(1)

(2)

a. Z = H b; Z = C,H₅ c: Z = D d: Z = CH₃

implies that there is specific transannular monoene–diene interaction[7] in **1c** as in **12c** leading to **13c**.

Rearrangement of bicyclo[4.2.1]nona-2,4,7-trien-9-yl cations has been extended to acid catalyzed elimination of syn-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene **(19)**[8] and isomerization of 9-methylenebicyclo[4.2.1]-nona-2,4,7-triene **(10)**. Alcohol **19** was prepared (86% yield) from **16** and methylmagnesium bromide at 0° and subsequent acidification; **20** was obtained (77%

20
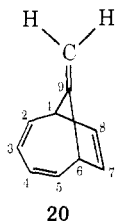
yield) from **16** and methylenetriphenylphosphorane in dimethyl sulfoxide at 74°. Dehydration of **19** and isomerization of **20** by p-toluenesulfonic acid in benzene at 74° give 2-methylindene **(14d, >80% yields)**; 1-methylindene **(9d)** and 3-methylindene **(10d)** were not detectable in these experiments by sensitive gas chromatographic methods. The conversions of **19** and **20** to **14d** are analogous to that of **17** to **14c** and indicate that the 9-methylbicyclo[4.2.1]nona-2,4,7-trien-9-yl cation **(1d)** rearranges by a specific bridging mechanism as in eq 2. The cationic conversion of **20** to **14d** reveals also that there is no formal initial stereochemical requirement at C-9 for entry into the rearrangement system of eq 2.[9] It is noted further that the previous exclusive conversion of **15** by p-toluenesulfonic acid to 2-phenylindene **(14b)**[2b] and the pyrolyses of syn-9-acetoxy-9-methylbicyclo-[4.2.1]nonatriene and syn-9-benzoyloxy-9-phenylbicyclo-[4.2.1]nonatriene at 184° in o-dichlorobenzene to **14d** and to **14b**, respectively,[2c] are now understandable via the reaction path of eq 2.

What is not yet definitive, however, are the structural and environmental factors which allow bicyclo[4.2.1]-

nona-2,4,7-trien-9-yl cationic reactions to occur via rearrangement processes as in eq 1. A major fact yet to be determined is whether sequences which begin as in eq 2 give products which presently appear to have been derived via eq 1. Based on the present information, however, it may be that bicyclo[4.2.1]nona-2,4,7-trien-9-yl cations, stabilized by electron-donor delocalizing groups at C-9 and possibly by solvent interaction at C-9 from the sterically available anti direction, do not bring out sufficient monoene–diene interaction from below as in **12**, and thus migration of C-2 or C-5 of the diene bridge to C-9 becomes the effective entry to cis-8,9-dihydroindenyl derivatives.

An Extension of the Nitrosyl–Aryldiazo Analogy.
The Structure of an Aryldiazo Group Coordinated to
Rhodium in a Doubly Bent Fashion

Sir:

Since the first unequivocal structural evidence for a bent M–N–O linkage in transition metal chemistry was presented,[1] chemical and structural interest in these systems has expanded rapidly. A recent tabulation[2] includes eight transition metal nitrosyl complexes out of 52 in which the M–N–O angle is between 120 and 128°. The analogy between NO⁺ (linear M–N–O) and RN₂⁺ (R = aryl) on the one hand and between NO⁻ (M–N–O angle, 120°) and RN₂⁻ on the other is an obvious one and suggests that the aryldiazo[3] ligand has the same amphoteric nature as does nitric oxide. We wish to report the first structural

(7) The physical constants of all intermediates and products compare favorably with literature values. The deuterium contents (~100%) of all labeled materials were confirmed by mass spectral and nmr methods.

(8) Alcohol **19** is identical with that prepared previously from dilithium cyclooctatetraenide and acetyl chloride and hydrolysis.[2a]

(9) The importance of hybridization at C-9 and the shape of bicyclo-[4.2.1]nona-2,4,7-triene systems is also indicated by the recent observations that, based on photoelectron spectra, there is considerable interaction of the π systems in **20** but none in bicyclo[4.2.1]nona-2,4,7-triene: M. T. Reetz, R. W. Hoffmann, W. Schäfer, and A. Schweig, *Angew. Chem.*, **85**, 45 (1973).

(1) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968); D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(2) B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Phys. Chem.*, **11**, 33 (1972).

(3) Consistent with the nomenclature proposed for C₆H₅NNH, phenyldiazene, and with that for C₆H₅NN⁺, phenyldiazonium ion, we adopt the names phenyldiazeno, instead of phenyldiimido, and phenyldiazo, instead of phenylazo, when these moieties are coordinated to a metal; phenyldiazo is used for both forms, RN₂⁺ and RN₂⁻. See E. M. Kosower, *Accounts Chem. Res.*, **4**, 193 (1971).
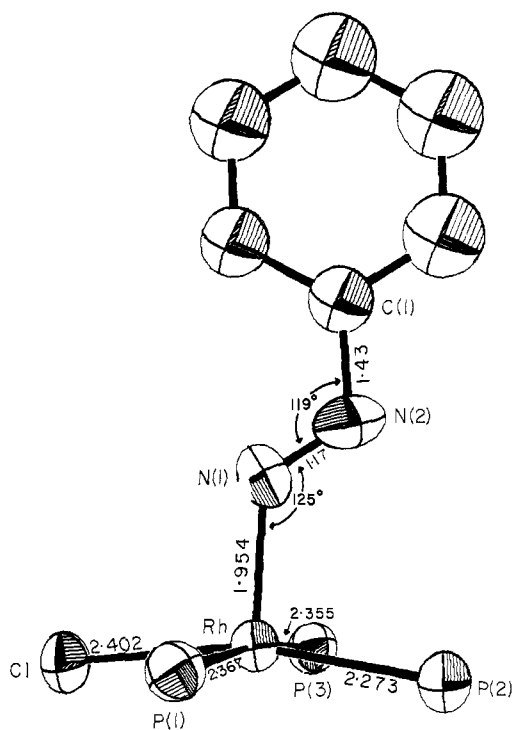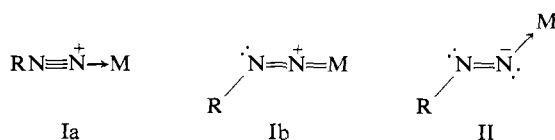
Figure 1. A perspective view of the inner coordination geometry of [Rh(C₆H₅P((CH₂)₃P(C₆H₅)₂)₂)Cl(N₂C₆H₅)]⁺. The methylene carbon atoms of the tridentate chelate ligand have been omitted for clarity. Estimated standard deviations on bond distances are Rh–P, 0.004; Rh–Cl, 0.003; Rh–N, 0.008; N–N, 0.02; and N–C, 0.01 Å. Estimated error in the angles is 1.0° in both cases.

example of the aryldiazo analog of NO⁻, in which the M–N–N–R linkage is doubly bent, II. The four previously determined aryldiazo structures all show singly bent diazo linkages, corresponding to RN_2^+.[4–7]

$$RN\!\!\equiv\!\!\overset{+}{N}\!\!\rightarrow\!\!M \qquad \overset{\cdot\cdot}{N}\!\!=\!\!\overset{+}{N}\!\!=\!\!M \qquad \overset{\cdot\cdot}{N}\!\!=\!\!\overset{\cdot\cdot}{N}\!\!\diagup^{M}$$

$$\qquad\qquad\qquad R\diagup \qquad\qquad R\diagup$$

$$\text{Ia} \qquad\qquad \text{Ib} \qquad\qquad \text{II}$$

The preparation of complexes of the type [RhLCl-(X)]⁺, where L = PhP((CH₂)₃PPh₂)₂, has been described.[8] When X = NO, a bent Rh–N–O linkage (M–N–O angle = 131°) is found[8] corresponding formally to NO⁻ bonded to Rh(III). The analogous complex with X = N₂Ph has been prepared[8] as the PF₆⁻ salt, and its structure was determined. The material crystallizes in space group C_1^1-$P\bar{1}$ with two formula units of the complex and two solvent molecules, CH₂Cl₂, in a cell of dimensions a = 12.675 (7), b = 13.254 (7), c = 15.092 (10) Å; α = 94.78 (5), β = 99.46 (5), γ = 112.40 (8)°; and V = 2282.3 Å³. Observed and calculated densities are 1.50 (1) and 1.506 g/cm³, respectively. At the present stage of least-squares refinement

based on 4031 absorption corrected data, the R index is 0.072. A difference Fourier map clearly reveals all of the 44 hydrogen atoms.

The geometry of the inner coordination sphere is approximately square pyramidal with the phenyldiazo group occupying the apical position (Figure 1). The apical ligand is formulated as phenyldiazo rather than phenyldiazene[9] since the region surrounding the nitrogen atoms is devoid of significant electron density within a radius of 1.7 Å. Spectral evidence also supports this formulation. The infrared spectrum shows neither an Rh–H nor an N–H stretching band.[9] The ¹H nmr spectra of both the ¹⁴N═¹⁴NPh and ¹⁵N═¹⁴NPh complexes show no evidence for either a hydride ligand attached to Rh or for a proton attached to N(1). However, treatment of the unlabeled material with HCl results in a broad resonance at τ −2.8, indicative of protonation of a nitrogen atom.

The bonding in the tetragonal plane agrees with that found in the corresponding nitrosyl complex.[8] The stereochemistry about the N–N bond is trans. The Rh–N(1) distance is approximately equal to that in the corresponding nitrosyl complex[8] and is considerably longer than the M–N distances in a number of singly bent aryldiazo complexes.[4–7] The M–N distances in aryldiazo complexes are thus consistent with comparable data on NO⁺ and NO⁻ complexes.[2] The bond angle of 125° at N(1) completes the analogy with the bonding in NO⁻, and suggests formulation of the complex as $Rh^{III}(N_2Ph^-)$. These results seem to confirm the suggestion[9–14] that certain aryldiazonium complexes of Rh, Ir, and Pt possess doubly bent aryldiazo groups.

The infrared spectrum of the complex (Nujol mull, KBr pellet) shows, in addition to absorptions arising from PF₆⁻ and RhLCl, two bands at 1627 (m) and 1561 (m) cm⁻¹ which persist in solution (CH₂Cl₂). The infrared spectrum of [RhLCl(¹⁵N═¹⁴NPh)][PF₆⁻] is identical with that of the unlabeled material except that these two bands are shifted to lower energy by 14 and 12 cm⁻¹, respectively, and are thus associated with the –N═N– linkage. The origin of the two frequencies associated with the –N═N– linkage is not known with certainty. However, two absorption bands are frequently observed in complexes which exhibit lower values of ν(NN), see Table I.

There are inadequacies in using the N–O stretching frequency to diagnose the mode of nitrosyl coordination to a transition metal because of the large overlapping region (1600–1720 cm⁻¹) between NO⁺ and NO⁻ complexes.[15] Based on accumulated data on transition metal–NO geometries,[2] we put forward the following empirical rules to bring the various NO stretching frequencies to a common scale: (1) subtract 50 cm⁻¹ for first-row metals and 30 cm⁻¹ for second-row metals; (2) subtract 80 cm⁻¹ for singly charged and 140 cm⁻¹ for doubly charged cationic complexes; (3) add 40 or

(4) V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, Chem. Commun., 1083 (1970).

(5) G. Avitabile, P. Ganis, and M. Nemiroff, Acta Crystallogr., Sect. B, 27, 725 (1971).

(6) J. A. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, Inorg. Chem., 12, 1676 (1973). We are indebted to Professor Eisenberg for a preprint of that work.

(7) B. L. Haymore and J. A. Ibers, unpublished results. An independent determination of the structure of the Ru aryldiazo complex is in good agreement with the results of McArdle, et al. (ref 6).

(8) T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner, and J. A. Ibers, J. Amer. Chem. Soc., 95, 4194 (1973).

(9) K. R. Laing, S. D. Robinson, and M. F. Uttley, J. Chem. Soc., Chem. Commun., 176 (1973).

(10) B. L. Haymore and J. A. Ibers, J. Amer. Chem. Soc., 95, 3052 (1973).

(11) G. W. Parshall, J. Amer. Chem. Soc., 89, 1822 (1967); 87, 2133 (1965).

(12) S. Cenini, R. Ugo, and G. LaMonica, J. Chem. Soc. A, 3441 (1971).

(13) A. J. Deeming and B. L. Shaw, J. Chem. Soc. A, 1128 (1969).

(14) M. C. Baird and G. Wilkinson, J. Chem. Soc. A, 865 (1967).

(15) D. M. P. Mingos and J. A. Ibers, Inorg. Chem., 10, 1479 (1971).

Table I

Compound[a]	Geometry[b]	ν(NN)[c]	ν'(NN)[d]
I OsBr₃P₂L[e,f]		1850	1850
II RuCl₃P₂L[e,g]	Ia ↔ Ib[o]	1882	1852
III [RhClP₂L][PF₆][h]		1899	1789
IV [IrClP₂L][PF₆][g]		1868	1788
V [Ir(PP)₂L][PF₆]₂[h]		1697	1627
VI [IrClP₃L][PF₆][g]		1651	1611
VII [Fe(CO)₂P₂L][BF₄][i,j,k]	Ib[h]	1723	1593
VIII [RhCl(PPh₂CH₃)₃L][PF₆][h,l]		1653	1583
IX RhCl₂P₂L[e,f]		1614, 1549	1551
X [RhCl(PPP)L][PF₆][m]	II	1627, 1561	1524
XI IrCl₂(CO)P₂L[g]		1464	1464
XII [IrCl(PP)₂L][PF₆][h]		1463, ~1440	1442
XIII [RhCl(PP)₂L][PF₆][h]		1493, 1466	1440
XIV PtCl(PEt₃)₂L[n]		1440	1440
XV RuCl(CO)₂P₂L[h]		1455	1425

[a] Key: Ph = C_6H_5, Et = C_2H_5, L = PhN_2, P = PPh_3, PP = $(Ph_2PCH_2)_2$, PPP = $PhP(CH_2CH_2CH_2PPh_2)_2$. [b] Crystal structure of compound or closely related one is known. [c] Frequencies given as cm^{-1}. [d] When two frequencies are observed, the average is taken in computing this value. [e] Reference 9. [f] S. D. Robinson, private communication. [g] Reference 10. [h] Reference 7. [i] F. J. Lalor, private communication. [j] D. Sutton, private communication. [k] Spectra in CH_2Cl_2 solution of analytically pure samples of $[Ru(CO)_2P_2L][PF_6]$ show three ν(CO)'s at 2080, 2051, and 1995 and three ν(NN)'s at 1681, 1607, and 1556 indicating the presence of either two different compounds or two stereochemical forms of the same compound. [l] Reference 14. [m] Reference 8. [n] Reference 11; $[PtP_3L]^+$ and $PtIP_2L$ were omitted because the assigned values for ν(NN) were not substantiated by isotopic substitution and because the reported values are in sharp contrast to those for XIV; see ref 12. [o] Reference 6.

70 cm^{-1} for complexes with three or four tertiary phosphines, respectively. These rules, which are primarily applicable to diamagnetic complexes of group VIII metals,[16] greatly reduce the region of overlap noted above. Several of the complexes whose modified values of ν(NO) fall in or near the region of overlap may exhibit an intermediate M–N–O geometry.

If we apply these rules to the observed values of ν(NN)[17] in phenyldiazo complexes of group VIII metals, we obtain (Table I) the modified frequencies, ν'(NN). The PhN_2 complexes then fall into three groups except for IX which is a borderline case: (A) those with values of ν'(NN) lower than 1540–1560 cm^{-1} corresponding to the doubly bent geometry (II); (B) those with values between 1540–1560 and 1700–1740 cm^{-1} corresponding to the singly bent geometry (Ib); (C) those with values greater than 1700–1740 cm^{-1} corresponding to the singly bent geometry, but tending toward the totally linear case (Ia). Despite the relatively small number of diazo complexes known, the proposed empirical rules seem to be useful in categorizing these complexes into three groups. When more diazo complexes are found, we anticipate that ν'(NN) will be more useful than ν(NN) in characterizing the mode of diazo coordination. In the above, we have considered what appear to be the three most important canonical structures contributing to the ground states of the phenyldiazo ligand; we have ignored those canonical formulations involving reduced forms for the phenyl ring.

(16) Similar rules for group VIb and VIIb metals can be formulated.
(17) ν(NN) refers to the frequency(s) arising from the diazo linkage as established by ^{15}N substitution.

Arthur P. Gaughan, Jr., Barry L. Haymore, James A. Ibers*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

William H. Myers, Thomas E. Nappier, Jr., Devon W. Meek
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received May 24, 1973

Novel Nonphenol Oxidative Coupling[1]

Sir:

Oxidative coupling of phenols as a mode of carbon–carbon bond formation holds a prominent position in the biosynthesis and synthesis of complex alkaloids and other polycyclic compounds.[2,3] Recent reports have also described efficient intramolecular coupling in monophenolic compounds.[4,5] Although the electro-oxidative coupling of *nonphenolic* substrates has been reported, prior attempts to effect chemical coupling of such substrates have apparently been unsuccessful.[6] We wish to report herewith the smooth intermolecular and intramolecular coupling of *nonphenolic* benzylisoquinolines upon treatment with vanadium oxytrifluoride. The usefulness of the novel reaction is exemplified by the efficient synthesis of the unusual spirodienone **10**, an *Erythrina* alkaloid precursor.

Papaverine (**1**), a readily available nonphenolic alkaloid, was a convenient starting material for the initial studies. Based on our previous experience,[5] VOF_3 in trifluoroacetic acid (TFA) was chosen as the oxidizing system. In the event, a surprisingly facile reaction ensued which afforded an 80% yield of the aryl-to-aryl intermolecularly coupled product, **2**:[7] mp 180–182°; uv λ_{max}^{EtOH} (log ϵ) 239 (5.06), 284 (4.14), 314 (3.85), 328 (3.91) nm; nmr ($CDCl_3$) δ 8.23 (d, J = 6 Hz, 2 H-3), 7.23 (d, J = 6 Hz, 2 H-4), 6.93 (s, 4 ArH), 6.72 (s, 2 ArH), 6.50 (s, 2 ArH), 4.23 (s, 4 H, 2 Ar-CH_2-Ar'), 3.91, 3.79, 3.70, 3.50 (each s, all 6 H, 8-OCH_3); mass spectrum m/e (%) 676 (19, M⁺), 475 (100). Assignment of the 6'-6' linkage in the structure of the dimer, favored by analogy to the products of other reactions of papaverine,[8] was confirmed by oxidation to the tetramethoxydiphenic acid **3**.[9–11]

(1) This investigation was supported by grants from the National Cancer Institute (CA-12059 and CA-11760).
(2) W. I. Taylor and A. R. Battersby, Ed., "Oxidative Coupling of Phenols," Marcel Dekker, New York, N. Y., 1967.
(3) T. Kametani and K. Fukumoto, *Synthesis*, 657 (1972).
(4) M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *J. Amer. Chem. Soc.*, **95**, 612 (1973).
(5) S. M. Kupchan and A. J. Liepa, *ibid.*, **95**, 4062 (1973).
(6) L. L. Miller, F. R. Stermitz, and J. R. Falck, *ibid.*, **95**, 2651 (1973); *cf.* D. H. R. Barton, *Proc. Chem. Soc., London*, 293 (1963).
(7) All new compounds were characterized by concordant analytical and spectral data.
(8) *Cf.* P. Mathieu and J. Gardent, *C. R. Acad. Sci., Ser. C*, 1416 (1968).
(9) Reduction of the dimer 2 with Zn–40% aqueous HOAc at 90° to the bistetrahydro derivative was followed by CH_3I methylation and Hofmann degradation to the bismethine.[10] Oxidation with aqueous $KMnO_4$ yielded a crude dialdehyde, which was oxidized with $KMnO_4$–acetone to the diacid **3**: mp 251–254° (lit.[11] mp 251–253°); mass spectrum m/e (%) 362 (80, M⁺), 344 (48), 317 (100).

Communications to the Editor