have been found to correlate with the distribution of ions in tetrahedral and octahedral sites in crystal lattices[15] and with the variations in heat released upon dissolving a series of MCl_4^{2-} salts ($M = Mn^{2+}$–Zn^{2+}) in water,[18] a process involving a tetrahedral to octahedral transition. Studies of the copper protein azurin[19] have revealed that apparent metal affinities did not correlate well with changes in LFSE assuming an octahedral to tetrahedral conversion, a fact ascribed to the highly distorted nature of this metal-binding site. Our results suggest that the LFSE changes incumbent in binding metal ions in tetrahedral sites in proteins is an important determinant in specificity for zinc over other divalent first-row transition metals. This observation pertains to the "zinc finger" proteins and to other proteins that appear to have metal ions bound in tetrahedral sites formed from short stretches of amino acid sequence such as the bacteriophage gene 32 protein[20] and the steroid receptor family[21] as well as to other proteins with tetrahedral sites.

Acknowledgment. The National Institutes of Health (BRSG SO7 RR7041, GM-38230) and the Camille and Henry Dreyfus Foundation are gratefully acknowledged for their support of this work.

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Nickel-Catalyzed Cyclodimerization of [5]Cumulene (Hexapentaene). Synthesis of a Novel [4]Radialene System

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Received December 20, 1988

Although the cyclooligomerization of allenes using nickel catalysts has been investigated in detail,[1,2] only a few examples are known of the nickel-catalyzed cyclooligomerization of higher cumulenes. Recently, we have reported the nickel-catalyzed cyclodimerization and trimerization of [3]cumulenes (butatrienes).[3] The cyclooligomerization of [3]cumulenes has importance in organic synthesis, because this reaction provides access to novel compounds of potential theoretical and synthetic interest. We now report a nickel-catalyzed cyclodimerization of [5]cumulenes (hexapentaenes), which produce unique [4]radialene derivatives.

Tetra-*tert*-butyl[5]cumulene (3,8-di-*tert*-butyl-2,2,9,9-tetramethyldeca-3,4,5,6,7-pentaene) dimerizes thermally at 200 °C to give tetrakis(di-*tert*-butylvinylidene)cyclobutane as the cyclic dimer. In contrast, copper-catalyzed decomposition of the anion derived from tetrahydropyranyl ether of 3-hydroxy-3-methyl-1-butyne produces octamethylcyclododeca-1,3,7,9-tetrayne via [6 + 6]cyclodimerization of the corresponding [5]cumulene, which is formed through the coupling of isobutenylidenecarbene.[5] The formation of the cyclic tetraacetylene may be favored in the thermal cyclodimerization of tetraalkyl[5]cumulenes.[6]

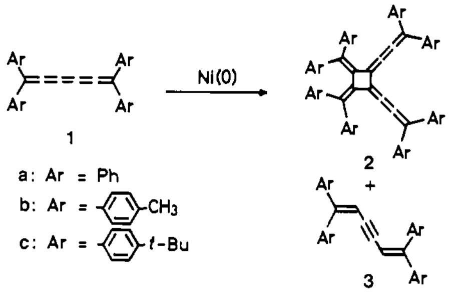
The thermal reaction of tetraarylhexapentaenes has never been reported to give cyclic dimers, presumably owing to thermal instability of these [5]cumulenes. Therefore, we investigated the cyclodimerization of tetraarylhexapentaenes with zero-valent nickel catalysts. As shown in Table I, the reaction of tetraphenylhexapentaene (**1a**) with $Ni(PPh_3)_4$ proceeds smoothly at room temperature to give the cyclic dimer **2a**[7,8] in 40–64% yields. This cyclization gave the same dimer in THF, DMF, and benzene as the solvent, and the formation of the reduction product **3a**[9] was observed as byproduct in the reaction in benzene. As for the nickel catalysts, $Ni(CO)_2(PPh_3)_2$[3] can be also employed for the dimerization of **1a**. Thus, treatment of **1a** with 10 mol % of $Ni(CO)_2(PPh_3)_2$ in refluxing benzene afforded **2a** in 61% yield. Under similar reaction conditions, dimerization of tetrakis(4-methylphenyl)hexapentaene (**1b**)[10] produced **2b**[11] in 57% yield.

Table I. Reaction of Tetraarylhexapentaene **1a–c** with Nickel(0) Complexes

starting material	Ni(0) complex	mol %	solv	temp (°C)	time (min)	yield (%) **2**	yield (%) **3**
1a	$Ni(PPh_3)_4$[a]	50	THF	25	60	53	0
1a	$Ni(PPh_3)_4$[a]	50	DMF	25	10	41	3
1a	$Ni(PPh_3)_4$[a]	20	DMF	25	30	64	0
1a	$Ni(PPh_3)_4$[a]	50	benzene	25	60	40	10
1a	$Ni(CO)_2(PPh_3)_2$	10	benzene	80	30	61	0
1b	$Ni(CO)_2(PPh_3)_2$	25	benzene	80	30	57	0
1c	$Ni(CO)_2(PPh_3)_2$	50	benzene	80	30	13[b]	0
1c	$Ni(CO)_2(PPh_3)_2$	100	benzene	80	30	34	0

[a] Prepared from $NiBr_2(PPh_3)_2$, PPh_3, and zinc in a 1:2:4 molar ratio. [b] The starting material (23%) was recovered.

Scheme I



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(7) **2a**: deep blue needles, mp 210 °C dec; MS, *m/z* 760 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 10 H), 7.11–7.06 (m, 14 H), 6.98 (t, J = 8.0 Hz, 2 H), 6.88 (t, J = 8.0, 2 H), 6.83 (d, J = 8.0, 4 H), 6.73 (t, J = 8.0, 4 H), 6.68 (t, J = 8.0, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 141.1, 140.5, 139.5, 138.7, 138.4, 136.7, 136.5, 131.0, 130.7, 130.2, 129.5, 129.2, 129.0, 128.3, 127.8, 127.7, 127.6, 127.43, 127.36, 127.2, 123.1; UV–vis (THF) λ_{max} (log ϵ) 230 (4.63), 293 (4.58), 384 sh (4.76), 413 (4.95), 623 nm (4.22); IR (KBr) 2028, 1970 cm^{-1}; Raman (KBr) 2030, 1970 cm^{-1}.

(8) Satisfactory elemental analyses were obtained on all new compounds except for **2c**.

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(11) **2b**: dark blue needles, mp 210 °C dec; MS, *m/z* 872 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0, 4 H), 7.06 (d, J = 8.2, 4 H), 7.05 (d, J = 8.2, 4 H), 6.99 (d, J = 8.2, 4 H), 6.88 (d, J = 8.0, 4 H), 6.69 (d, J = 8.0, 4 H), 6.54 (d, J = 8.2, 4 H), 6.52 (d, J = 8.0, 4 H), 2.42 (s, 6 H), 2.17 (s, 6 H), 2.14 (s, 6 H), 2.12 (s, 6 H); UV–vis (THF) λ_{max} (log ϵ) 238 (4.64), 310 (4.62), 385 sh (4.66), 424 (4.97), 694 nm (4.21); Raman (KBr) 2029, 1972 cm^{-1}.

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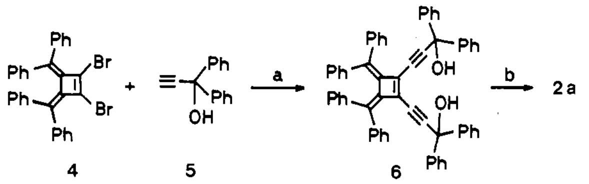
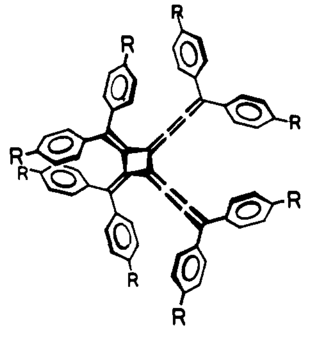
Scheme II[a]



[a] Reagents: (a) $PdCl_2(PPh_3)_2$, CuI, Et_3N, 85 °C, 2.5 h; (b) $SnCl_2 \cdot 2H_2O$, 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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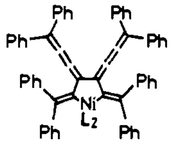
The uncertainty in the structural determination of **2a–c** could not be eliminated completely by using their spectroscopic analysis. Therefore, we carried out the synthesis of **2a** by the stepwise, independent pathway. The palladium-catalyzed coupling[14] of **4**[15] with the ethynyl alcohol **5** 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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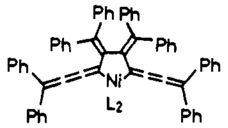

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(12) This compound was prepared from 4,4′-di-*tert*-butylbenzophenone: Buu-Hoi, N. P.; Royer, R.; Xuong, N. D.; Thang, K. V. *Bull. Soc. Chim. Fr.* **1955**, 1204–1207.

(13) **2c**: dark blue fine crystals, mp 200 °C dec; MS m/z 1208 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, AA′BB′, 8 H), 7.30 (d, $J = 8.7$, 4 H), 7.29 (br d, $J = 8.4$, 4 H), 7.16 (d, $J = 8.7$, 4 H), 6.93 (br d, $J = 8.4$, 4 H), 6.89 (d, $J = 8.1$, 4 H), 6.82 (br d, $J = 8.1$, 4 H), 1.40 (br s, 18 H), 1.25 (s, 18 H), 1.24 (s, 18 H), 1.11 (br s, 18 H); UV–vis (THF) λ_{max} (log ϵ) 234 (4.68), 303 (4.67), 390 sh (4.67), 416 (4.83), 515 sh (4.09), 623 nm (4.19).

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Dichloromethane Is a Coordinating Solvent

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Received January 18, 1989

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—ClCH₂Cl 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, $\alpha = 114.23$ (2)°, $\beta = 100.54$ (2)°, $\gamma = 91.42$ (2)°, $V = 790.1$ Å^3, $Z = 1$, $T = -130$ °C, $\rho_{calcd} = 3.40$ g cm^{-1}, $F(000) = 728.0$. Nicolet R3m diffractometer, $\theta/2\theta$ scans, $4° < 2\theta < 55°$; $\pm h,-k,\pm l$; 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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(7) (a) Fernandez, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672. (b) Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

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