Table IV. Weighted Least-Squares Planes[a]

Plane	Equation	Angles between planes, deg
1. $N_1N_2N_3N_4$	$0.1119x - 0.8226y + 0.5574z = 1.552$	10.0 (6)
2. $C_1N_1C_3N_3$	$0.2338x - 0.8669y + 0.4403z = 0.862$	7.1 (7)
3. $C_2N_2C_4N_4$	$0.0237x - 0.7771y + 0.6289z = 2.374$	17.1 (7)
4. C_{11}–C_{16}	$-0.1360x - 0.9359y + 0.3250z = 1.230$	
5. C_{21}–C_{26}	$0.5919x - 0.6986y + 0.4026z = 3.675$	
6. C_{31}–C_{36}	$-0.5686x + 0.0578y + 0.8206z = 6.906$	

Distances of Atoms from Planes,[b] Å

1. N_1, −0.004; N_2, 0.004; N_3, 0.003; N_4, −0.004; Rh, 0.1256; O_1, −0.108; O_2, −0.125; O_3, 0.006; O_4, −0.025; C_1, −0.210; C_2, −0.162; C_3, −0.204; C_4, −0.128
2. N_1, 0.001; N_3, −0.001; C_1, −0.002; C_3, 0.002; Me_1, 0.075; Me_3, −0.026; O_1, −0.133; O_3, −0.033; Rh, −0.144
3. N_2, 0.006; N_4, −0.005; C_2, −0.017; C_4, 0.016; Me_2, −0.217; Me_4, 0.021; O_2, −0.146; O_4, −0.053; Rh, −0.061
4. C_{11}, −0.012; C_{12}, 0.009; C_{13}, 0.003; C_{14}, −0.020; C_{15}, 0.008; C_{16}, 0.011
5. C_{21}, 0.006; C_{22}, −0.017; C_{23}, 0.014; C_{24}, 0.005; C_{25}, −0.017; C_{26}, 0.009
6. C_{31}, −0.002; C_{32}, −0.002; C_{33}, 0.003; C_{34}, 0.002; C_{35}, −0.007; C_{36}, 0.006.

[a] The orthogonal coordinates (x,y,z) are directed along the crystal axes a, b, and c^*, respectively, and are in ångströms. The weight given to each atom i in forming the planes is $w_i = [a\sigma_{xi}b\sigma_{yi}c\sigma_{zi}]^{-2/3}$. [b] Average esd's of atomic positions are (Å): Rh, 0.0004; N, 0.004; O, 0.004; C_1–C_4, 0.006; Me, 0.008; C_{11}–C_{16}, 0.008; C_{21}–C_{26}, 0.007; C_{31}–C_{36}, 0.007.

Table V. Intermolecular Contacts Less than van der Waals Radii

Atoms		
Molecule A	Molecule B	Distance, Å
Cl	C_{13}	3.695 (7)
O_3	Me_1	3.364 (8)
O_3	Me_2	3.258 (8)
Me_2	Me_3	3.89 (1)
Me_2	Me_4	3.99 (1)

to their specific bonding requirements. Thus distances from 2.11 Å $[Mo_2(OAc)_4]$[17] to 2.72 Å $[Cu_2(O_2CH)_4NCS^{2-}]$[18] have been observed. Moreover, in several cases where isoelectronic systems with and without bridging carboxylato groups can be compared, such a constraining effect is at best slight. Thus the Mo–Mo distances in $Mo_2(O_2CCH_3)_4$ and $Mo_2Cl_8^{4-}$ are 2.11 and 2.14 Å, respectively.[17,19] Again, the Re–Re distances in $Re_2(O_2CC_6H_5)_4Cl_2$ and $Re_2Cl_8^{2-}$ are 2.235 and 2.241 Å, respectively.[20,21] It therefore seems unlikely that the Rh–Rh distance in the acetate is shortened to any significant extent over a hypothetical case where no bridging carboxylates are present.

Acknowledgment. We thank Dr. Alan S. Parkes for assistance with the intensity data collection, and the National Science Foundation for funds used to purchase the automated diffractometer.

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Reactions of Coordinated Ligands. Synthesis of a New Dinitrogen Complex

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Abstract: The reactions of *trans*-$[RuCl(NO)(das)_2]Cl_2$ [das is *o*-phenylenebis(dimethylarsine)] with nitrogen bases have been studied and found to involve nucleophilic attack at the nitrosyl nitrogen atom. With hydrazine as the nucleophile, the product formed is *trans*-$[RuN_3Cl(das)_2]$. This azide complex undergoes a novel reaction with $NOPF_6$ to yield the stable dinitrogen complex *trans*-$[RuClN_2(das)_2][PF_6]$. In the presence of oxygen, *trans*-$[RuN_3Cl(das)_2]$ is photochemically converted to the nitro complex, *trans*-$[RuCl(NO_2)(das)_2]$, which may also be prepared by the reaction of *trans*-$[RuClNO(das)_2]Cl_2$ with aqueous NaOH. ^{15}N-substituted complexes have been prepared and their infrared spectra utilized to determine the course of these reactions. Proton nmr spectra show that the complexes have the trans configuration.

The coordinated nitrosyl ligand is known to be rather inert to displacement by electron-pair donors such as cyanide, hydroxide, carbon monoxide, tertiary phosphines, etc. This inertness to displacement is undoubtedly due in part to the strong bonds formed between the transition metal and the nitrosyl group.

The fact that the nitrosyl group is not readily displaced suggests that reactions may be carried out on the coordinated ligand itself.

Indeed, it has long been recognized[1] that the NO group in $[Fe(CN)_5NO]^{2-}$ is readily attacked by bases forming complexes in which the entering base is attached to the nitrogen of the nitrosyl group. The best known example is the reaction of $[Fe(CN)_5NO]^{2-}$ with hydroxide

$$[Fe(CN)_5NO]^{2-} + 2OH^- \longrightarrow [Fe(CN)_5NO_2]^{4-} + H_2O \tag{1}$$

Many of these reactions have been summarized in two review articles.[2,3] While the reactions between the nitrosyl group and oxygen bases have received some attention, there has been no systematic investigation of the reaction between the nitrosyl group and nitrogen-containing bases. Most of the previous studies have dealt with the reactions of iron nitrosyl species. However, since the ruthenium complexes undergo similar reactions, but produce more stable products, the ruthenium nitrosyl compounds were chosen for the investigations outlined below.

Experimental Section

The $RuNOCl_3$ used in these experiments was obtained from Englehard Industries, while the $RuCl_3 \cdot 3H_2O$ was obtained from the Bishop Chemical Co. The ^{15}NO (95%) was used as obtained from Biorad Laboratories. The ligands, *o*-phenylenebis(dimethylarsine) and *cis*-1,2-bis(dimethylarsino)ethylene, were prepared using published procedures.[4,5] The nitrogen gas used was purified by passing it over BTS catalyst from BASF, followed by drying over activated molecular sieve. The infrared spectra were obtained using a Beckman Model 12 or a Perkin-Elmer Model 337 spectrophotometer. The nmr spectra were measured on a Varian Model A60 using tetramethylsilane as an internal or external standard. The mass spectra were measured on a Hitachi Perkin-Elmer Model RMU-6e mass spectrometer. The X-ray photoelectron spectra were obtained using Mg Kα radiation (1253.6 eV) using a double-focusing magnetic spectrometer.[6] Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo., and by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Dichloride. A solution of $RuNOCl_3$ (2.66 g) and *o*-phenylenebis(dimethylarsine) (6.94 g) in methanol (370 ml) was refluxed for 90 hr in a nitrogen atmosphere. The solution was evaporated to dryness under reduced pressure and the resulting solid was washed with diethyl ether and finally recrystallized from ethanol–ether to yield the desired product as yellow microprisms (5.53 g). The complex was dried at 100° (0.1 mm). The complex is diamagnetic.

Anal. Calcd for $C_{20}H_{32}As_4Cl_3NORu$: C, 30.1; H, 4.3; Cl, 12.6; N, 1.7; O, 2.0. Found: C, 30.1; H, 4.4; Cl, 12.2; N, 1.7; O, 2.5. The ^{15}N analog was prepared in the following way. A mixture of ruthenium metal (0.2 g) and NaOCl (50 ml, 5% solution) was stirred for 12 hr at 20°. The solution was cooled to 0° and a cold mixture of ethanol (10 ml) and concentrated hydrochloric acid (10 ml) was added. The solvent was removed under reduced pressure and the residue was dissolved in a mixture of water (20 ml) and concentrated hydrochloric acid (1 ml). The resulting solution was stirred at 20° in an atmosphere of ^{15}NO for 12 hr, after which the solvent was removed under reduced pressure. The residue (0.6 g) and *o*-phenylenebis(dimethylarsine) (0.4 g) reacted in methanol (as described above) to give $[RuCl(^{15}NO)(das)_2]Cl_2$ (0.057 g).

Chloronitrosylbis[*cis*-1,2-bis(dimethylarsino)ethylene]ruthenium Dichloride. A solution of $RuNOCl_3$ (0.15 g) and *cis*-1,2-bis(dimethylarsino)ethylene (*cis*-edas) (0.40 g) in methanol (50 ml) was refluxed for 4 hr. The volume of the solution was reduced by boiling and diethyl ether was added to precipitate a yellow solid. After washing with dichloromethane and recrystallization from ethanol, 0.20 g of complex was obtained.

Anal. Calcd for $C_{12}H_{28}As_4Cl_3NORu$: C, 20.3; H, 4.0; N, 2.0. Found: C, 20.3; H, 4.2; N, 1.6. The complex is diamagnetic.

Azidochlorobis[*o*-phenylenebis(dimethylarsine)]ruthenium(II). Hydrazine (3.5 ml) was added to a solution of $[RuClNO(das)_2]Cl_2$ (0.36 g) in methanol (15 ml). The solution became brown and then deposited microcrystals (0.23 g) which were filtered, washed with methanol, and dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_{21}H_{35}As_4ClN_3ORu$: C, 32.2; H, 4.7; Cl, 4.6; N, 5.4; O, 2.1; Ru, 12.9. Found: C, 31.35; H, 4.3; Cl, 4.8; N, 5.0; O, 2.4; Ru, 13.7. A sample dried at 100° (0.1 mm) contained no methanol.

Anal. Calcd for $C_{20}H_{32}As_4ClN_3Ru$: C, 32.0; H, 4.3; Cl, 4.8; N, 5.6; O, 0.0; Ru, 13.5. Found: C, 32.0; H, 4.4; Cl, 5.0; N, 5.3; O, 0.2; Ru, 13.3. The complex is diamagnetic.

The ^{15}N-substituted complex was similarly prepared from $[RuCl(^{15}NO)(das)_2]Cl_2$. The ^{15}N complex was identified by its infrared spectrum and by decomposition with ceric sulfate–water. A total of 28.7 mg of $[Ru(^{15}NN_2)Cl(das)_2]$ was placed in an open-ended ampoule in a flask containing ceric sulfate (0.3 g) and water (10 ml). The flask was evacuated and the ceric sulfate solution was degassed by freeze–thaw techniques. The complex and solution were then mixed and the composition of the evolved gas was measured by mass spectrometry.

Azidochlorobis[*cis*-1,2-bis(dimethylarsino)ethylene]ruthenium(II). Hydrazine (1 ml) was added to a solution of $[RuClNO(edas)_2]Cl_2$ (0.10 g) in methanol (5 ml). The solution was stirred under nitrogen for 2 hr, and the volume was reduced to 2 ml. The product (0.03 g) precipitated as a gold-colored powder.

Anal. Calcd for $C_{12}H_{28}As_4ClN_3Ru$: C, 22.1; H, 4.3; Cl, 5.5; N, 6.4. Found: C, 21.8; H, 4.2; Cl, 5.7; N, 6.2. The complex is diamagnetic.

Chloro(oxophenyltriazeno)bis[*o*-phenylenebis(dimethylarsine)]ruthenium(II) $[RuCl(N(O)N_2HPh)(das)_2]$. Phenylhydrazine (1 ml) was added to a solution of $[RuCl(NO)(das)_2]Cl_2$ (0.2 g) in methanol (10 ml). The resulting white precipitate (0.15 g) was separated by centrifuging, washed successively with methanol, water, and methanol, and finally dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_{26}H_{38}As_4ClN_3ORu$: C, 37.0; H, 4.6; Cl, 4.2; N, 5.0; O, 1.9. Found: C, 37.1; H, 4.6; Cl, 4.5; N, 4.8; O, 1.9. The complex is diamagnetic.

Chloronitrobis[*o*-phenylenebis(dimethylarsine)]ruthenium(II). The complex $[RuClNO(das)_2]Cl_2$ (0.19 g) was dissolved in water (10 ml). The solution was stirred and aqueous NaOH (0.358 *M*, 5 ml) was added. The pale yellow precipitate which formed was separated by centrifugation. The complex (0.12 g) was washed with water and dried at 100° (0.1 mm) over P_2O_5.

Anal. Calcd for $C_{20}H_{32}As_4ClNO_2Ru$: C, 31.8; H, 4.3; Cl, 4.7; N, 1.9; O, 4.3. Found: C, 31.5; H, 4.3; Cl, 5.1; N, 1.8; O, 4.6. The complex is diamagnetic.

Reactions of $[RuClNO(das)_2]Cl_2$ with Amines. In a typical experiment, the nitrosyl complex (0.10 g) was dissolved in methanol (25 ml) and treated with excess of aqueous ammonia (2 ml). The solution was set aside for several hours and the resulting pale yellow precipitate (0.09 g) was removed by filtration. The complex was washed with methanol and dried at 100° (0.1 mm). The materials obtained from all of these reactions were shown to be the nitro complex described above. A typical analysis of the product from the reaction with ammonia follows.

Anal. Calcd for $C_{20}H_{32}As_4ClNO_2Ru$: C, 31.8; H, 4.3; Cl, 4.7; N, 1.9; O, 4.3; Ru, 13.4. Found: C, 31.6; H, 4.3; Cl, 5.1; N, 2.0; O, 4.1; Ru, 13.0.

Reactions with other amines also gave the nitro complex which was identified by its infrared spectrum. These amines follow, together with reaction time and percentage yield: $(CH_3)_2NNH_2$ (15 min, 25%), $C_6H_5NH_2$ (11 days, 10%), $(C_2H_5)_3N$ (2 days, 77%), $(C_2H_5)_2NH$ (18 hr, 62%), $C_2H_5NH_2$ (18 hr, 79%).

Photolysis of Aziodochlorobis[*o*-phenylenebis(dimethylarsine)]ruthenium(II). A solution of $[RuN_3Cl(das)_2]$ (0.013 g) in dichloromethane (3 ml) was irradiated for 10 hr with light from a fluorescent tube (estimated flux 2 × 10^4 ergs/cm^2). A yellow precipitate formed, which was filtered and washed with methanol (yield, 0.007 g). The product was shown to be $[RuCl(NO_2)(das)_2]$ by its infrared spectrum and elemental analysis.

Chloro(dinitrogeno)bis[*o*-phenylenebis(dimethylarsine)]ruthenium(II) Hexafluorophosphate. A stirred suspension of $[RuN_3Cl$-

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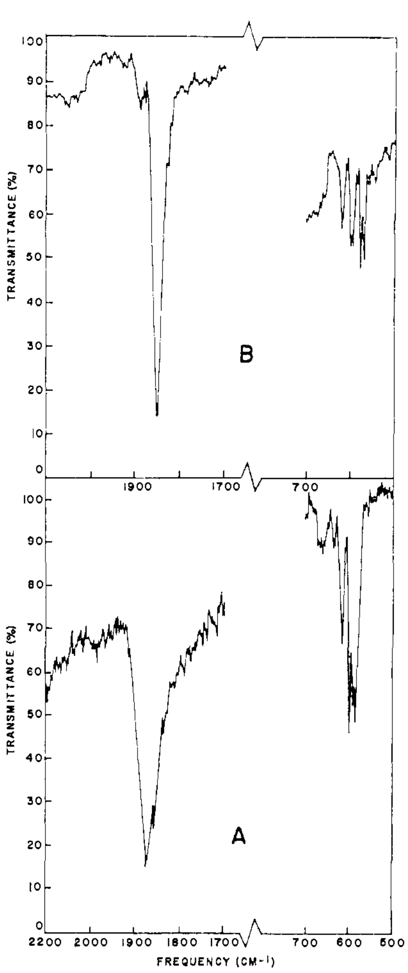

Figure 1. The infrared spectra of (A) $[RuCl(^{14}NO)(das)_2]Cl_2$ and (B) $[RuCl(^{15}NO)(das)_2]Cl_2$ in the 600- and 1800-cm^{-1} regions.

$(das)_2]$ (0.91 g) in methanol (60 ml) was treated with 1.5 g of $NOPF_6$. After 5 min the precipitate was filtered, recrystallized four times from acetone–water (with charcoal), and dried at 100° (0.1 mm) to give 0.06 g of colorless plates. The complex was found to decompose over 200°. A sample of the complex (0.106 g) was pyrolyzed at 200° *in vacuo* for 2 hr. The gas evolved (3.11 mg or 93%) was shown by mass spectroscopy to consist entirely of N_2. The residue contained less than 0.1% nitrogen.

Anal. Calcd for $C_{20}H_{32}As_4ClF_6N_2PRu$: C, 27.0; H, 3.7; Cl, 4.0; N, 3.2; P, 3.5; F, 13.0. Found: C, 27.4; H, 3.8; Cl, 4.3; N, 3.2; P, 4.0; F, 13.3. The complex is diamagnetic.

***trans*-Chloro(carbonyl)bis[*o*-phenylenebis(dimethylarsine)]ruthenium(II) Tetraphenylborate.** Carbon monoxide was passed through a refluxing solution of $RuCl_3 \cdot 3H_2O$ (0.447 g) in 2-methoxyethanol (20 ml) for 18 hr. Then, *o*-phenylenebis(dimethylarsine) (1.15 g) was added to the pale yellow solution which was then refluxed for 5 min in a carbon monoxide atmosphere. The solvent was removed under reduced pressure and the residue dissolved in methanol (5 ml). To the filtered solution was added a solution of $NaB(C_6H_5)_4$ (1 g) in methanol (5 ml). The resultant precipitate was separated by filtration and recrystallized from dichloromethane–methanol as pale yellow microcrystals (yield, 0.65 g). The complex was dried at 150° for analysis, but some dichloromethane remained in the solid.

Anal. Calcd for $C_{45}H_{52}As_4BClORu$: C, 51.3; H, 5.0; O, 1.5; Cl, 3.5. Found: C, 50.6; H, 5.1; O, 1.7; Cl, 4.1. The complex is diamagnetic.

Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium Dihexafluorophosphate. **Method 1.** A solution of KPF_6 (0.033 g) in water (3 ml) was added to a solution of *trans*-$[RuClNO(das)_2]Cl_2$ (0.57 g) in water (10 ml). The resulting yellow precipitate (0.47 g) was filtered, washed with water, and dried at 100° (0.1 mm).

Anal. Calcd for $C_{20}H_{32}As_4ClF_{12}NOP_2Ru$: C, 23.4; H, 3.2; Cl, 3.5; N, 1.4; P, 6.0; F, 22.2. Found: C, 23.6; H, 3.4; Cl, 3.7; N, 1.5; P, 6.0; F, 22.2.

Method 2. A suspension of $[RuN_3Cl(das)_2]$ (0.192 g) in methanol (40 ml) was treated with small portions of $NOPF_6$ (a total of 0.355 g) during a 5-min period. The precipitate (0.08 g) was filtered, washed with methanol, and dried at 100° (0.1 mm). The infrared spectrum of this product was identical with the spectrum of a sample obtained using method 1.

Results and Discussion

Ruthenium Nitrosyl Complexes. The orange ruthenium nitrosyl complex containing one *o*-phenylenebis(dimethylarsine) (das) ligand has been previously prepared[7] by treatment of $RuNOCl_3$ with *o*-phenylenebis(dimethylarsine) in refluxing ethanol. We find that the yellow complex, $[RuClNO(das)_2]Cl_2$, may also be prepared by refluxing $RuNOCl_3$ for a prolonged period with *o*-phenylenebis(dimethylarsine) in methanol followed by recrystallization from ethanol–ether. Both $[RuCl_3NO(das)]$ and $[RuClNO(das)_2]Cl_2$ undergo similar reactions with nitrogen bases, but the products containing two of the tertiary arsine ligands are more stable.

The complex $[RuCl^{15}NO(das)_2]Cl_2$ was prepared by treating an aqueous solution of $RuCl_3 \cdot 3H_2O$ with ^{15}NO. The uptake of ^{15}NO was approximately 90% of the theoretical. The resulting solution contained only $Ru^{15}NO^{3+}$ species and starting material. This solution, of the solid material obtained from evaporation of the solvent, served as the source of the ^{15}N complexes prepared in this research. The *o*-phenylenebis(dimethylarsine) complex was obtained from the reaction of this ^{15}NO-containing solid with *o*-phenylenebis(dimethylarsine) in refluxing methanol.

The nmr spectrum of $[RuClNO(das)_2]Cl_2$ was obtained in D_2O. The nmr spectrum consisted of an AA′-BB′ pattern near 7.5 ppm and two methyl singlets at 1.99 and 2.14 ppm. Both cis and trans isomers are possible for a six-coordinate complex $[MX_2(das)_2]^{n+}$. Bailar[8] has shown that for the cis isomer, there are four separate peaks in the methyl region, while for the trans isomer, only one methyl resonance is found. This is to be expected, since there are clearly four types of methyl groups in the cis complex, while there is only one type of methyl group in the trans complex. However, for a trans complex of the type $[MXY(das)_2]^{n+}$ there should be two types of methyl groups, those adjacent to X and those adjacent to Y. For the cis isomer, there is a total of eight different methyl groups. Since only two methyl resonances were observed, $[RuClNO(das)_2]Cl_2$ must have a trans arrangement of the chloride and nitrosyl groups.

The infrared spectra of the ^{15}N-enriched and unenriched complexes, *trans*-$[RuClNO(das)_2]Cl_2$, are compared in Figure 1. The strong NO stretching frequency at 1883 cm^{-1} in the ^{14}N complex is shifted by 36.5 cm^{-1} in the ^{15}N complex. In addition, the metal–nitrogen frequencies can be identified by this isotopic substitution. The 600-cm^{-1} region of the infrared spectrum of $[RuCl^{14}NO(das)_2]Cl_2$ consists of four absorption bands at 626.5, 605.0, 595.5, and 591.5 cm^{-1}. The two bands at 626.5 and 605.0 cm^{-1} are always present in complexes of *o*-phenylenebis(dimethylarsine) and moreover were not appreciably shifted upon isotopic substitution by ^{15}N. Both components of the doublet at 595.5 and 591.5 cm^{-1} were shifted, with replacement of ^{14}N by ^{15}N. These data are listed in Table I. Miki[9] has in-

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Table I. Observed and Calculated Vibrational Frequencies (cm^{-1}) for (Ru–^{14}NO)$^{3+}$ and (Ru–^{15}NO)$^{3+}$ Complexes

Assignment	*trans*-[RuClNO(das)$_2$]Cl$_2$				*trans*-[RuClNO-(edas)$_2$]Cl$_2$	K$_2$[RuCl$_5$NO][a]			
	^{14}NO	^{15}NO	Δ(obsd)	Δ(calcd)	^{14}NO	^{14}NO	^{15}NO	Δ(obsd)	Δ(calcd)
NO str (A$_1$)	1883 (s)	1847 (s)	36.5		1847 (s)	1904 (vs)	1875 (vs)	39	40
RuN str (A$_1$)	596 (w)	593 (w)	3.0	6.5	*b*	606 (w)	600 (w)	6	6
RuNO bend (E)	592 (m)	578 (m)	14.0	14.1	594 (m)	588 (s)	572 (s)	16	16

[a] See ref 9. [b] Obscured by C–As stretch.

Table II. Infrared Absorption Bands of Coordinated and Uncoordinated Azides

Assignment	(^{14}N–^{14}N–^{14}N)	(^{15}N–^{14}N–^{14}N)[a]	(^{14}N–^{15}N–^{14}N)	[Ru(N$_3$)Cl(das)$_2$] (^{14}N)	[Ru(N$_3$)Cl(das)$_2$] (^{15}N)	[Ru(N$_3$)Cl(edas)$_2$] (^{14}N)
ν_3 NN str (antisym)	2037 (s)	2025 (s)	1991 (s)	2038 (s)	2026 (s)	2028 (s)
ν_1 NN str (sym)	(1358)[b]	(1337)[c]	*b*	1317 (m)	1294 (m) (1294.5)[c]	1310 (m)
ν_2 N$_3$ bend	640 (m)	637 (m)	626 (m)	*d*	*d*	*d*

[a] See ref 12. [b] Raman active, not observed in the infrared spectrum. [c] Calculated. [d] Not identified; see text.

vestigated the infrared spectra of K$_2$RuCl$_5$NO and K$_2$RuBr$_5$NO. He identified the three fundamental Ru–N–O frequencies in each of these compounds by use of ^{15}NO. Our assignments, the observed frequencies, and the observed frequency shifts agree closely with Miki's results (Table I). The observed frequency shifts agree with those calculated for the three-body problem using a valence force field and confirm the assignments of these frequencies.

Ruthenium nitrosyl trichloride also reacts readily with *cis*-1 2-bis(dimethylarsine)ethylene[10] (edas) to form the complexes [RuCl$_3$NO(edas)] and [RuClNO(edas)$_2$]Cl$_2$ under conditions similar to those used for the preparation of the nitrosyl complexes of *o*-phenylenebis(dimethylarsine). The Ru–N–O frequencies were readily identified by comparison with other complexes of *cis*-1,2-bis(dimethylarsino)ethylene and with *trans*-[RuClNO-(das)$_2$]Cl$_2$. The nmr spectrum of [RuClNO(edas)$_2$]Cl$_2$ in D$_2$O consisted of a singlet at 7.78 ppm due to the ethylenic protons and two methyl singlets at 2.15 and 2.00 ppm. Thus, the complex [RuClNO(edas)$_2$]Cl$_2$ also exists exclusively as the trans isomer.

Reactions with Hydrazine and Substituted Hydrazines. Hydrazine hydrate rapidly reacts with solutions and suspensions of *trans*-[RuClNO(das)$_2$]Cl$_2$ in methanol, producing a complex with an easily identifiable new band in the infrared spectrum at 2038 cm^{-1}. This compound is relatively insoluble in most solvents. It did prove sufficiently soluble in dichloromethane to obtain the conductivity and a crude molecular weight by vapor-pressure osmometry. The molecular weight corresponds to that of a monomeric species, and the compound is a nonelectrolyte in dichloromethane. Under the initial conditions of preparation, the compound was contaminated by variable amounts of [RuCl$_2$(das)$_2$] which could not be removed owing to the insolubility of both complexes. The elemental analyses of this compound proved to be very erratic because of the contamination by the dichloride and because of the difficulty of analyzing for Ru, As, and Cl in the presence of each other. This gave rise to the incorrect formulation of the azide as a complex of dinitrogen.[11]

The method of preparation and the analyses presented in the Experimental Section gave reliable and reproducible results. The overall reaction between hydrazine and *trans*-[RuClNO(das)$_2$]Cl$_2$ is represented by

$$3N_2H_4 + [RuClNO(das)_2]Cl_2 \longrightarrow [RuN_3Cl(das)_2] + 2N_2H_5Cl + H_2O \quad (2)$$

Equation 2 requires hydrazine to attack the nitrosyl group at the nitrogen atom, with the subsequent loss of water and hydrogen ions. In order to verify this postulate, the reaction was carried out with ^{15}N-enriched (95%) *trans*-[RuCl^{15}NO(das)$_2$]Cl$_2$. The product from the reaction with hydrazine had an infrared spectrum which differed from that of the unenriched compound. The strong absorption band in the infrared spectrum at 2038 cm^{-1} in the unenriched complex is shifted by 12 cm^{-1} to 2026 cm^{-1} in the compound prepared from the 95%-enriched ^{15}N nitrosyl. The ^{15}N azide was decomposed with aqueous ceric sulfate, and a mass spectrum of the gas evolved was obtained. Both ^{15}N–^{14}N and ^{14}N–^{14}N were present in the gas obtained from the decomposition of [Ru(^{15}N–N$_2$)Cl(das)$_2$]. These results show that the nitrogen of the nitrosyl is retained in the product from these reactions. This same azide complex was also prepared from the reaction of NaN$_3$ with *trans*-[RuClNO(das)$_2$]Cl$_2$ in water.

The infrared spectra of the azide ion isotopically substituted with ^{15}N at the central position, the terminal position, and at all three positions have been reported.[12] The frequencies observed for the ^{15}N-substituted azide ion are compared with those of [Ru(^{15}N–N$_2$)Cl(das)$_2$] obtained from the reaction of the ruthenium nitrosyl with hydrazine (Table II). The terminally substituted azide group, (^{15}N–N–N)$^-$, has frequency shifts for the antisymmetric stretching frequency, ν_3, and the N$_3^-$ bending frequency, ν_2, of 12 and 3 cm^{-1}, respectively. The azide ion with the central nitrogen substituted with ^{15}N has much larger frequency shifts: $\Delta\nu_3$ is 46 and $\Delta\nu_2$ is 12 cm^{-1}. Within experimental error, the frequency shift in ν_3 for the complex [Ru(^{15}N–N$_2$)-Cl(das)$_2$] is identical with that found for the terminally substituted azide ion. Therefore, the azide ion in the complex [Ru(^{15}N–N$_2$)(das)$_2$] must have a terminal ^{15}N atom. There are two terminal positions for ^{15}N

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(10) (a) H. G. Metzger, Ph.D. Dissertation, University of Arizona, 1970; (b) NDEA Predoctoral Fellow, 1967–1969.

(11) R. D. Feltham, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 49.

(12) T. Theophanides and G. C. Turrell, *Spectrochim. Acta, Part A*, **23**, 1927 (1967).

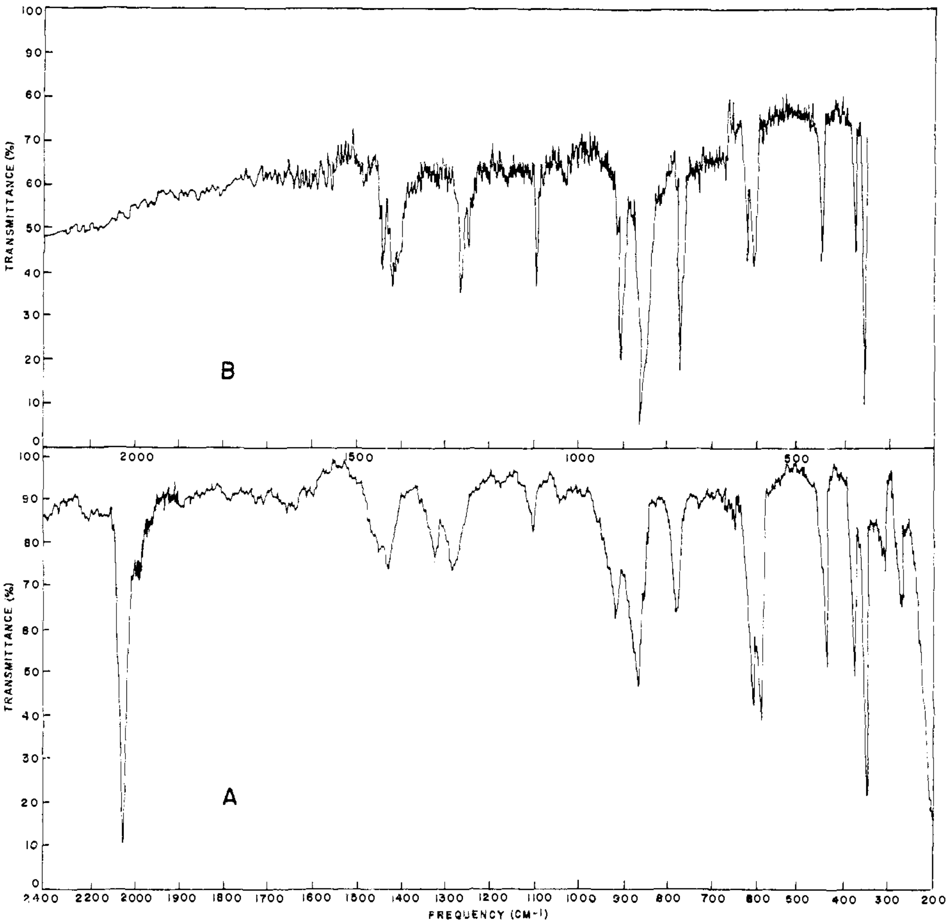

Figure 2. The infrared spectra of (A) [$RuN_3Cl(das)_2$] and (B) *trans*-[$RuCl_2(das)_2$].

in a coordinated azide ion, one in which the ^{15}N is bound to the ruthenium, and one not coordinated to ruthenium. The infrared spectra of [$Ru(^{14}N_3)Cl(das)_2$] and [$Ru(^{15}N-N_2)Cl(das)_2$] were carefully compared in the region of the infrared spectrum between 300 and 700 cm^{-1}. While the $Ru-^{14}NO$ and $Ru-^{15}NO$ frequencies were easily identified (*vide supra*), it was not possible to identify the ruthenium azide frequencies in this region. Unfortunately there were no absorption bands in the infrared spectrum between 300 and 700 cm^{-1} which could be attributed to the coordinated azide ligand. Moreover, no frequency shifts were observed in this region upon ^{15}N substitution. In order to fully identify the infrared absorption bands of a coordinated azide ion, the complex *trans*-[$Co(N_3)_2(das)_2$][ClO_4] was prepared. The three fundamental frequencies of the azide ion, 1327 (ν_1), 2038 (ν_3), and 657 cm^{-1} (ν_2), were readily identified in this complex. However, there were no new absorption bands which could be attributed to the coordinated $Co-N_3$ bending and stretching modes. There is one shoulder present in the cobalt complex at 430 cm^{-1} which is in the frequency range expected[13] for $Co-N_3$, but, without further information, it cannot be definitely assigned. However, comparison of the ruthenium complexes [$Ru(N_3)Cl(das)_2$] and [$RuCl_2(das)_2$] (Figure 2) confirms the assignment of the antisymmetric stretching frequency, ν_3, and the symmetric stretching frequency, ν_1, to the absorption bands at 2038 and 1317 cm^{-1}, respectively.

The X-ray photoelectron spectrum of the azide complex was also obtained. The XPS spectrum consists of two photopeaks with an intensity ratio of approximately 2:1 (Table III). The XPS spectrum of sodium azide is very similar to that obtained for the ruthenium azide complex, and to that obtained for the cobalt azide complex, *trans*-[$Co(N_3)_2(das)_2$][ClO_4]. The photopeak due to the terminal azido nitrogens was not split. A preliminary single-crystal X-ray investigation of the complex [$RuN_3Cl(edas)_2$] shows that the ruthenium atom is surrounded by a planar arrangement of four arsenic atoms and consequently has a trans configuration.[14]

Table III. Nitrogen 1s Binding Energies

Compound	Binding energies, eV	Approximate intensity ratios
NaN_3	403.7, 399.3	1:2
trans-[$Co(N_3)_2(das)_2$][ClO_4]	403.2, 400.1	1:2
trans-[$RuN_3Cl(das)_2$]	403.9, 399.2	1:2

The complex *trans*-[$RuClNO(edas)_2$]Cl_2 also reacts with hydrazine under conditions similar to those used for the *o*-phenylenebis(dimethylarsine) complex to produce [$RuN_3Cl(edas)_2$]. This complex has two bands in the infrared spectrum at 2028 and 1310 cm^{-1} which are attributable to the coordinated N_3^- ligand (Table

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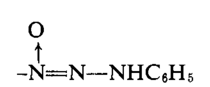
(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(14) J. Enemark, private communication.

II). Again, it proved impossible to identify any absorption bands of the Ru–N_3 group.

The formation of an azide from the reaction of the NO group with hydrazine requires the loss of oxygen from the nitrosyl group and four protons from the hydrazine moiety. In order to isolate a possible intermediate, the reaction was carried out between phenylhydrazine and *trans*-$[RuClNO(das)_2]Cl_2$. The product obtained from this reaction in methanol has a composition corresponding to $[RuCl(NON_2HC_6H_5)(das)_2]$. The presence of a phenyl ring was clearly demonstrated by elemental analyses and the presence of absorption bands in the infrared spectrum at 695, 751, 1500, and 1596 cm^{-1} which are characteristic for a monosubstituted phenyl group. In addition to these bands, there is a weak absorption at 3255 cm^{-1} which can be assigned to an N–H stretching frequency (Figure 3). For these reasons, the ligand formed from the reaction of phenylhydrazine with the coordinated nitrosyl group is formulated as the oxophenyltriazeno group

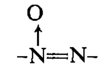


$$-\overset{\overset{O}{\uparrow}}{N}{=}N{-}NHC_6H_5$$

The infrared spectrum of this complex was carefully compared with the spectra of azoxy compounds in order to obtain structural information regarding the disposition of the oxygen in this ligand. The infrared spectra of several azoxy compounds have been reported. Jander and Haszeldine[15] have made assignments of the absorption bands observed for the compounds

$$CF_3N{=}\overset{\overset{O}{\uparrow}}{N}CF_3 \quad CH_3\overset{\overset{O}{\uparrow}}{N}{=}NCH_3$$

to the fundamental vibrations of the



$$-\overset{\overset{O}{\uparrow}}{N}{=}N-$$

group. Unfortunately, it has been impossible to unequivocally assign the azoxy frequencies of azoxybenzene, and thus no further structural information could be extracted from the infrared spectrum of $[RuCl(NON_2HC_6H_5)(das)_2]$.

The reactions of this compound do, however, provide information regarding its structure. Treatment of the complex with HCl gives the nitrosyl $[RuClNO(das)_2]Cl_2$ as the major product. This indicates that the nitrosyl group must be essentially intact in $[RuCl(NON_2HC_6H_5)(das)_2]$.

The reactions between hydrazine and phenylhydrazine are summarized by the following equations

$$[RuClNO(das)_2]^{2+} + 3H_2N{-}NHR \longrightarrow [RuCl(NONNHR)(das)_2] + 2NH_3NHR^+ \quad (3)$$

followed by the loss of water when R = H

$$[RuCl(NONNH_2)(das)_2] \longrightarrow [RuN_3Cl(das)_2] + H_2O \quad (4)$$

Reaction 3 is reversible in the sense that addition of acid regenerates $[RuClNO(das)_2]^{2+}$. Such reverse reactions are well established for oxygen base adducts of $[Fe(CN)_5NO]^{2-}$

$$[Fe(CN)_5NO_2]^{4-} + 2H^+ \longrightarrow [Fe(CN)_5NO]^{2-} + H_2O \quad (5)$$

(reverse reaction of eq 1).

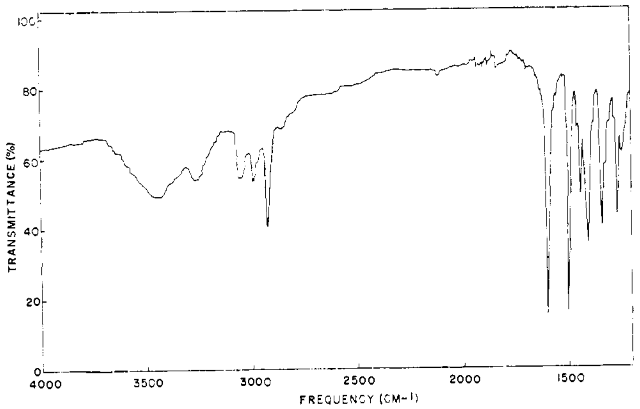


Figure 3. The infrared spectrum of $[RuCl(NON_2HC_6H_5)(das)_2]$ from 1200 to 4000 cm^{-1}.

Reactions with Amines. Reactions were carried out between $[RuClNO(das)_2]^{2+}$ and a series of amines including ammonia, aniline, methylamine, and dimethylamine, with the expectation that reactions similar to those with hydrazine might occur. In all of the reactions, the solvents used contained traces of water. The only compound which was isolated from any of these reactions was the nitro complex $[RuClNO_2(das)_2]$ formed by the attack of the hydroxide ion on the nitrosyl (eq 1). The same nitro compound is produced from the reaction of $[RuClNO(das)_2]^{2+}$ with sodium hydroxide in water in the absence of any amine base. The nitro group was readily identified by elemental analyses and by the three bands in the infrared spectrum at 1313, 1218, and 820 cm^{-1} which are characteristic of a coordinated nitro group.

Reactions with the Nitrosonium Ion. Nitrous acid is known to react with hydrazoic acid to form N_2O and N_2 quantitatively, presumably by the attack of the NO^+ group on the azide.[16] Consequently, it was felt that $[RuN_3Cl(das)_2]$ might be converted to a dinitrogen complex by the reaction with NO^+. It was found that the azide reacts readily with $NOPF_6$ in methanol to give a mixture of starting material, $[RuClN_2(das)_2][PF_6]$, and $[RuClNO(das)_2][PF_6]_2$. $[RuClN_2(das)_2][PF_6]$ can be readily separated by recrystallization from acetone–water mixtures. The compound $[RuClN_2(das)_2][PF_6]$ has two absorption bands in the infrared spectrum which are due to the dinitrogen ligand. There is a strong absorption band at 2130 cm^{-1} and one of medium intensity at 489 cm^{-1} which were identified as the N_2 stretching frequency and an Ru–N_2 frequency, respectively. These positions are very similar to those found by Allen[17] for $[Ru(NH_3)_5N_2][PF_6]_2$ of 2167 and 474 cm^{-1}. An nmr spectrum of the dinitrogen complex was obtained in dimethyl-d_6 sulfoxide. There were two sharp singlets at 1.88 and 1.84 ppm, which demonstrates that $[RuClN_2(das)_2][PF_6]$ has a trans configuration. Kane-Maguire, *et al.*, have also prepared complexes of dinitrogen from the reactions of ruthenium azides with nitrous acid.[18]

To obtain information concerning the course of the reaction between the coordinated azide group and NO^+,

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(15) J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 919 (1954).

(16) L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

(17) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsaln, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

(18) L. A. P. Kane-Maquire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *ibid.*, 90, 5295 (1968).

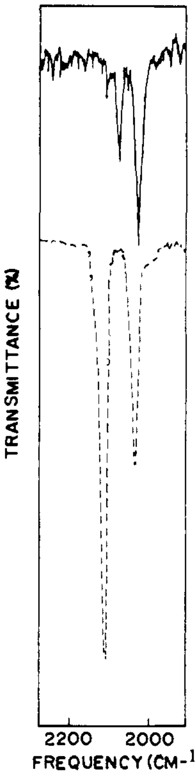


Figure 4. The infrared spectrum in the 2000-cm^{-1} region of the material from the reaction of $NOPF_6$ with $[Ru(^{14}N_3)Cl(das)_2]$ (---) and $[Ru(^{15}N\text{-}N_2)Cl(das)_2]$ (—).

the complex $[Ru(^{15}NN_2)Cl(das)_2]$ was treated with an insufficient amount of $NOPF_6$ in methanol. The usual mixture of products from this reaction was obtained. There were three absorption bands in the infrared spectrum between 2000 and 2500 cm^{-1} (Figure 4). The predominant band at 2029 cm^{-1} is due to the presence of a large amount of unreacted starting material, while the small band at 2130 cm^{-1} is readily identified as $[RuCl(^{14}N^{14}N)(das)_2][PF_6]$. However, most of the dinitrogen complex which is formed in this reaction consists of $[Ru(^{15}N^{14}N)Cl(das)_2[PF_6]$. The absorption band at 2095 cm^{-1} is shifted from that of the unsubstituted complex at 2130 cm^{-1} by 35 cm^{-1} compared with the isotopic shift expected for coordinated $^{15}N^{14}N$ of 35.8 cm^{-1}. The Ru–N_2 bending frequency in the ^{15}N-substituted dinitrogen complex has been shifted from 489 to 477.5 cm^{-1}. The calculated frequency for the ruthenium–nitrogen bend for the dinitrogen complex in which the ^{15}N is attached to the ruthenium is 477.7 cm^{-1}, in good agreement with the observed value of 477.5 cm^{-1}. No linkage isomerism such as that described by Taube[19] was observed over a 24-hr period.

The complex $[RuCl(CO)(das)_2]^+$ was prepared so that its properties might be compared with those of the dinitrogen complex. The carbonyl cation, isolated as the tetraphenylborate salt, had a strong CO stretching frequency at 1950 cm^{-1} and two singlets at 1.88 and 1.81 ppm in the nmr spectrum in DMSO-d_6.

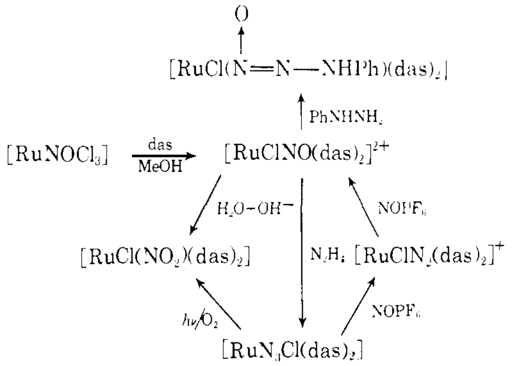
Photochemical Reactions of $[RuN_3Cl(das)_2]$. During attempts at purification, it was observed on numerous occasions that the azide complex was converted to another compound. This compound contains only one nitrogen per ruthenium, and its infrared spectrum and elemental analysis correspond to the nitro complex, $[RuCl(NO_2)(das)_2]$, prepared independently. Dichloromethane solutions of $[RuN_3Cl(das)_2]$ are stable in the absence of light. However, even in Pyrex vessels, these same solutions photolyze in the presence of air to form the nitro complex in good yields

$$[RuN_3Cl(das)_2] + O_2 \xrightarrow[h\nu]{CH_2Cl_2} [RuCl(NO_2)(das)_2] + N_2 \quad (6)$$

It was shown that both oxygen and light were necessary for this reaction to take place. In the absence of either oxygen or light, the nitro complex is not produced. In order to isolate any possible reactive nitrene intermediates, this photochemical reaction was carried out with cyclohexene in the absence of oxygen. No ruthenium complexes containing cyclohexene could be isolated from this mixture.

Conclusions

The reactions[20] of the ruthenium complexes described above are summarized in the following diagram.



The ruthenium–nitrogen bonds in these complexes are so stable that the ligands bound to ruthenium can readily be transformed to other ligands without disruption of the ruthenium–nitrogen bond. Thus, the nitrosyl complex, *trans*-$[RuClNO(das)_2]^{2+}$, was readily converted under mild conditions into the azide complex, $[RuN_3Cl(das)_2]$. The coordinated azide ion also reacted with $NOPF_6$ under somewhat more vigorous conditions to give moderately good yields of the dinitrogen complex, *trans*-$[RuClN_2(das)_2][PF_6]$. The course of these reactions was followed by the use of ^{15}N. The ^{15}N which was initially coordinated to the ruthenium is retained throughout the entire reaction sequence. The retention of the ^{15}N fragment coupled with the positive identification of the Ru–^{15}N stretching frequencies show that the Ru–N bond is not ruptured during the course of these reactions.

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

[20] For a preliminary account of portions of these results, see P. G. Douglas, R. D. Feltham, and H. G. Metzger, *Chem. Commun.*, 889 (1970).