Experimental Section

Analyses were performed by Galbraith Laboratories, Inc. The compounds rich in aziridine presented some difficulty in handling since aziridine is readily sublimed from the sample under normal room conditions.

The thermal decompositions were run in an Abderhalden condenser. Decomposition was continued until the sample weight became constant.

Magnetic moments were determined by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as standard. Diamagnetic corrections were made using Pascal's constants.

Electronic absorption spectra were recorded with a Cary 14 spectrophotometer. Absorption of solids was measured with Nujol mulls on filter paper.

All chemicals were of reagent grade. Aziridine was supplied by Dow Chemical Co., Midland, Mich.

Hexaaziridinenickel(II) Chloride, $[Ni(Az)_6]Cl_2$.—A heterogeneous reaction between aziridine and anhydrous nickel(II) chloride is run in a beaker surrounded by ice. The resulting violet mass is treated with dry ether to improve the physical form and filtered. After several washings with dry ether, the solid product is dried in a desiccator over KOH pellets. Care must be taken in handling this compound because it readily loses aziridine on standing. It was difficult to obtain satisfactory analytical data for this reason. $[Ni(Az)_6]Cl_2$ can also be prepared by the direct reaction of aziridine with $Ni(Az)_4Cl_2$ or $Ni(Az)_2Cl_2$.

Dichlorotetraaziridinenickel(II), $Ni(Az)_4Cl_2$.—To a solution of hydrated nickel(II) chloride in methanol, an excess of aziridine is added. The addition is made at ice bath temperature with stirring, producing a deep blue color. Slow addition of a small amount of ether causes precipitation of the blue product which is isolated by filtration and dried in a desiccator over KOH pellets. $Ni(Az)_4Cl_2$ can also be prepared by dissolving $Ni(Az)_2Cl_2$ in an ethanol solution of aziridine and isolating the product in the same manner described above.

Dichlorodiaziridinenickel(II), $Ni(Az)_2Cl_2$.—$Ni(Az)_2Cl_2$ is prepared by the thermal decomposition of $[Ni(Az)_6]Cl_2$ or $Ni(Az)_4Cl_2$ in an Abderhalden apparatus at 100° and a pressure of approximately 5 Torr. All attempts to prepare this compound directly from nickel(II) chloride have been unsuccessful.

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Preparation and Reactivity of New Azido-Bridged Complexes of Rhodium(I)

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Although azido-bridged complexes have been presumed by several authors,[1-4] it is recently that such complexes have been fully characterized.[5-7]

This paper reports the preparation of new Rh^I azido-bridged complexes by a general method which can be extended to the synthesis of analogous transition metal complexes.

Experimental Section

Materials.—The compounds $[(CO)_2RhCl]_2$,[8] $[C_8H_{12}RhCl]_2$,[9] $[C_{10}H_{12}RhCl]_2$,[9] $[C_7H_8RhCl]_2$,[10] $[C_8H_8RhCl]_2$,[11] and $[(P(C_6H_5)_3)_2RhCl]_2$[12] were synthesized as described in the literature. Tetrabutylammonium azide was prepared as described by Gutmann.[13] Absolute methanol was dried and purified by distillation after refluxing over $Mg(OCH_3)_2$. All the chemicals used were reagent grade.

Preparation of $[(CO)_2RhN_3]_2$.—To a stirred suspension of 0.388 g (1 mmol) of $[(CO)_2RhCl]_2$ in 20 ml of dry methanol, 0.140 g (2.15 mmol) of sodium azide was added in a nitrogen atmosphere at room temperature. Immediately the solution turned yellow-brown while a deep red precipitate was formed. After 1 hr the solution was filtered and the dimeric compound was recrystallized from dichloromethane–methanol. The yield was almost quantitative (mp 120–125° dec). The compound is air stable in the solid state, although it decomposes in solution to a dark insoluble solid (probably a polymeric form). The complex $[(CO)_2RhN_3]_2$ is soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in methanol, and insoluble in hydrocarbons.

Preparation of $[(diene)RhN_3]_2$.—These complexes were prepared in an almost quantitative yield by the following procedure.

To a suspension of 0.1 mmol of $[(diene)RhCl]_2$ in dry methanol a twofold molar excess of solid NaN_3 was added with stirring in a nitrogen atmosphere. After 4–5 hr the reaction mixture was filtered and washed with a few milliliters of water to remove the excess of sodium azide, methanol, and ether. All the complexes prepared with the procedure described above were recrystallized from dichloromethane–hexane. Analytical data and physical properties of $[(diene)RhN_3]_2$ are reported in Table I.

Preparation of $(P(C_6H_5)_3)_2Rh(CO)N_3$.—A solution of 0.200 g (0.5 mmol) of $[(CO)_2RhN_3]_2$ in CH_2Cl_2 was treated with an excess of triphenylphosphine (0.500 g) in a nitrogen atmosphere. After a few minutes the solution turned from orange-yellow to pale yellow, and after 20 min the solvent was removed leaving a yellow solid which was washed several times with hexane and crystallized from CH_2Cl_2–hexane.

Its ir spectrum and physical properties are identical with those of the compound prepared according to the literature procedure by metathesis from $(P(C_6H_5)_3)_2Rh(CO)Cl$ and $N(C_2H_5)_4N_3$.[14,15]

Preparation of $(diene)Rh(P(C_6H_5)_3)N_3$.—A stirred suspension of 0.100 g $[(diene)RhN_3]_2$ (diene = C_7H_8, C_8H_{12}, $C_{10}H_{12}$) in petroleum ether (bp 40–60°) was treated dropwise with a petroleum ether solution containing the stoichiometric amount of triphenylphosphine. After 10 hr the mixture was filtered and the yellow residue was washed with hexane. The complexes (diene)-$Rh(P(C_6H_5)_3N_3$ were characterized by their elemental analysis and ir spectra (see Tables I and II).

Reactions of Azido-Bridged Complexes with Carbon Monoxide.—When carbon monoxide was bubbled through a CH_2Cl_2 solution of $[(CO)_2RhN_3]_2$ or $[(diene)RhN_3]_2$ for 24 hr at room temperature, the complex $[(CO)_2Rh(NCO)]_2$ was obtained in both cases, after evaporation of the solvent and recrystallization from CH_2Cl_2–pentane. The red $[(CO)_2Rh(NCO)]_2$ complex melts with decomposition at 170–175° and is stable in air in the solid state but decomposes very slowly in solution. It dissolves in chlo-

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(1) P. I. Paetzold, M. Gayoso, and K. Dehnicke, *Chem. Ber.*, **98**, 1173 (1965).

(2) K. Dehnicke, J. Strahle, D. Seybold, and J. Muller, *J. Organometal. Chem.*, **6**, 298 (1966).

(3) N. Wiberg and K. H. Schmid, *Chem. Ber.*, **100**, 741 (1967).

(4) J. Muller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **350**, 113 (1967).

(5) W. Beck, W. P. Fehlhammer, P. Pollmann, and R. S. Tobias, *Inorg. Chim. Acta*, **2**, 467 (1968).

(6) V. G. Lange and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **344**, 167 (1966).

(7) S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, **4**, 813 (1965).

(8) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211.

(9) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(10) E. W. Abel, M. A. Bennet, and G. Wilkinson, *ibid.*, 3187 (1959).

(11) M. A. Bennett and J. D. Saxby, *Inorg. Chem.*, **7**, 321 (1968).

(12) D. N. Lawson and C. Wilkinson, *J. Chem. Soc.*, 1900 (1965).

(13) V. Gutmann, G. Hampel, and O. Leitmann, *Monatsh. Chem.*, **95**, 1034 (1964).

(14) J. P. Collman, M. Kubota, and J. W. Hosking, *J. Amer. Chem. Soc.*, **89**, 4809 (1967).

(15) W. Bech, M. Bauder, W. P. Fehlhammer, P. Pollmann, and H. Schachl, *Inorg. Nucl. Chem. Lett.*, **4**, 143 (1968).

TABLE I

COLORS, DECOMPOSITION TEMPERATURES, AND ANALYTICAL DATA FOR AZIDO COMPLEXES

			Analyses, %					
			C		H		N	
Complex[a]	Color	Dec pt, °C	Calcd	Found	Calcd	Found	Calcd	Found
$[(C_8H_{12})RhN_3]_2$	Yellow	187–190	37.96	38.5	4.78	4.6	16.60	16.6
$[(C_7H_8)RhN_3]_2$	Yellow	174–176	35.46	35.2	3.40	3.3	17.73	17.8
$[(C_{10}H_{12})RhN_3]_2$	Yellow	179–182	44.34	44.6	4.36	4.3	15.16	15.2
$[(C_8H_8)RhN_3]_2$	Yellow	173–177	38.57	38.8	3.24	3.2	16.87	16.7
$(C_7H_8)Rh(P(C_6H_5)_3)N_3$	Yellow	138–143	60.13	61.2	4.64	4.5	8.41	8.3
$(C_8H_{12})Rh(P(C_6H_5)_3)N_3$	Yellow	105–108	60.58	61.6	5.28	5.4	8.15	8.3
$(C_{10}H_{12})Rh(P(C_6H_5)_3)N_3$	Brown-yellow	104–108	62.34	63.0	5.04	5.3	7.79	7.9
$[(CO)_2RhN_3]_2$	Red	120–125	11.95	12.2	...	...	20.91	20.6
$(CO)Rh(P(C_6H_5)_2N_3$	Yellow	167–171	65.20	65.1	4.43	4.4	6.17	6.2
$[(CO)_2Rh(NCO)]_2$	Red	170–175	17.92	18.25	...	0.03	6.97	6.82

[a] C_8H_{12} = cycloocta-1,5-diene, C_7H_8 = norbornadiene, $C_{10}H_{12}$ = dicyclopentadiene, and C_8H_8 = cyclooctatetraene.

TABLE II

INFRARED BANDS (CM^{-1}) OF $[(CO)_2RhX]_2$ (X = N_3, NCO, Cl, Br) COMPLEXES[a]

Compound	ν(CO)	$\nu_{as}(N_3)$ ν_{as}(NCO)	$\nu_s(N_3)$ ν_s(NCO)	Other bands
$[(CO)_2RhN_3]_2$	2135 w, 2087 s, 2063 vw, 2029 s, 1994 w[b]	2092 s[b]	1279 m[c]	723 w, 610 m, 554 w, 501 w, 449 w[c]
$[(CO)_2Rh(NCO)]_2$	2139 w, 2089 s, 2063 vw, 2035 s, 1995 w[b]	2185 s[b]	1336 m[c]	721 vw, 618 w, 607 w, 583 m, 509 vw, 431 vw[c]
$[(CO)_2RhCl]_2$[d]	2105 m, 2089 s, 2080 vw, 2035 s, 2003 w			610 m, 483 m
$[(CO)_2RhBr]_2$[d]	2100 m, 2087 s, 2075 vw, 2032 s, 2001 w			599 m, 475 m

[a] Abbreviations: v, very; s, strong; m, medium; w, weak. [b] Cyclohexane solution. [c] Nujol mull. [d] Data from C. W. Garland and J. R. Wilt, *J. Chem. Phys.*, **36**, 1094 (1962).

rinated solvents to give yellow solutions like the analogous $[(CO)_2RhN_3]_2$.

Attempted Preparation of $[(P(C_6H_5)_3)_2RhN_3]_2$.—To a stirred suspension of 0.265 g (0.2 mmol) of $[(P(C_6H_5)_3)_2RhCl]_2$ in 20 ml of dry methanol 0.013 g of NaN_3 was added under nitrogen at room temperature. After 4 hr the resulting solution was evaporated to dryness. The yellow-orange solid was dissolved in dichloromethane and precipitated with hexane. The analysis was not consistent with a compound of the formula $[(P(C_6H_5)_3)_2RhN_3]_2$. Further attempts to purify the yellow solid either by chromatography on alumina or by fractional crystallization were unsuccessful.

Instrumentation.—Ir spectra were recorded on a Perkin-Elmer 621 double-beam spectrophotometer. Conductivity measurements were carried out with a LKB 5300 B conductivity bridge.

Results and Discussion

It has been shown that in complexes of the type $[(L_\pi)_2RhCl]_2$ (L_π = CO, $^1/_2$(diolefin)) the chloride can be easily replaced by other anions, such as Br^-, I^-, carboxylate, nitrate, thiocarbonate, sulfate, etc.,[9–12] leading to the corresponding dimeric complexes. The same reaction occurs with the azide ion

$$[(L_\pi)_2RhCl]_2 + 2N_3^- \longrightarrow [(L_\pi)_2RhN_3]_2 + 2Cl^-$$

L_π = CO, $^1/_2$(cycloocta-1,5-diene), $^1/_2$(norbornadiene), $^1/_2$(dicyclopentadiene), $^1/_2$(cyclooctatetraene).

Carbonyl Derivatives.—When a methanolic suspension of $[(CO)_2RhCl]_2$ is allowed to react with the stoichiometric amount of NaN_3, a red precipitate is formed slowly and the stable compound $[(CO)_2RhN_3]_2$ is obtained. This compound was characterized by its elemental analysis and ir spectrum.

It is a nonconducting compound in dichloromethane and air stable in the solid state but decomposes in solutions of most common organic solvents to give a dark solid which is probably a polymeric form. In the solid state it is dichroic, suggesting the presence of metal–metal bonds, as in rhodium carbonyl chloride itself.[12–16] It dissolves in chlorinated solvents giving yellow solutions.

The ir spectrum of $[(CO)_2RhN_3]_2$ in cyclohexane solution shows an additional band at 2092 cm^{-1} (s), with respect to the analogous $[(CO)_2RhX]_2$ (X = Cl, Br, NCO), due to $\nu_{as}(N_3)$ (Table II). The reaction product does not exhibit bands in the 200–400-cm^{-1} region due to the ν(Rh–Cl), whereas a new medium-strong band appears at 1279 cm^{-1} attributable to $\nu_s(N_3)$ in the azido-bridged complex.

Diene Derivatives.—Following the same preparative route described for the carbonyl derivatives, dimeric compounds of the type $[(diene)RhN_3]_2$ were obtained. Analytical data and some physical properties of these complexes are reported in Table I. They are soluble in chlorinated solvents, slightly soluble in hydrocarbons, and insoluble in alcohols. These complexes are air stable in the solid state and decompose in solution to give brown unidentified materials. In their ir spectra, reported in Table III, the positions of $\nu_{as}(N_3)$ and $\nu_s(N_3)$

TABLE III

FREQUENCIES OF THE FUNDAMENTAL N_3 VIBRATIONS OF DIOLEFIN–AZIDO COMPLEXES OF Rh^I [a]

Complex	ν_{as}, cm^{-1}	ν_s, cm^{-1}	δ, cm^{-1}
$[(C_8H_{12})RhN_3]_2$	2058 vs	1279 s	574 w
$[(C_7H_8)RhN_3]_2$	2059 vs	1281 s	578 vw, 558 w
$[(C_{10}H_{12})RhN_3]_2$	2062 vs	1278 s	577 w
$[(C_8H_8)RhN_3]_2$	2058 vs	1284 s	579 vw, 568 vw
$(C_7H_8)Rh(P(C_6H_5)_3)N_3$	2025 vs	1278 m	...
$(C_8H_{12})Rh(P(C_6H_5)_3)N_3$	2038 vs	1282 m	...
$(C_{10}H_{12})Rh(P(C_6H_5)_3)N_3$	2046 vs	1278 w	...

[a] Abbreviations: v, very; s, strong; m, medium; w, weak. Spectra taken in Nujol mull.

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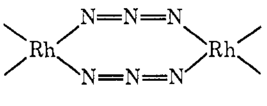
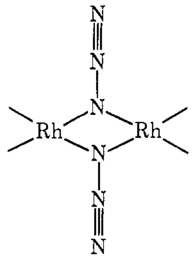
(16) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, **83**, 1761 (1961).

are practically unchanged by varying the coordinated diolefins. It can be seen that the $\nu_{as}(N_3)$ in the $[(CO)_2RhN_3]_2$ dimer is higher than that of the analogous diene derivatives and of other d^8 azido-bridged complexes.[5,7]

For the $[(L_\pi)_2RhN_3]_2$ two structures are possible



A



B

Both structures have D_{2h} symmetry and so cannot be distinguished on the basis of the number of infrared-active vibrations. However, the appearance of ν_s in the ir spectra of the azido-bridged complexes as a medium-strong band strongly supports structure B in which a single atom is bridging.

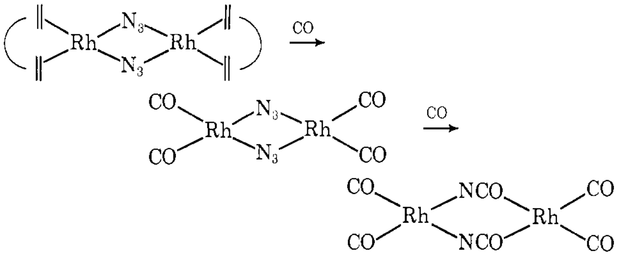
Bridge-Splitting Reactions of the $[(L\pi)_2RhN_3]_2$ Complexes.—To study the reactivity of the dimeric complexes, we have carried out some bridge-splitting reactions with triphenylphosphine and amines.

The reactions of $[(L_\pi)_2RhN_3]_2$ with triphenylphosphine are similar to those observed for the analogous chloro-bridged complexes, the monomeric $[(L_\pi)_2Rh(P(C_6H_5)_3)N_3]$ being obtained. The infrared spectra of these products show that the $\nu_{as}(N_3)$ is lower (~30 cm^{-1}) than that of the corresponding dimeric compounds.

In the case of amines such as pyridine or *p*-toluidine, no reaction occurs even with a large excess of ligand. The attempted preparation of the monomeric compounds (diene)RhN_3(amine) by methathesis from the chloro derivatives was unsuccessful and in fact $[(diene)RhN_3]_2$ was isolated from the reaction of (diene)Rh(amine)Cl with N_3^-. This behavior reflects the greater stability of the azido-bridged complexes with respect to the corresponding chloro compounds.

Reactions of $[(L_\pi)_2RhN_3]_2$ with CO.—It has been shown[14,15] that azido complexes of the types $(CO)ML_2N_3$ (M = Rh, Ir) and $M(N_3)_2L_2$ (M = Pd, Pt) react with carbon monoxide to give the corresponding cyanato complexes. A similar reaction occurs with the $[(L_\pi)_2RhN_3]_2$ complexes. These compounds and the diene derivatives react with carbon monoxide in dichloromethane at room temperature to give the cyanato-bridged complex $[(CO)_2Rh(NCO)]_2$. The cyanato-bridged compound has been characterized by elemental analysis (Table I) and its ir spectrum (Table II). It dissolves in chlorinated solvents giving yellow solutions. Its infrared spectrum in cyclohexane solution shows bands at 2185 (s) and 1303 cm^{-1} (m) attributed to $\nu_{as}(NCO)$ and $\nu_s(NCO)$, respectively.[17]

The following scheme is likely for the reaction of $[(diene)RhN_3]_2$ with carbon monoxide



This is in agreement with the fact that the overall reaction is complete after 1 day, whereas it is known that the displacement of the olefin by CO in complexes of the type (diene)RhLCl is fast (~1 hr).[18] Moreover, an ir spectrum of the reaction mixture taken after 3 hr shows $\nu_{as}(NCO)$ and $\nu_{as}(N_3)$ at 2185 and 2092 cm^{-1}, respectively, indicating that no olefin derivative is present.

The method reported in this paper for the preparations of the azido- and cyanato-bridged complexes of Rh^I appears to be of general applicability, although it was not possible to isolate $[(P(C_6H_5)_3)_2RhN_3]_2$. The preparation of other azido-bridged complexes of Pt^{II} and Pd^{II} is in progress and will be reported in a further publication.

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[17] J. Nelson and S. M. Nelson, *J. Chem. Soc. A*, 1597 (1969).

[18] J. W. Kang and P. M. Maitlis, *Can. J. Chem.*, **46**, 897 (1968).

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Platinum(II)-Olefin Complexes Containing Amino Acids. I. Preparation and Structure of Several Platinum(II)-Ethylene Complexes with Amino Acids[1]

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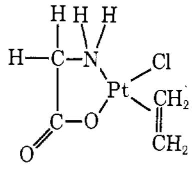
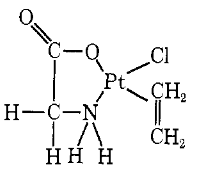
Recently, Kieft and Nakamoto[2] and Panunzi, *et al.*,[3] prepared a novel Pt(II) complex, chloro(glycino)(ethylene)platinum(II), by treating Zeise's salt with glycine. They proposed structure I in which the nitrogen



I (N-trans isomer)



II (O-trans isomer)

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[2] J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **30**, 3103 (1968).

[3] A. Panunzi, R. Palumbo, C. Pedone, and G. Paiaro, *J. Organometal. Chem.*, **5**, 586 (1966).