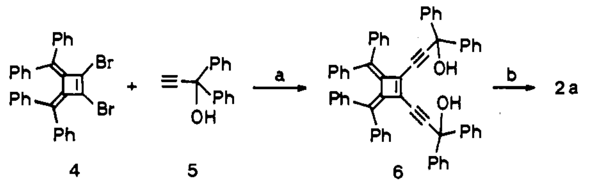
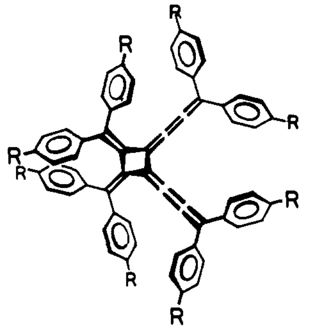
Scheme II[a]



[a] Reagents: (a) $PdCl_2(PPh_3)_2$, CuI, Et_3N, 85 °C, 2.5 h; (b) $SnCl_2$·$2H_2O$, HCl, ether, -50 °C, 30 min.

In the case of tetrakis(4-*tert*-butylphenyl)hexapentaene (**1c**),[12] 1 equiv of $Ni(CO)_2(PPh_3)_2$ was required for the reaction, and the dimer **2c**[13] was obtained only in 34% yield, owing to a steric repulsion between the large *tert*-butyl groups.

The molecular models show that the dimer **2** has a twisted structure with C_2 symmetry. Thus, each benzene ring should be located at a relatively short distance. In agreement with this consideration, ^1H NMR spectra of these dimers show upper field shifts of aryl protons due to the shielding effect of the closely situated neighboring benzene ring. Electronic spectra of the dimers show broad, strong absorptions tailing up to 750 nm, corresponding to the deep blue color in solution. The dimers have 1,2,3,5,6,7-octahexaene structures which may cyclize to give 1,2-divinylidenecyclobutene derivatives. However, **2a–c** are rather stable in prolonged heating or nickel catalysts.



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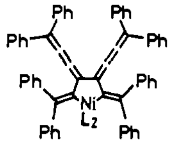
The uncertainty in the structural determination of **2a–c** could not be eliminated completely by using their spectroscopic analysis. Therefore, we carried out the synthesis of **2a** by the stepwise, independent pathway. The palladium-catalyzed coupling[14] of **4**[15] with the ethynyl alcohol **5** gave the diol **6** in 73% yield (Scheme II). Reduction of **6** with $SnCl_2$[16] in ether containing hydrogen chloride gave **5a** in 68% yield. The compound thus synthesized exhibited spectral data identical with those of the nickel-catalyzed dimer.

The selective formation of **2a–c** reveals that the complexation and reaction of [5]cumulenes with nickel occur not at the central cumulenic sp–sp bond but at the lateral cumulenic sp–sp bond, i.e., the C_2–C_3 or C_4–C_5 bond of hexapentaene. The nickel-catalyzed cyclooligomerization of [3]cumulenes proceeds via a five-membered nickelacycle intermediate.[17] Therefore, the mechanism for the cyclooligomerization of tetraarylhexapentaenes can be recognized as follows. The first step is the formation of the hexapentaene (C_2–C_3)–nickel complex, followed by the *syn*-bishexapentaene π-complex. The regioselective π–π coupling at C_2 or C_3 carbons results in the formation of the nickelacyclopentane **7** or **8**. Finally, reductive elimination of the nickelacyclopentane produces the head-to-head dimers **2a–c**.



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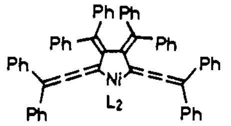

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Dichloromethane Is a Coordinating Solvent

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Of all the common solvents available to the synthetic chemist, dichloromethane is perhaps the only one that is commonly thought of as "polar but noncoordinating".[4] We now report the structure of $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (I), shown in Figure 1.[5] The structural results leave no doubt that dichloromethane can coordinate to metal ions, that it can use both chlorine atoms to form four-membered chelate rings, and, if a metal ion is unsaturated enough, that more than one dichloromethane molecule can coordinate to it. We also report two different spectroscopic methods for determining whether or not dichloromethane is coordinated to a metal ion.

Until recently, the weak bonding between metal ions and chlorine atom lone pairs of chlorocarbon solvents, while suspected by many chemists, had not been confirmed. IR and NMR spectral data strongly suggested the coordination of dichloromethane to the $[CpMo(CO)_3^+]$[6] and $[CpRe(NO)(PPh_3)^+]$[7] cations, respectively. The structure of $[Ph_3C^+][PtCl_5(CH_2Cl_2)^-]$ suggested a Pt—$ClCH_2Cl$ bonding interaction, but reliable metrical details of this interaction could not be determined because of disorder and "the questionable quality of the data due to crystal decom-

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(1) Colorado State University.

(2) Middle Tennessee State University.

(3) Alfred P. Sloan Research Fellow, 1987-1989.

(4) This terminology has been used in hundreds of papers. A recent example is as follows: Bond, A. M.; Ellis, S. R.; Hollenkamp, A. F. *J. Am. Chem. Soc.* **1988**, *110*, 5293.

(5) For $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$: triclinic $P\bar{1}$, a = 8.923 (2) Å, b = 9.953 (3) Å, c = 9.985 (2) Å, α = 114.23 (2)°, β = 100.54 (2)°, γ = 91.42 (2)°, V = 790.1 Å^3, Z = 1, T = -130 °C, ρ_{calcd} = 3.40 g cm^{-1}, $F(000)$ = 728.0. Nicolet R3m diffractometer, $\theta/2\theta$ scans, 4° < 2θ < 55°; $\pm h,-k,\pm l$; 3399 reflections with $|F_o| > 2.55\sigma|F_o|$. Lorentz and polarization corrections; empirical absorption correction, μ(Mo Kα) = 63.1 cm^{-1}, T = 0.730–0.958. Weighted least-squares refinement on F with neutral atom scattering factors and anomalous dispersion, anisotropic thermal parameters for non-H atoms, 196 parameters, H atoms in idealized positions; R = 0.041, R_w = 0.045, GOF = 1.63, slope of normal probability plot = 1.42.

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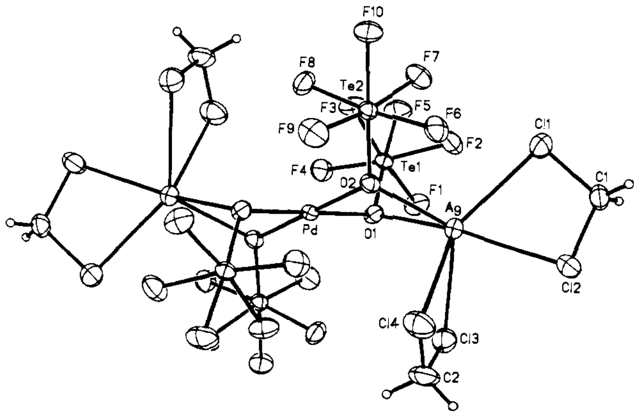

Figure 1. Drawing of the $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ molecule (50% probability ellipsoids). Selected bond distances and angles are as follows: Ag–Cl1, 2.775 (2) Å; Ag–Cl2, 2.811 (2) Å; Ag–Cl3, 2.859 (2) Å; Ag–Cl4, 2.882 (2) Å; Ag–O_{av}, 2.468 (6) Å; Pd–O_{av}, 2.011 (6) Å; Cl1–C1–Cl2, 109.4 (4)°; Cl3–C2–Cl4, 111.3 (4)°; O1–Ag–O2, 66.9 (2)°.

position."[8] A recent report from our laboratory described the synthesis and structure of $[AgOTeF_5(1,2\text{-}C_2H_4Cl_2)]_2$ (II), in which chlorine atoms of a related chlorocarbon solvent are coordinated to silver(I) ions.[9] The bonding between iodocarbons and metal ions has been the subject of several recent investigations.[10-15] Perhaps because of the apparent difference in both strengths RI–M > RCl–M,[10-12] many more compounds containing coordinated iodocarbons have been isolated and structurally characterized by X-ray diffraction.[10-12]

Compound I was prepared from $AgOTeF_5$[9,16] and anhydrous $PdCl_2$ as shown in eq 1. The same products were generated in

$$4AgOTeF_5 + PdCl_2 \xrightarrow[24\ h,\ 25\ ^\circ C]{CH_2Cl_2} 2AgCl + Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4 \quad (1)$$

the presence of excess $PdCl_2$; no $Pd(OTeF_5)_2$ was formed. After removing AgCl from the reaction mixture by filtration, amber crystals of I were grown by slowly cooling a concentrated dichloromethane solution to −20 °C. These extremely hygroscopic crystals readily effloresce (by loss of dichloromethane) in a N_2-filled glovebox at 25 °C. Nevertheless, crystals of I were isolated, examined, and mounted on the diffractometer without allowing the crystals to warm to above −20 °C.[5]

Two symmetry-related $Ag(CH_2Cl_2)_2^+$ moieties are bridged by the centrosymmetric $Pd(OTeF_5)_4^{2-}$ core, which contains a planar PdO_4 array. To within experimental error, the two bidentate dichloromethane ligands are unperturbed from the gas-phase structure of dichloromethane: bound C–Cl_{av} = 1.76 (2) Å, Cl–C–Cl_{av} = 110.4 (6)°; free C–Cl = 1.7724 (5) Å, Cl–C–Cl = 111.78 (2)°.[17] The ligand containing Cl is bound more strongly to the Ag(I) ion (Ag–Cl_{av} = 2.793 (3) Å) than the ligand containing C2 (Ag–Cl_{av} = 2.871 (3) Å). Both chelates have small "bites" (Cl1–Ag–Cl2 = 62.1 (1)°, Cl3–Ag–Cl4 = 60.6 (1)°), which is a common feature of four-membered chelate rings with second-row donor atoms (cf. transition-metal dithiocarbamates[18]). The bond angles at the chlorine atoms span a small range, 92.1 (2)–94.5 (3)°. The "optimum" M–Cl–C angle is not known, since no complex with a monodentate chlorocarbon has been structurally characterized. For the 1,2-dichloroethane five-membered chelate rings in II, the average Ag–Cl–C angle is 103.0 (8)°.[9] For two monodentate iodocarbon complexes, the M–I–C angles are 106.9 (8)° (M = Ir(III); average of two values)[11] and 102.5 (5)° (M = Re(I)).[12]

While the results above show that the structure of dichloromethane is not significantly changed upon coordination to silver(I), X-ray diffraction is not as sensitive a probe as some spectroscopic techniques. IR spectroscopy could potentially probe changes in carbon–chlorine bonding that occur upon coordination, if ν(CCl) bands could be assigned reliably. For dichloromethane, the $\nu(CCl)_{asym}$ stretching normal mode is mixed with the $\delta(CH_2)$ rocking normal mode (both have B_2 symmetry);[19,20] a pair of strong bands that are predominantly $\delta(CH_2)$ and $\nu(CCl)_{asym}$ were found at 1262 and 743 cm^{-1}, respectively, for dichloromethane dispersed in Nujol. For dichloromethane-d_2, these bands were shifted to 952 and 716 cm^{-1}, demonstrating that deuterium substitution can be used to assign one of the carbon–chlorine stretching bands of coordinated dichloromethane. For $[AgOTeF_5(CH_2Cl_2)]_2$,[9] III, a band at 738 cm^{-1} was assigned to $\nu(CCl)_{asym}$, since it was absent from the IR spectrum of $[AgOTeF_5(CD_2Cl_2)]_2$ (Figure 2, Supplementary Material). Since $\nu(CCl)_{asym}$ only decreased by 5 cm^{-1} for this compound, *very* little change in carbon–chlorine bonding was apparent. Coordination of dichloromethane may be stronger in I than in III, since $\nu(C\text{–}Cl)_{asym}$ for I shifted by 18 cm^{-1} to 725 cm^{-1} (this band was absent from the spectrum of I-d_8).

Another sensitive probe of M–Cl–C bonding is ^{35}Cl nuclear quadrupole resonance (NQR) spectroscopy. It can distinguish between chlorine atoms that are bonded to metal ions and those that are not[21] and has been used to characterize metal complexes of the 2,6-dichlorophenolate ion and related ligands, which can form five-membered chelate rings containing M–Cl–C linkages.[21c,d,f,22] For example, the compound Ag(2,4,6-trichlorophenolate)$(PPh_3)_2$ contains a weak Ag–Cl bond of 3.160 (2) Å between the silver ion and one of the two ortho chlorine atoms.[23] At 77 K, the ^{35}Cl NQR frequency of the coordinated ortho chlorine atom was 1.500 MHz lower than the frequency of the noncoordinated ortho chlorine atom.[23] Similar shifts were observed for compounds I–III at 77 K: free dichloromethane, 35.991 MHz;[24] I, 35.483, 34.827 (double intensity, presumably due to overlap of two signals), and 34.640 MHz; III, 34.498 and 34.230 MHz; free 1,2-dichloroethane, 34.361 MHz;[24] II, 32.036, 31.828 (double intensity, presumably due to overlap of two signals), and 31.700 MHz. Except for two pairs of overlapped signals, each

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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]

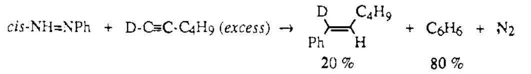
An interesting feature in the reaction chemistry of the protic diazenes is that while they are generally synthesized as the trans geometrical isomers, a trans → cis isomerization is usually invoked as a crucial (rate-determining) prerequisite to N_2 extrusion. For example, the involvement of *cis*-NH=NH 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.

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

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

$$R{-}C{\equiv}C{-}R + NH{=}NH \rightarrow \textit{cis}\text{-}CHR{=}CHR + CH_2R{-}CH_2R + N_2 \quad (3)$$

The reaction of $[\textit{trans,trans}\text{-}W(NH{=}NPh)(CO)_2(NO)(PPh_3)_2^+][PF_6^-]$ (**1**)[7] with $[n\text{-}Bu_4N^+][Br^-]$ 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 $[H{-}C{\equiv}C{-}C_4H_9] \gg [\mathbf{2}]$), (*E*)-1-phenylhexene can be isolated from the reaction mixture in about 20% total yield based on **1** (eq 4).[8]



(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 ^1H 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.*

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

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

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