from C-H bonds of alcohols to form radical pairs (e.g., $PhCH_2\cdot + \cdot CH_2OH$) which would recombine with high efficiency to give the C-H "insertion" products in the matrix environment, whereas in the liquid phase the members of the pairs would diffuse apart to yield **2** and **3**. The facts that the yield of bibenzyl drops markedly as the reaction phase is changed from liquid to solid and **5** increases significantly in colder and presumably harder −196 °C matrix[10] are apparently related to the relative diffusibility of radicals.

The reason for the marked reduction in the ether yields at lower temperature is uncertain. A rapid decay of the initially formed singlet carbene to the triplet in rigid matrix seems unlikely since styrene, an intramolecular product of singlet PhCMe,[11] was formed in high yield even in −196 °C matrix and, further, rapid and reversible singlet-triplet equilibrium has been assumed[1,5] to be involved in phenylcarbene reactions. There is a possibility, however, that the O-H insertion reaction could be more significantly assisted by solvation, which might become less important in solid phase, compared with the other radical processes, since ionic species,[1a] i.e., benzyl cation and/or ylide, have been proposed to be involved in the reaction. Thus, matrix might affect the kinetics of the competitive intermolecular singlet and triplet carbene processes occurring within it.[5]

The low temperature photolysis[3] of diphenyldiazomethane in *tert*-butyl alcohol matrix gave a completely different picture than irradiation in other alcoholic matrices. There was no sign of the C-H insertion product being formed; instead, there was formed azine (**8**), ethylene (**9**), and ethane (**10**)

$$\underset{\mathbf{6}}{Ph_2CN_2} \xrightarrow[\substack{t\text{-BuOH}\\ 70\text{-}80\%}]{h\nu} \underset{\mathbf{7}}{Ph_2CHO\text{-}t\text{-}Bu} + \underset{\mathbf{8}}{Ph_2C{=}NN{=}CPh_2} + \underset{\mathbf{9}}{Ph_2C{=}CPh_2} + \underset{\mathbf{10}}{Ph_2CHCHPh_2}$$

	Relative yields, %			
T, °C	**7**	**8**	**9**	**10**
27	97.5	2.5	0	0
−72	3.0	56.6	26.9	13.5
−196	0.8	26.6	72.6	0

all of which were only minor products (<5%) in the photolysis in other alcohols.[12] The high yield formation of the olefinic dimer (**9**) in *tert*-butyl alcohol matrix is especially noteworthy since solution-phase photolysis of **6** in inert solvent gave[13] predominantly azine but no trace of ethylene. Presumably, molecules are not matrix isolated but coherent with large dislocation in matrix of *tert*-butyl alcohol which does not form glass but crystallizes upon cooling,[14] and, hence, carbenes or radicals derived from them in the solid would dimerize or attack the neighboring diazo compound inside the molecular aggregates of **6**. Whether the olefinic dimer arises from combination of two triplet carbenes[15] or an action of a carbene on a diazo compound[16] is an interesting question.[17] There is particularly sound precedence for the former in this special condition since triplet phenylcarbenes are known[18] to have enough lifetime to encounter each other at this temperature. Drastic decrease in the azine yield at lower temperature would suggest that the azine could be formed via electrophilic attack by singlet carbene on the terminal nitrogen of the diazo linkage as has been suggested[15] previously, if one assumes that the temperature dependence of intermolecular singlet carbene processes is general.[5]

In conclusion the present results provide a carbene route to the C-H insertion products into alcohols as well as important informations on chemical behaviors of carbenes in rigid matrix and the relationship between the multiplicities and the reaction pathways of carbenes. Further we hope the observed matrix effect would be extended to a unique low temperature synthesis of unstable ethylenes (e.g., tetra-*tert*-butylethylene) via carbenes.

References and Notes

(1) (a) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971; (b) R. A. Moss and M. Jones, Jr., Ed., "Carbenes", Vol. I and II, Wiley, New York, N.Y., 1974 and 1975.

(2) See, for example, D. R. Morton and N. J. Turro, *Adv. Photochem.*, **9**, 197-309 (1974).

(3) The degassed and sealed quartz tubes containing alcohol solution of diazo compounds were suspended in a transparent quartz Dewar flask filled with coolant and irradiated with a Halos 300-W high-pressure mercury lamp. When the irradiation was performed in solid phase, the mixture was periodically warmed in the dark until the rigid glass or solid melted so that mixing could occur.

(4) The melting points of pure methanol, ethanol, and 2-propanol are −97.8, −114.1, and −88.5 °C, respectively: "The Merck Index", 9th ed, M. Windholz, Ed., Merck and Co., Rahway, N.J., 1976.

(5) R. A. Moss and U.-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954-960 (1971); R. A. Moss and M. A. Joyce, *ibid.*, **99**, 1262-1264 (1977).

(6) A. M. Trozzolo, *Acc. Chem. Res.*, **1**, 329-335 (1968).

(7) The emission spectrum of **6** in ethanol glass at −196 °C was identical with that of triplet diphenylmethylene.[6]

(8) A possible alternative source[1b] of **5** might involve the intervention of the $Ph\dot{C}N_2$ radical, since photolysis of diazomethane in an Argon matrix at 8 K is reported to yield substantial amounts of the corresponding diazo radical: J. F. Ogilvie, *Photochem. Photobiol.*, **9**, 65 (1969). This may seem less likely since the comparative chemistry in different matrix at different temperature would considerably differ.

(9) The sensitized decomposition of diazomalonate in 2,3-dimethylbutane yielded slightly more tertiary C-H insertion product than did the direct: M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycky, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Am. Chem. Soc.*, **94**, 7469-7479 (1972).

(10) Although the exact temperature at which the reactions occur is not clear, the significant differences between −110 and −196 °C matrix results (in methanol and 2-propanol) suggest that most of the reaction occur in the matrices.

(11) Y. Yamamoto, S.-I. Murahashi, and I. Moritani, *Tetrahedron*, **31**, 2663-2667 (1975).

(12) (a) Although photolysis of **1** in *tert*-butyl alcohol matrix at −196 °C also yielded *trans*-stilbene and benzalazine, quantitative studies have not been made since the control experiments showed that some of the azine was formed on thawing the matrix at 25 °C (melting point of *tert*-butyl alcohol). (b) Moss et al.[5] have also observed that *trans*-stilbene became the more important product in the irradiation of **1** in *crystalline* olefinic matrices at −196 °C than in solution. (c) Absence of *cis*-stilbene in low temperature matrix experiments is reminiscent of the almost exclusive formation of trans isomer in the photoisomerization of stilbene at low temperature: D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 3907-3918 (1968).

(13) W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 19-30 (1958).

(14) Similar striking effects of host on the course of low temperature photochemical reactions have been observed previously: (a) W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874-5879 (1959); (b) V. Dvorák, J. Kolc, and J. Michl, *Tetrahedron Lett.*, 3443-3446 (1972); (c) J. Kolc, *ibid.*, 5321-5324 (1972).

(15) H. E. Zimmerman and D. Paskovich, *J. am. Chem. Soc.*, **86**, 2149-2160 (1964).

(16) H. Reimlinger, *Chem. Ber.*, **97**, 339-348 (1964).

(17) **9** was not formed in the photolysis of **8** in methanol: J. Gorse, III, and R. W. Binkley, *J. Org. Chem.*, **37**, 575-578 (1972).

(18) W. A. Gibbons and A. M. Trozzolo, *J. Am. Chem. Soc.*, **88**, 172-173 (1966).

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Binuclear Rhodium(I) Complexes. Molecular A Frames

Sir:

The design, synthesis and characterization of binuclear complexes in which d^8 metal centers are held in close, fixed proximity, represents an important objective in the systematic study of multicentered reagents and catalysts.[1] The primary approach to this objective involves the use of bridging ligands to achieve the desired structure and orientation of the metal centers.[2-7] The bridging ligands can also serve to introduce additional functionality into the complex which can be utilized in the binding and activation of substrates. The binuclear Rh(I)

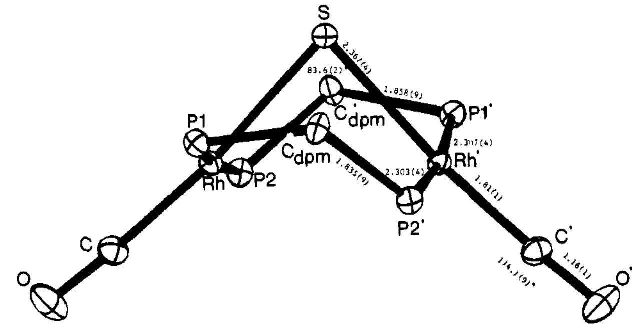
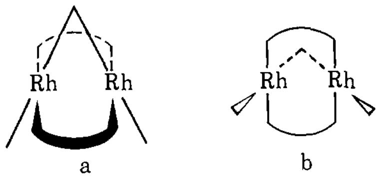


Figure 1. Drawing of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$ without phenyl rings. Selected distances and angles are shown. Sulfur lies on a crystallographic C_2 axis and the unprimed atoms represent one asymmetric unit. Other bond angles include C-Rh-P1, 97.6 (3)°; P1-Rh-P2, 173.51 (9)°; P1-Rh-S, 84.3 (1)°; P2-Rh-S, 89.4 (1)°; S-Rh-C, 172.9 (3)°; and C-Rh-P2, 88.8 (3)°.

complexes which we report herein exemplify these features and possess the novel "A-frame"-type structure I.



I

The addition of Na_2S to a methanolic suspension of $[Rh_2Cl_2(CO)_2(dpm)_2]$ (dpm = bis(diphenylphosphino)methane),[2] produces an immediate color change followed by precipitation of red crystals of $[Rh_2(\mu\text{-}S)(CO)_2(dpm)_2]$, **1.** This complex is obtained analytically pure and exhibits ν_{CO} of 1910 and 1923 cm^{-1}. Treatment of **1** with MeNC leads to CO evolution and the formation of the analogous isocyanide complex $[Rh_2(\mu\text{-}S)(CNMe)_2(dpm)_2]$, **2,** with ν_{CN} of 2160 and 2185 cm^{-1}.

The structure of **1** was established by a single-crystal x-ray diffraction study. Complex **1** crystallizes in space group *Pccn* in a cell of dimensions $a = 13.72$ (2), $b = 17.49$ (3), $c = 19.29$ (4) Å ($Z = 4$; $\rho_{calcd} = 1.525$ g/cm^3; $\rho_{obsd} = 1.51$ (1) g/cm^3). Intensity data were collected using Mo Kα radiation by the θ-2θ scan technique in the range $3° \leqslant 2\theta \leqslant 45°$. The structure was solved by the usual Patterson-least-squares-Fourier methods, and refined to final discrepancy factors R and R' of 0.0459 and 0.0541, respectively, for 240 parameters and 1884 observations.[8] All nonhydrogen atoms were refined anisotropically and three of the four independent phenyl rings were treated as rigid groups (vide infra).

The structure of complex **1,** which has crystallographic C_2 symmetry, is shown in Figures 1 and 2. Complex **1** possesses the "A-frame" structure I with each Rh(I) ion in square-planar coordination sharing a common sulfide ligand. Important structural parameters (see Figure 1) include Rh-C, Rh-S, and average Rh-P bond lengths of 1.81 (1), 2.367 (4), and 2.305 (4) Å. The two square planes are approximately orthogonal with a dihedral angle between least squares planes of 83.3° and a Rh···Rh separation of 3.155 (4) Å. The structural parameters of Figure 1 suggest the possibility of binding diatomic substrates to both Rh(I) centers on the endo side of the A-frame arrangement. However, this site for substrate binding is blocked in the present structure by two symmetry-related *endo*-phenyl rings of the bridging dpm ligands (Figure 2). In addition, the other *endo*-phenyl rings show very close nonbonded contacts with the terminal CO ligands (C—H···C—O ~2.2 Å) resulting in extremely anisotropic thermal parameters for several of the phenyl ring C atoms and slight deviations from planarity when this phenyl ring is refined as individual atoms.

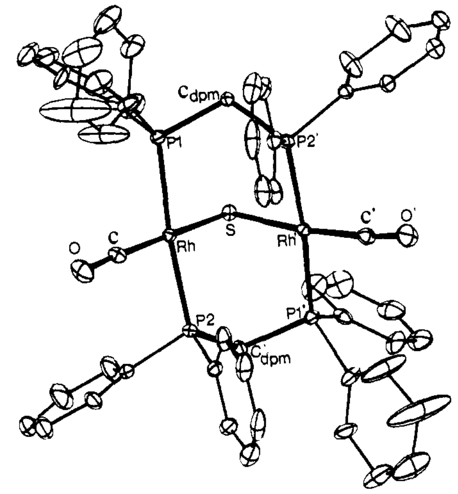
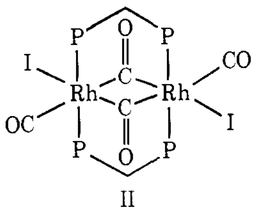


Figure 2. Drawing of $[Rh_2S(CO)_2(dpm)_2]$ with all nonhydrogen atoms.

These observations regarding the conformation of the Rh-dpm-Rh unit and the orientation of the phenyl substituents underscore a consideration in the design of other A-frame systems. For example, 1,3-diisocyanopropane[5] may prove more suitable as a bridging ligand for A-frame-type structures in which accessibility to the Rh···Rh unit is desired for cooperative substrate binding and activation. Recently, Balch and coworkers[9] have reported the isoelectronic complexes $[Pd_2(\mu\text{-}CNR)(CNR)_2(dpm)_2]^{2+}$ which also exhibit the A-frame structure similar to that reported here. The scope of these systems may be quite general.

The initial chemical characterization of **1** with various electrophilic reagents indicates that the bridging sulfur is quite reactive and competes effectively with the individual Rh(I) centers. For example, the reaction of **1** with $(OEt_3)(PF_6)$ leads to the formation of the monoalkylated complex $[Rh_2(\mu\text{-}SEt)(CO)_2(dpm)_2](PF_6)$, **3** ($\nu_{CO}$ 1963, 1980 cm^{-1}; $\Lambda_M = 75\ \Omega^{-1}$ cm^2 mol^{-1} in nitromethane) while reaction with HBF_4 yields a monoprotonated species which is also a 1:1 electrolyte. The addition of HCl to **1** regenerates the starting complex $[Rh_2Cl_2(CO)_2(dpm)_2]^2$ with H_2S formation. The most intriguing reaction involves the interaction of MeI or EtI with **1** followed by treatment with CO to yield complex **4** having ν_{CO} of 1962 (vs, br) and 1850 (s, br) cm^{-1}, and a ^1H NMR spectrum which shows only dpm resonances. Complex **4** can also be prepared from $[Rh_2Cl_2(CO)_2(dpm)_2]$ + LiI in THF followed by CO treatment, strongly supporting the notion that the reaction of **1** with R-I leads to sulfur alkylation and removal. Treatment of **4** with Na_2S regenerates **1.** Complex **4** is proposed as $[Rh_2I_2(\mu\text{-}CO)_2(CO)_2(dpm)_2]$ with structure II. Because of the binuclear arrangement imposed by the dpm ligands, each Rh(I) is precluded from adopting a TBP geometry, as would be anticipated for $RhI(CO)_2L_2$, and instead the complex assumes structure II in which CO bridges are formed. Because of their high ν_{CO}, the bridging carbonyls in **4** may be unsymmetrical, and the potentially fluxional nature of the carbonyl ligands in this system should be explored.



II

Reactivity of **1** at the metal centers is suggested by the reversible formation of a purple SO_2 adduct in benzene solution and by catalytic hydrogenation of ethylene in methylene chloride-benzene. Details will be published separately. It seems evident that the synthesis of other A-frame molecules and their use as multifunctional reagents holds great promise.

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References and Notes

(1) E. L. Meutterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975), and references therein.

(2) J. T. Mague, *Inorg. Chem.*, **8**, 1975 (1969); J. T. Mague and J. P. Mitchener, *ibid.*, **8**, 119 (1969).

(3) R. G. Hayter, *Inorg. Chem.*, **3**, 301 (1964), and references therein.

(4) P. Kalck and R. Poilblanc, *Inorg. Chem.*, **14**, 2779 (1975); J. J. Bonnet, J. Galy, D. deMontauzon, and R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, 47 (1977).

(5) N. S. Lewis, K. R. Mann, J. G. Gordon II, and H. B. Gray, *J. Am. Chem. Soc.*, **98**, 7461 (1976).

(6) A. L. Balch, *J. Am. Chem. Soc.*, **98**, 8049 (1976).

(7) A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 120 (1977).

(8) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. The programs and procedures are similar to those reported previously by S. Z. Goldberg, C. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **14**, 1650 (1975).

(9) A. L. Balch, personal communication; M. M. Olmstead, H. Hope, L. S. Benner, and A. L. Balch, *J. Am. Chem. Soc.*, **99**, 5502 (1977).

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Configurational Isomerism in Bis(dimethyl metal)-*N*,*N'*-dialkyloxamides of Aluminum and Gallium

Sir:

We wish to report the discovery by ^1H and ^{13}C NMR and the elucidation by crystal structure analysis of a new type of configurational isomerism in main group metal complexes.

According to a general scheme,[1] trialkyl derivatives of group 3B elements react with *N,N'*-dialkyloxamides to yield covalently bonded products of the general structural formula $(R_2'M)_2(CONR)_2$. Three representative compounds, **1-3**, are shown below; they have been characterized as 2:1 products by elemental analysis, and have been demonstrated to exist in monomeric form.[2]

Table I. Crystallographic Data[a] for the Bis(dimethyl metal)-oxamide Complexes **1-3**

	1	2	3
Space group	$P\bar{1}$	Cm	$P1$
a, Å	5.7438 (9)	11.774 (2)	8.8300 (6)
b, Å	9.466 (1)	5.7068 (6)	11.6355 (5)
c, Å	6.5750 (8)	8.9852 (8)	6.4533 (4)
α, degree	94.78 (1)	90.0	93.74 (1)
β, degree	111.02 (1)	112.00 (1)	99.51 (1)
γ, degree	101.21 (1)	90.0	95.54 (1)
Z	1	2	2
R	0.040	0.040	0.067

[a] Intensity and lattice parameter data were measured with crystals maintained at ca. −150 °C (Syntex LT-1 low temperature device) on a Syntex $P\bar{1}$ autodiffractometer operating in an ω-scan mode. Each data set was collected with one crystal; reference reflections measured periodically during data collection showed neither systematic nor significant variations in their respective intensities.

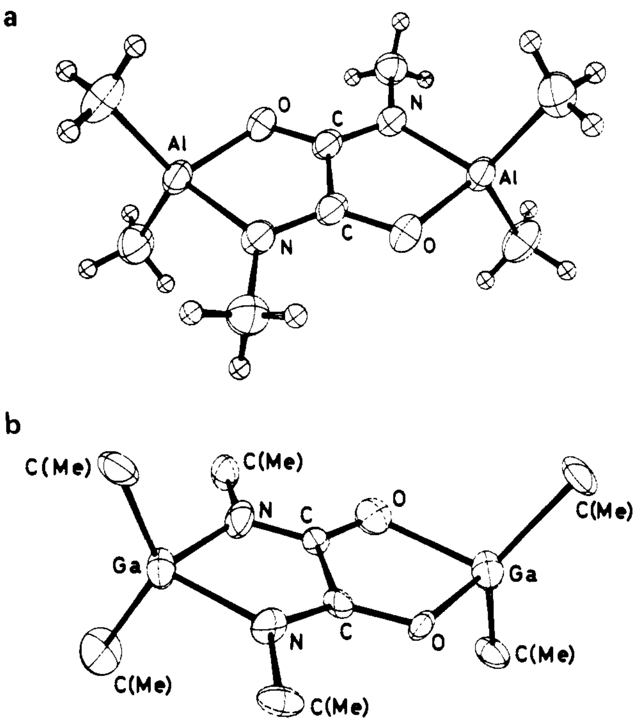

Figure 1. Chemical structure of (a) bis(dimethylaluminum)-*N,N'*-dimethyloxamide (**1**) and (b) bis(dimethylgallium)-*N,N'*-dimethyloxamide (**3**, cis configuration **3B**) (thermal ellipsoids are represented at the 75% probability level).

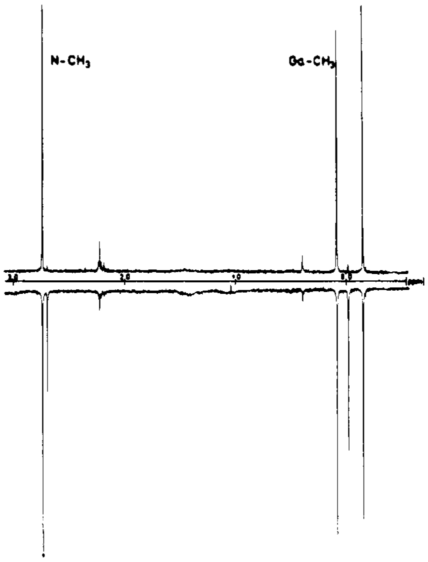

Figure 2. ^1H NMR spectra (C_6D_6 solutions, 30 °C) of a single crystal of **3** (100-200 μg) (top) and a 50-mg random sample of **3** (inverted trace) (bottom).

$$2(CH_3)_3M + (CONHR)_2 \xrightarrow{-2CH_4} (CH_3)_2M(CONR)_2M(CH_3)_2$$

1, M = Al; R = CH_3
2, M = Ga; R = H
3, M = Ga; R = CH_3

A fused five-membered-ring structure has been established for the corresponding bis(dimethylgallium) oxalate;[3] the same structural principle has now been verified for the *N*-methylaluminum derivative **1**. The crystalline complex, utilizing a crystallographic center of symmetry, displays the oxamide ligand in the trans configuration **1A**, Figure 1a, which provides