unique coordinated chlorine atom gave rise to a discrete signal. Furthermore, the observed shifts were generally in excess of the shifts that can be produced by solid-state effects.<sup>25</sup>

The extraordinary solubility of I-III in chlorocarbon solvents,<sup>9</sup> the high lability of the chlorocarbon ligands,<sup>9</sup> and the weak basicity of the ancillary teflate ( $OTeF_5^{-}$ ) ligands<sup>26</sup> may combine to yield a new class of reactive homonuclear and heteronuclear metal complexes. The chemical properties, usefulness, and limitations of I-III and similar compounds will be the subjects of forthcoming papers from our laboratory.

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Supplementary Material Available: IR spectra of I,  $I-d_8$ , III, and III- $d_4$  (Figure 2) and tables of atomic coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters for I (5 pages); table of observed and calculated structure factors for I (20 pages). Ordering information is given on any current masthead page.

## Reactions of Terminal Alkynes with *cis*-Phenyldiazene, NH==N( $C_6H_5$ )

Milton R. Smith III and Gregory L. Hillhouse\*

Searle Chemistry Laboratory Department of Chemistry, The University of Chicago Chicago, Illinois 60637 Received January 13, 1989

Diazenes (NR=NR') comprise one of the most simple, rudimentary classes of nitrogen-containing compounds, but while the moderately thermally robust disubstituted derivatives (R, R' = carbyl function) have been well studied,<sup>1</sup> fundamental questions concerning the chemistry of the highly unstable protic diazenes (NH=NH and NH=NR) remain. The chemistries of the latter (where facile loss of dinitrogen dominates) differ significantly from that of their disubstituted counterparts.<sup>2,3</sup> Interest in these protic diazenes stems in large part from the established synthetic utility of diazene in stereoselective cis hydrogenations of olefins and acetylenes,<sup>4</sup> from the intriguing possibilities the monosubstituted diazenes offer for analogous reductions of olefins and acetylenes in a new type of carbon-carbon bond-forming reaction as well as from a desire to better understand some important organic reactions in which NH=NR species are thought to be key intermediates (e.g., oxidations of hydrazines, Wolff-Kishner reductions, and reductive deaminations).<sup>5</sup>

An interesting feature in the reaction chemistry of the protic diazenes is that while they are generally synthesized as the trans geometrical isomers, a trans  $\rightarrow$  cis isomerization is usually invoked as a crucial (rate-determining) prerequisite to N<sub>2</sub> extrusion. For example, the involvement of *cis*-NH=NH in the diazene reductions of olefins and acetylenes is usually cited to explain the observed stereochemistries of the products (eqs 1-3).<sup>4</sup> Unfor*cis*-CHR=CHR + ND=ND  $\rightarrow$ 

meso-CHDR—CHDR +  $N_2$  (1)

trans-CHR=CHR + ND=ND 
$$\rightarrow$$
 dl-CHDR-CHDR + N<sub>2</sub>
(2)

$$R - C \equiv C - R + NH = NH \rightarrow cis - CHR = CHR + CH_2R - CH_2R + N_2 (3)$$

tunately, protic diazenes possessing cis geometries were unknown until recently, so notions regarding a special (or enhanced) reactivity of the cis isomers with respect to the trans isomers could not be tested. Our recent report of a general method for preparing monosubstituted *cis*-aryldiazenes, by a high yield displacement reaction of the diazene from a transition-metal complex,<sup>6</sup> affords the first opportunity for studying details of the chemistry of this elusive molecular class, and herein we describe the reactivity of *cis*-phenyldiazene with some simple alkynes.

The reaction of  $[trans, trans-W(NH=NPh)(CO)_2(NO)-(PPh_3)_2^+][PF_6^-](1)^7$  with  $[n-Bu_4N^+][Br^-]$  at 5 °C can be used to cleanly generate synthetically useful quantities of *cis*-NH=NPh (2).<sup>6</sup> Because 1 is soluble in a variety of organic solvents (including aromatic hydrocarbons) and since 2 exhibits moderate thermal stability in the absence of air, the displacement reaction provides a powerful, flexible method for surveying the reactivity of 2 with potentially reactive organic substrates. When 2 is generated and allowed to react (CH<sub>2</sub>Cl<sub>2</sub> solution, 5 °C, 3 h) in the presence of a large excess of 1-hexyne (i.e., "trapping conditions" with [H-C=C-C\_4H\_9] >> [2]), (E)-1-phenylhexene can be isolated from the reaction mixture in about 20% total yield based on 1 (eq 4).<sup>8</sup>

$$cis-NH=NPh + D-C\equiv C-C_4H_9 (excess) \rightarrow \sum_{Ph}^{D} \frac{C_4H_9}{H} + C_6H_6 + N_2 \qquad (4)$$

With 1-hexyne- $d_1$  reduction with 2 gives the alkene- $d_1$  in which the label is incorporated specifically at the former C-1 carbon of the alkyne. We do not observe the Z isomer when the reaction is monitored by <sup>1</sup>H NMR, suggesting at least an 8:1, E:Z specificity.<sup>9</sup> As in the reductions of alkynes with NH=NH, the reaction shown in eq 4 proceeds with formal cis addition of H<sup>\*</sup> and Ph<sup>\*</sup> from 2 to the alkyne.<sup>2,4</sup> However, when 2 is allowed to react with an excess of 1-phenylethyne (same conditions as above), both cis- and trans-stilbene can be isolated (4:1, cis:trans) from the reaction mixture in about 15% total yield based on 1 (D-C=C-Ph yielding solely stilbenes- $d_1$ ) (eq 5).<sup>8</sup> Thus, the major olefinic product in eq 5, cis-stilbene, arises from a formal trans addition of H<sup>\*</sup> and Ph<sup>\*</sup> from 2 to 1-phenylethyne.

cis-NH=NPh + D−C≡C−Ph (excess) → CDPh=CHPh + C<sub>6</sub>H<sub>6</sub> + N<sub>2</sub> (5) 12% cis 85% 3% trans

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<sup>(9)</sup> The *E* stereochemistry is assigned on the basis of its characteristic vinylic proton coupling constant,  ${}^{3}J_{HH} = 16$  Hz.

Phenyl radicals are thought to be involved in the aerobic reactions of trans-NH=NPh,<sup>3</sup> and we have strong evidence, from displacements of 2 from 1 in the presence of radical traps, that they are also important in the anaerobic reaction chemistry of 2. For example, when 2 is generated and allowed to react in benzene- $d_6$ , biphenyl- $d_5$  is produced in about 11% yield based on 1 (eq 6); similarly o-, m-, and p-tolylbenzene isomers are produced

$$H^{N=N}_{Ph} \xrightarrow{-N_2} \xrightarrow{-N_2} \xrightarrow{-10\%} \xrightarrow{\sim} 0\% \xrightarrow{d_5} (6)$$

(10% total yield) when the displacement is effected in toluene (eq 7).<sup>10</sup> In the presence of excess BrCCl<sub>3</sub>, 2 reacts to afford bromobenzene in a higher (70%) yield (eq 8).<sup>11</sup> The products in eq 6-8 are typical ones of cage-escaped phenyl radicals, and we feel that they are also involved in the reactions of 2 with alkynes (eq 4 and 5) because of the following reasons: (1) The regiochemistries of the products are consistent with a Kharasch-type addition of Ph<sup>•</sup> to the alkyne terminus to give a vinyl radical intermediate that subsequently abstracts H<sup>•</sup> to give the olefin.<sup>12</sup> The observation that 1-hexyne reacts with ND=NPh (2-d, > 95%) $d_1$ ) to give (E)-1-phenylhexene that is only partially deuterated  $(\sim 50\% d_1)$  supports such an H<sup>•</sup> abstraction mechanism (not simple H-transfer) for the reaction in eq 4 (similar label loss occurs in the reaction of 2-d with PhC=CH). (2) Isomerization of the stilbenyl radical is fast, and the observed ratio of *cis:trans*-stilbene formed in the reduction of phenylethyne by 2 (eq 5) is in accord with the known partition of cis- and trans-stilbene formed from stilbenyl radicals prepared by other means (eq 9).<sup>13</sup> (3) The overall yields of olefinic products in eq 4 and 5 are similar to the yields of Ph<sup>•</sup> trapped products in eq 6 and 7 (corresponding to  $\sim$ 10–15% radical cage escape).



In summary, the results reported herein provide insight into the mode of reaction of cis-NH=NPh with terminal alkynes. In contrast to reductions of alkynes involving NH=NH, where reduction proceeds in a highly stereoselective (cis) fashion, the reactions of cis-NH=NPh with terminal alkynes appear to be radical processes involving Ph\* transfer, and the stereoselectivities of the reductions are consequently sensitive to the nature of the substrate.

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Supplementary Material Available: Experimental details and spectral data (<sup>1</sup>H, <sup>13</sup>C NMR, GC/MS) for phenylethyne- $d_1$  and cis-NH=NPh with phenylethyne, 1-hexyne, benzene and toluene, and bromotrichloromethane (3 pages). Ordering information is given on any current masthead page.

## Catalytic Formation of $\alpha$ -Keto Acids by Artificial CO<sub>2</sub> Fixation

Koji Tanaka,\* Tatsuji Matsui, and Toshio Tanaka

Department of Applied Chemistry, Faculty of Engineering, Osaka University Yamada-oka, Suita, Osaka 565, Japan Received February 2, 1989

Artificial CO<sub>2</sub> fixation has been widely conducted in the viewpoints of the utilization of the ultimate oxidation product of organic molecules and mimicking biological carbon assimilation. Highly reduced species such as  $CH_4^{1,2}$  and  $CH_3OH^3$  have been obtained in some CO<sub>2</sub> reductions though most of the products in those reductions are CO and/or HCOOH.4-17 On the other hand, four CO<sub>2</sub> molecules are fixed in one complete turn of the reductive carboxylic acid cycle in photosynthetic bacteria.<sup>18-21</sup> Two of them are incorporated at the carbonyl carbon of  $CH_3C(O)SCoA$  and  $HOOCCH_2CH_2C(O)SCoA$  (CoASH = coenzyme A) to form  $\alpha$ -keto acids, pyruvate, and  $\alpha$ -ketoglutarate (eq 1), where reduced

$$\begin{array}{c} \text{RC}(\text{O})\text{SC}_{\text{O}}\text{A} + \text{CO}_2 + 2e^- \rightarrow \\ \text{RC}(\text{O})\text{COO}^- + \text{C}_{\text{O}}\text{AS}^- \\ (\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_2\text{COOH}) \end{array}$$
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