-$[RuCl(^{15}N^{14}N)(das)_2]^+$. The absence of any observable $(Ru^{14}N^{14}N)^+$, $(Ru^{14}N^{15}N)^+$, or $(Ru^{15}N^{15}N)^+$ species rules out any mechanism which involves the formation of dinitrogen-bridged dimers or the formation of the dinitrogen complex from atmospheric nitrogen. The mechanism proposed by Kane-Maguire, *et al.*,[15] to explain the reaction between acids and the ruthenium(III) azides cannot be eliminated from consideration on the basis of the distribution of the ^{15}N isotope alone. However, the products and the product distributions from the reactions of ruthenium(II) and ruthenium(III) azides with acid are quite different. First, no dinitrogen-bridged dimers were observed from the reaction of $(RuN_3)^+$ with acid, while the dimer $(Ru\text{-}N_2\text{-}Ru)^{4+}$ was a major product from the reaction of $(RuN_3)^{2+}$ with acid. Second, although attack of the "nitrene," $[RuClNH(das)_2]^+$, on $[RuN_3Cl(das)_2]$ could lead to the observed distribution of the ^{15}N isotope, the dinitrogen complex which would be formed from this reaction would be $(RuN_2)^+$ rather than $(RuN_2)^{2+}$. For these two reasons, the Kane–Maguire mechanism probably does not apply to the reaction of *trans*-$[RuN_3Cl(das)_2]$ with acid.

A third possible mechanism would involve the prior oxidation of *trans*-$[RuN_3Cl(das)_2]$ to *trans*-$[RuN_3Cl$-

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$(das)_2]^+$ by acid followed by decomposition of the ruthenium(III) azide in a manner similar to $[Ru(NH_3)_5N_3]^{2+}$. In order to test this hypothesis, *trans*-$[RuN_3Cl(das)_2]$ was treated with an excess of bromine in methanol. A rapid reaction took place resulting in the formation of an unstable green solid. An ir spectrum of this material obtained as soon as possible after drying (5 min) initially consisted of three bands in the 2000-cm^{-1} region at 2125 (m), 2000 (s), and 1870 (vw) cm^{-1}. After the solution was allowed to stand for several hours, the color of this solid changed from green to yellow, and the ir band at 2000 cm^{-1} had disappeared, while the band at 1870 cm^{-1} had markedly increased in intensity. The bands can be identified as the ruthenium(III) azide (2000 cm^{-1}), ruthenium(II) dinitrogen complex (2125 cm^{-1}), and $[RuClNO(das)_2]^{2+}$ (1870 cm^{-1}). Thus the products from the oxidation with bromine differ markedly from those obtained from the reaction with HCl. Although this evidence is not conclusive, it strongly suggests that the action of HCl does not involve oxidation of the ruthenium(II) azide, and that eq 4 and 5 represent the most likely route for the formation of the dinitrogen complex.

The ion *trans*-$[RuClN_2(das)_2]^+$ is very stable. Numerous attempts were made to reduce this dinitrogen complex with a variety of reagents including $NaBH_4$, $LiAlH_4$, and $Na_2S_2O_4$. In every case, the dinitrogen complex was recovered unchanged. The complex cannot be oxidized with iodine and is stable toward displacements by various ligands including CO.

Preparation and Reactions of *cis*-$[Ru(N_3)_2(das)_2]$. To further explore the reactions of ruthenium(II) azide complexes, *cis*-$[Ru(N_3)_2(das)_2]$ was prepared by metathesis from the corresponding dichloride with NaN_3. The cis stereochemistry of these compounds was established by proton nmr spectra listed in Table I. The diazide does not undergo reactions analogous to those of *trans*-$[RuN_3Cl(das)_2]$. Reaction of the cis diazide with HCl in methanol gives the cis dichloro complex exclusively, while photolysis in dichloromethane also gives the dichloro complex. Reactions with NO^+ and NO_2^+ also did not lead to products containing the coordinated N_2 group.

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Mechanism of Thermal Decomposition of Di-*n*-butylbis(triphenylphosphine)platinum(II)[1]

George M. Whitesides,* John F. Gaasch,[2] and Erwin R. Stedronsky[3]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received August 4, 1971*

Abstract: The thermal decomposition of di-*n*-butylbis(triphenylphosphine)platinum(II) (**1**) in methylene chloride to *n*-butane, 1-butene, and a complex of platinum(0) is proposed to take place by an intramolecular process involving an initial dissociation of 1 equiv of triphenylphosphine from **1** to yield a three-coordinate intermediate **5**, elimination of platinum hydride from one butyl group of **5** with concomitant transfer of the resulting 1-butene to the vacant coordination site, several cycles composed of rapid addition of platinum hydride to the coordinated butene and subsequent rapid reelimination of platinum hydride from the resulting butylplatinum complexes, and a final reductive elimination of *n*-butane from an intermediate having both hydride and butyl moieties bonded to platinum. Three significant conclusions concerning the mechanism of thermal decomposition of **1** have emerged from this study. First a vacant coordination site on platinum is a prerequisite for thermal decomposition under the conditions studied. Second, the identity of the rate-limiting step for the overall decomposition reaction depends upon the concentration of triphenylphosphine added to the solution: in the absence of added triphenylphosphine, the rate-limiting step is the dissociation of **1** to **5**; in the presence of *ca.* 1 equiv of added triphenylphosphine, the rate-limiting step is the reductive elimination of butane. Third, the olefins participating in the platinum hydride addition–elimination sequence are coordinated in the intermediate platinum complexes sufficiently firmly that they do not exchange with 1-butene free in solution.

Information concerning the mechanisms of thermal decomposition of alkyl derivatives of transition metals is pertinent both to theoretical discussions of the electronic structure of carbon–metal σ bonds and practical applications of transition metal organometallic compounds in organic synthesis and catalysis. Mechanisms involving both the homolytic scission of carbon–metal σ bonds and the β elimination of metal hydrides have been proposed for these thermal decompositions;[4,5] however, the latter course has been established as the more common for *n*-alkyl derivatives

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[2] National Institutes of Health Predoctoral Fellow, 1967–1968; E. B. Herschberg Fellow, 1966–1967.

[3] National Institutes of Health Predoctoral Fellow, 1967–1970.

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