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.[25]

The extraordinary solubility of I–III in chlorocarbon solvents,[9] the high lability of the chlorocarbon ligands,[9] and the weak basicity of the ancillary teflate ($OTeF_5^-$) ligands[26] 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.

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

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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,[1] 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.[2,3] Interest in these protic diazenes stems in large part from the established synthetic utility of diazene in stereoselective cis hydrogenations of olefins and acetylenes,[4] 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).[5]

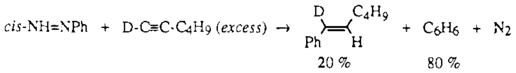
An interesting feature in the reaction chemistry of the protic diazenes is that while they are generally synthesized as the trans geometrical isomers, a trans → cis isomerization is usually invoked as a crucial (rate-determining) prerequisite to N_2 extrusion. For example, the involvement of *cis*-NH=NH in the diazene reductions of olefins and acetylenes is usually cited to explain the observed stereochemistries of the products (eqs 1–3).[4] Unfortunately, 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,[6] 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.

$$\textit{cis}\text{-CHR=CHR} + \text{ND=ND} \rightarrow \textit{meso}\text{-CHDR—CHDR} + N_2 \quad (1)$$

$$\textit{trans}\text{-CHR=CHR} + \text{ND=ND} \rightarrow \textit{dl}\text{-CHDR—CHDR} + N_2 \quad (2)$$

$$\text{R—C}{\equiv}\text{C—R} + \text{NH=NH} \rightarrow \textit{cis}\text{-CHR=CHR} + \text{CH}_2\text{R—CH}_2\text{R} + N_2 \quad (3)$$

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**).[6] 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_2Cl_2 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).[8]



$$\textit{cis}\text{-NH=NPh} + \text{D-C}{\equiv}\text{C-C}_4\text{H}_9\,(\textit{excess}) \rightarrow \underset{20\,\%}{\text{(D)(Ph)C=CH(C}_4\text{H}_9)} + \underset{80\,\%}{C_6H_6} + N_2 \quad (4)$$

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 ^{1}H NMR, suggesting at least an 8:1, *E*:*Z* specificity.[9] *As in the reductions of alkynes with NH=NH, the reaction shown in eq 4 proceeds with formal cis addition of H• and Ph• from 2 to the alkyne.*[2,4] 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).[8] *Thus, the major olefinic product in eq 5, cis-stilbene, arises from a formal trans addition of H• and Ph• from 2 to 1-phenylethyne.*

$$\textit{cis}\text{-NH=NPh} + \text{D—C}{\equiv}\text{C—Ph (excess)} \rightarrow \underset{\substack{12\%\ \text{cis}\\ 3\%\ \text{trans}}}{\text{CDPh=CHPh}} + \underset{85\%}{C_6H_6} + N_2 \quad (5)$$

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[8] Products were isolated by chromatography on silica gel and characterized by ^{1}H NMR, ^{13}C NMR, and GC/MS. Product ratios were quantified by GC by using a dodecane internal standard. See Supplementary Material for experimental details.

[9] The *E* stereochemistry is assigned on the basis of its characteristic vinylic proton coupling constant, $^3J_{HH}$ = 16 Hz.

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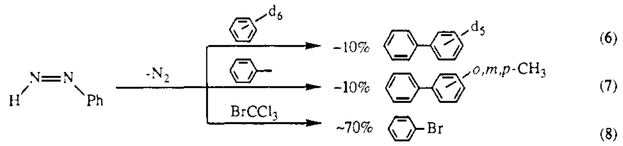
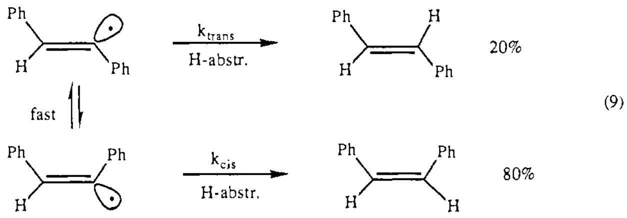
Phenyl radicals are thought to be involved in the aerobic reactions of *trans*-NH=NPh,[3] and we have strong evidence, from displacements of **2** from **1** in the presence of radical traps, that they are also important in the anaerobic reaction chemistry of **2**. For example, when **2** is generated 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 (10% total yield) when the displacement is effected in toluene (eq 7).[10] In the presence of excess $BrCCl_3$, **2** reacts to afford bromobenzene in a higher (70%) yield (eq 8).[11] 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• to the alkyne terminus to give a vinyl radical intermediate that subsequently abstracts H• to give the olefin.[12] The observation that 1-hexyne reacts with ND=NPh (**2-*d***, > 95% d_1) to give (*E*)-1-phenylhexene that is only partially deuterated (~50% d_1) supports such an H• 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).[13] (3) The overall yields of olefinic products in eq 4 and 5 are similar to the yields of Ph• trapped products in eq 6 and 7 (corresponding to ~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 (^1H, ^{13}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.

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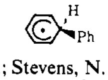

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Catalytic Formation of α-Keto Acids by Artificial CO_2 Fixation

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Artificial CO_2 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_2 reductions though most of the products in those reductions are CO and/or HCOOH.[4-17] On the other hand, four CO_2 molecules are fixed in one complete turn of the reductive carboxylic acid cycle in photosynthetic bacteria.[18-21] 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 α-keto acids, pyruvate, and α-ketoglutarate (eq 1), where reduced

$$\mathrm{RC(O)SCoA + CO_2 + 2e^- \rightarrow RC(O)COO^- + CoAS^-} \quad (\mathrm{R = CH_3, CH_2CH_2COOH}) \tag{1}$$

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