

σ^* orbitals ultimately derive from the octahedral e_g set of the metal d orbitals, with some admixture of s and p character.¹⁸ Surprisingly, the $\sigma \rightarrow \sigma^*$ transition energy for the $H_4Ru_4(CO)_{11}$ is nearly unchanged or even slightly blue-shifted compared to $H_4Ru_4(CO)_{12}$. However, the first absorption feature of $H_4Ru_4(CO)_{11}$ is much lower in energy and intensity than that for $H_4Ru_4(CO)_{12}$. The lower energy, weak absorption is consistent with a significant stabilization of a localized σ^* level that becomes the LUMO,¹⁹ in much the same way that coordinatively unsaturated mononuclear compounds are viewed, e.g., $Cr(CO)_5$ compared to $Cr(CO)_6$.^{1,2b}

The finding of clean loss of CO from $H_4Ru_4(CO)_{12}$ at 77 K prompts a consideration of the relative importance of metal-metal vs. metal-ligand bond cleavage in the photosubstitution of two-electron donor ligands, L, for CO at 298 K. If metal-metal bond homolysis is important to photosubstitution in fluid solution, associative substitution at two radical centers is expected to give some $H_4Ru_4(CO)_{10}(L)_2$ as a primary photoproduct, whereas none is expected in the thermal reaction of matrix-isolated $H_4Ru_4(CO)_{11}$ with excess L.²⁰ We thus used FTIR spectroscopy to determine product distributions at low-extent conversion (<20%) where secondary irradiation is negligible. Room temperature irradiation of 0.1 mM $H_4Ru_4(CO)_{12}$ in a deoxygenated alkane solution containing 2 mM PPh_3 results in clean FTIR and UV-vis spectral changes, Figure 1b, consistent with essentially quantitative formation of $H_4Ru_4(CO)_{11}(PPh_3)$ ¹⁶ ($\sim 2095\text{ cm}^{-1}$) at up to 95% conversion of $H_4Ru_4(CO)_{12}$ ($\sim 2081\text{ cm}^{-1}$). A portion of this same solution was photolyzed at 77 K to generate matrix-isolated $H_4Ru_4(CO)_{11}$. Warming of this glass results in net spectral changes at 298 K which are consistent with conversion of all $H_4Ru_4(CO)_{11}$ to $H_4Ru_4(CO)_{11}(PPh_3)$. These spectral changes are indistinguishable from spectral changes obtained in the 298 K photolysis at a similar extent conversion, Figure 1b. The absence of any $H_2Ru_4(CO)_{12}PPh_3$ ²¹ in the photolyzed mixture rules out loss of H_2 from $H_4Ru_4(CO)_{12}$ at 77 or 298 K. Thus, photosubstitution of $H_4Ru_4(CO)_{12}$ in fluid solution at 298 K is completely accounted for by the intermediacy of photogenerated $H_4Ru_4(CO)_{11}$. In support of loss of CO at 298 K as the dominant photoreaction, we note the absence of $H_4Ru_4(CO)_{10}(PPh_3)_2$ as a primary photoproduct, even at PPh_3 concentrations exceeding 0.1 M. An associative mechanism for photosubstitution is apparently ruled out by the fact that the quantum yield for substitution is independent of entering-group concentration.¹⁰

Our results are consistent with previous reports that added CO suppresses both the thermal^{18c,d,9a,c} and photochemical^{10,11} isomerization and hydrogenation of olefins when $H_4Ru_4(CO)_{12}$ is used as a catalyst. Preliminary studies show that photogenerated $H_4Ru_4(CO)_{11}$ reacts thermally with ethylene ($\sim 0.1\text{ M}$) in an alkane matrix at 77 K. The product has infrared spectral features in the carbonyl region characteristic of $H_4Ru_4(CO)_{11}L$ -type compounds¹⁶ different from those observed for $H_3Os_4(CO)_{11}(HC_2HR)$ products isolated²² from photolysis of solutions containing $H_4Os_4(CO)_{12}$ and $RCH=CH_2$. On the basis of these IR spectral features, we tentatively formulate this species as $H_4Ru_4(CO)_{11}(C_2H_4)$. Similar spectral features are observed when $H_4Ru_4(CO)_{12}$ is photolyzed in a neat 1-pentene matrix at 77 K. We are currently working to more fully characterize these " $H_4Ru_4(CO)_{11}(\text{olefin})$ " species and to investigate their significance in catalysis.

Note Added in Proof. Recent results show that near-UV irradiation of $H_4Ru_4(CO)_{12}$ in a methylcyclohexane matrix at 77

(18) Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *100*, 6088.

(19) Hoffmann, R., private communication.

(20) This technique has been successfully used to distinguish associative free radical substitution subsequent to metal-metal bond cleavage and competitive predissociation of CO in the photosubstitution of $Mn_2(CO)_{10}$ in fluid solution; see ref 4a.

(21) Foley, H. C.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7176.

(22) (a) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *J. Organomet. Chem.* **1976**, *113*, C42. (b) Bhaduri, S.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Raithby, P. R.; Rehani, S.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1979**, 562.

K yields CO loss but the $H_4Ru_4(CO)_{11}$ has a different structure than for the $H_4Ru_4(CO)_{11}$ in the 3-methylpentane matrix. Warmup of the $H_4Ru_4(CO)_{11}$ in methylcyclohexane yields the structure generated in 3-methylpentane. These findings will be elaborated in the full paper.

Acknowledgment. This research was supported in part by the Office of Naval Research and the National Science Foundation. We appreciate helpful discussions with Professor R. Hoffmann and the private communication of calculations relating to $H_4Ru_4(CO)_{11}$.

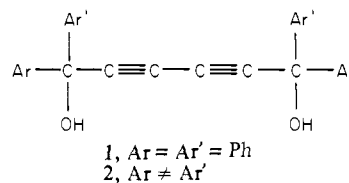
Molecular Design for Hosts in Crystalline Host-Guest Complexes

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In 1968 F. Toda reported¹ that diacetylenic diol **1** forms crystalline stoichiometric host-guest complexes² with a variety of small molecules. Thirty-five different guests, both polar



(ketones, aldehydes, esters, ethers, amides, amines, nitriles, sulfides, sulfides) and relatively nonpolar (arenes, alkenes, alkynes, haloalkanes), were mentioned. Recently Toda showed that chiral hosts **2** can discriminate between enantiomeric guests.³

Some X-ray structures of Toda's complexes have been determined.^{3,4} Features that contribute to complex formation are hydrogen bonding with the OH groups, the linear nature of the acetylenic bond, and π interactions with the aryl rings.

We thought that the overall molecular shape of **1** might also be important in its complex-forming capability. Toda's hosts contain a long molecular axis with sp^3 carbons at each end that bear large, relatively rigid groups. Such host molecules are likely to pack well only when aligned (roughly) along the long axis. The large end groups, however, act as "spacers" which prevent the hosts from packing closely, hence creating substantial voids in the crystal. These voids can then be occupied by guest molecules. In general, the voids might be expected to follow the long molecular axis, leading to channel-type complexes.^{4,5} If this structural feature⁶ of Toda's compounds is significant, it should be possible

(1) Toda, F.; Akagi, K. *Tetrahedron Lett.* **1968**, 3695.

(2) Hagan, M. M. "Clathrate Inclusion Compounds"; Reinhold: New York, 1962. Mandelcorn, L. "Non-Stoichiometric Compounds"; Academic Press: New York, 1964. Bhatnagar, V. M. "Clathrate Compounds"; Chemical Publishing Co.: New York, 1970. Cram, D. J.; Cram, J. M. *Science (Washington, D.C.)* **1974**, *183*, 803. MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. *Chem. Soc. Rev.* **1978**, *7*, 65. Vögtle, F., Ed. *Top. Curr. Chem.* **1981**, *98*; **1982**, *101*. Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177.

(3) Toda, F.; Tanaka, K.; Omata, T.; Nakamura, K.; Ōshima, T. *J. Am. Chem. Soc.* **1983**, *105*, 5151. Toda, F.; Tanaka, K.; Ueda, H. *Tetrahedron Lett.* **1981**, *22*, 4669. Toda, F.; Tanaka, K.; Ueda, H.; Ōshima, T. *J. Chem. Soc., Chem. Commun.* **1983**, 743. Toda, F.; Tanaka, K.; Mori, K. *Chem. Lett.* **1983**, 827.

(4) Toda, F.; Ward, D. L.; Hart, H. *Tetrahedron Lett.* **1981**, *22*, 3865. Toda, F.; Tanaka, K.; Hart, H.; Ward, D. L.; Ueda, H.; Ōshima, T. *Nippon Kagaku Kaishi* **1983**, 239.

(5) Some complexes have structures that simultaneously qualify for channel and clathrate descriptors.

(6) In our first X-ray paper,⁴ we described this shape as "wheel-and-axle". Because wheel may imply rotation, we think the term spacer may be more precise.

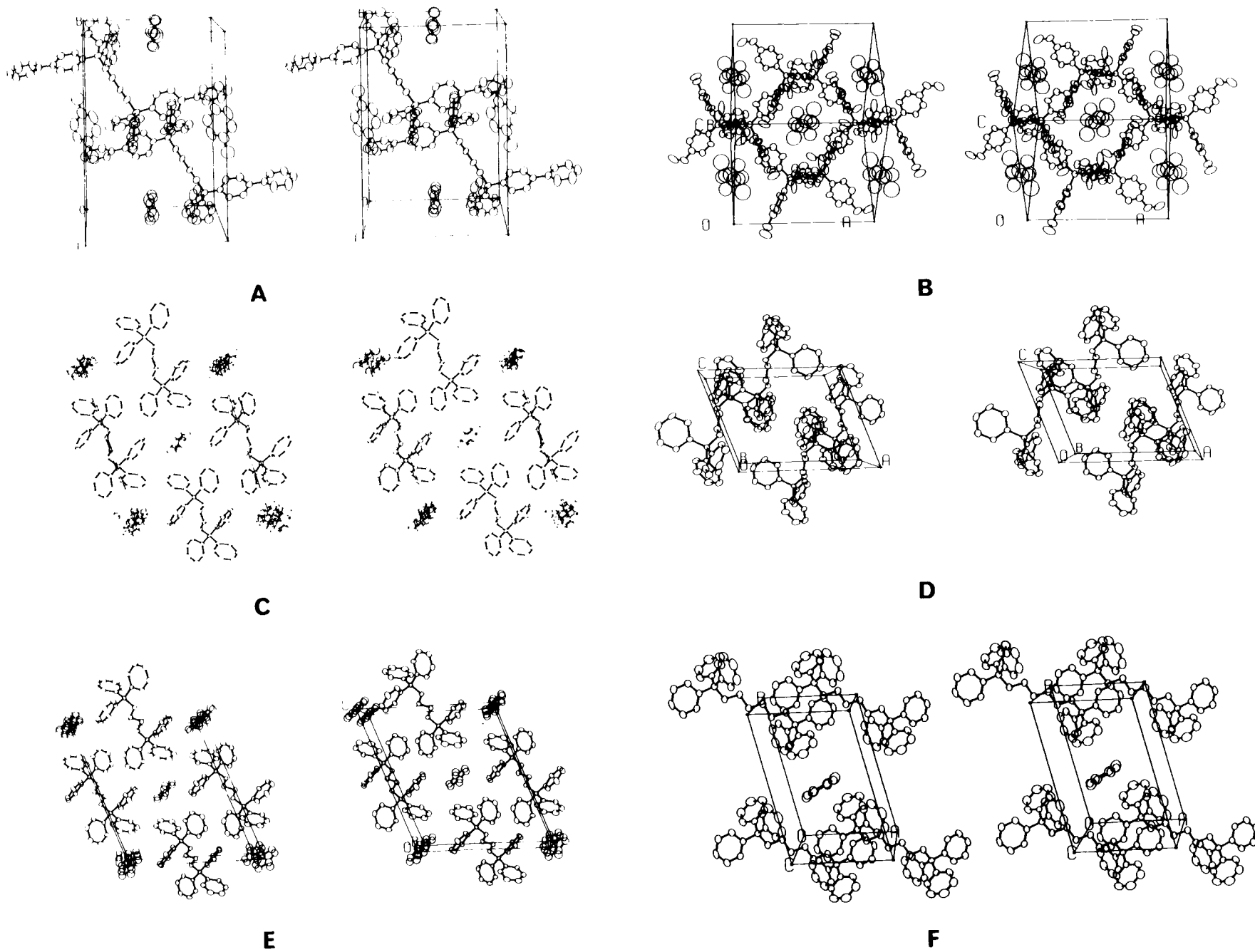


Figure 1. Unit cells of the 1:1 complexes of (A) 4 + *p*-xylene (triclinic, space group $P\bar{1}$), (B) 7 + CHCl_3 (cubic, space group $Pa3$), (C) 12 + toluene (monoclinic, space group $P2_1/n$), (D) 12 without guest (monoclinic, space group $P2_1/n$), (E) 13 + toluene (monoclinic, space group $P2_1/n$), (F) 14 + *p*-xylene (triclinic, space group $P\bar{1}$). Hydrogens are omitted from all drawings for clarity.

Table I. Complexes of $\text{Ar}_3\text{CC}\equiv\text{C}-\text{C}\equiv\text{CCAr}_3$ ^{a,b}

Ar ₃	C ₆ H ₆	C ₆ H ₅ ⁻ (CH ₃)	C ₆ H ₄ (CH ₃) ₂			CHCl ₃
			ortho	meta	para	
(Ph) ₃ (3)						1:1
(Ph) ₂ (BP) (4)						
(Ph)(BP) ₂ (5)	1:1	1:1	1:1	1:1	1:1	
(BP) ₃ (6)		1:2	1:2		1:1	
(MeOPh) ₃ (7)					1:1	1:1

^a Ph = phenyl; BP = *p*-biphenyl; MeOPh = 4-methoxyphenyl. ^b All ratios are host/guest.

Table II. Complexes of Hosts with Nonlinear Long Axes^a

host	C ₆ H ₅ ⁻ CH ₃	C ₆ H ₄ (CH ₃) ₂		
		ortho	meta	para
Ph ₃ CCH=CHCH=CHCPh ₃ (9)	3:1			
Ph ₂ (BP)CCH=CHCH=CHC(BP)Ph ₂ (10)			4:1	
Ph(BP) ₂ CCH=CHCH=CHC(BP) ₂ Ph (11)	1:2	1:2	2:1	
Ph ₃ CCH ₂ CH=CHCH ₂ CPh ₃ (12)	1:1			
Ph ₃ C(CH ₂) ₄ CPh ₃ (13)	1:1			
Ph ₃ C(CH ₂) ₆ CPh ₃ (14)				1:1

^a All C=C bonds are trans. Footnotes from Table I also apply.

to design other hosts with the same general shape but different structural details and expect them to form crystalline host-guest complexes. In this paper we show that this simple idea has merit.

We decided first to eliminate the hydrogen-bonding capability in the host by replacing the hydroxyl group in **1** with a third aryl group. To test for complexation, potential hosts were recrystallized from various solvents; the host/guest ratios in the resulting crystals were determined by one or more methods such as NMR integration, elemental analysis, and X-ray structure determination. To begin with, we studied only a small number of potential guests, mainly nonpolar aromatic hydrocarbons. Table I shows some of the results.^{7,8} Clearly this molecular design does lead to stoichiometric complexes.

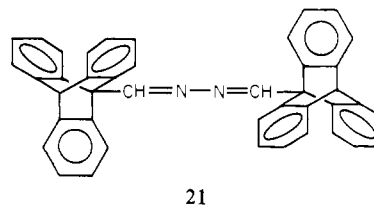
The axis may be lengthened. For example, Ph₃C—(C≡C)₃—CPh₃ (**8**) forms a stable 1:1 complex with *p*-xylene and somewhat less stable complexes with benzene, toluene, *o*-xylene, and chlorobenzene.

So that we could determine whether the long molecular axis could be "bent" instead of linear, sp² and sp³ carbons were incorporated (Table II).^{7,8} The chains between the spacers are in extended conformations, and these compounds do function as hosts.

With these successes, we added heteroatoms or functional groups to the long molecular axis. Azine Ph₃CCH=NN=CHCPh₃ (**15**), Ph₃COCH₂CH₂OCPH₃ (**16**), and Ph₃CNHCH₂CH₂NHCPH₃ (**17**) all form complexes with toluene.⁹ Oxygen functions may replace methylene groups in **13**; for example, Ph₃CC(=O)CH₂CH₂C(=O)CPh₃ (**18**), Ph₃CCH₂C(=O)C(=O)CH₂CPh₃ (**19**), and *trans*-Ph₃CCH₂CHCHOCH₂CPh₃ (**20**) all form 1:1 complexes with benzene.¹⁰ Since the guests in these complexes of **15**–**20** are nonpolar, hydrogen bonding to the oxygens or nitrogens cannot be a factor.

Although the trityl group and its analogues are excellent spacers, they are not essential. For example **21**, the triptycyl analogue of **15**, forms crystalline complexes with toluene and *m*- and *p*-xylenes.

Figure 1 shows one stereoview of the unit cell in five of the complexes and for comparison in one case (**12**) the host structure without a guest. These and other structures will be discussed in



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detail in full papers, but several features are worth mentioning here. As predicted, host molecules do tend to align along the long molecular axis. All complexes are of the channel type.^{5,11} In the toluene complexes of **12** and **13** (Figure 1C,E), all guests in any one channel are aligned head-to-tail, although among channels either orientation of the aryl-methyl bond is possible. It is significant that the plane of the toluene ring in the channel is not random, but well-defined, being determined as a consequence of π interactions with two phenyl substituents on each of four host molecules. Hence these complexes have aspects of both a channel and a clathrate (cage) structure. The same is true for the *p*-xylene complexes of **4** and **14** (Figure 1A,F).

The toluene complexes of **12** and **13** are nearly identical (monoclinic, space group $P2_1/n$; the cell dimensions (Å) are, respectively, $a = 14.786$, 14.772 , $b = 7.525$, 7.915 , $c = 17.063$, 16.685 ; $\beta = 107.98$, 110.98°). Clearly, the presence or absence of the carbon-carbon double bond in the long molecular axis of the host makes little difference.

Structures C and D (Figure 1) show **12** with and without a guest. Both crystals are monoclinic, space group $P2_1/n$. Although there are minor differences in the unit cell dimensions, the host arrangement in both crystals is similar, and the substantial channels in structure D are apparent.

These complexes may be used for separations. For example, **14** forms a stable complex with *p*-xylene (structure, F, Figure 1) but not with *m*-xylene. Recrystallization of **14** from a mixture of the two xylenes containing 30% or more of the *p*-isomer gives crystals containing *only* this isomer (<1% meta, the NMR detection limit). Other uses, including chiral recognition, are readily envisioned.

The molecular design for hosts outlined here, generalized from the elegant studies of Professor Toda, has great potential, which we are continuing to explore.

Acknowledgment. We are indebted to Dr. Yoshikazu Takehira for the synthesis of **3** and **7**, to Dr. Mary Smal for the synthesis of **5**, **6**, and **8**, and to Kwok-Keung Ng for the synthesis of **16**. We thank the National Science Foundation for financial support. We also thank Professor Fumio Toda for introducing us to this subject and for the collaboration that resulted in ref. 4.

Registry No. 3-CHCl₃, 90507-77-0; 4-2C₆H₅(CH₃), 90507-79-2; 4-*o*-C₆H₄(CH₃)₂, 90507-80-5; 4-*m*-C₆H₄(CH₃)₂, 90507-81-6; 4-*p*-C₆H₄(CH₃)₂, 90507-82-7; 5-C₆H₆, 90507-84-9; 5-C₆H₅(CH₃), 90507-85-0; 5-*o*-C₆H₄(CH₃)₂, 90507-86-1; 5-*m*-C₆H₄(CH₃)₂, 90507-87-2; 5-*p*-C₆H₄(CH₃)₂, 90507-88-3; 6-2C₆H₅(CH₃), 90507-90-7; 6-2-*o*-C₆H₄(CH₃)₂, 90507-91-8; 6-*p*-C₆H₄(CH₃)₂, 90507-92-9; 7-*p*-C₆H₄(CH₃)₂, 90507-94-1; 7-CHCl₃, 90507-95-2; 8-*p*-C₆H₄(CH₃)₂, 90507-97-4; 9-¹/₃C₆H₅CH₃, 90507-99-6; 10-¹/₄-C₆H₄(CH₃)₂, 90508-01-3; 11-2C₆H₅CH₃, 90508-03-5; 11-2-*o*-C₆H₄(CH₃)₂, 90508-04-6; 11-¹/₂-*m*-C₆H₄(CH₃)₂, 90508-05-7; 12-C₆H₅CH₃, 90530-59-9; 13-C₆H₅CH₃, 90508-06-8; 14-*p*-C₆H₄(CH₃)₂, 90508-08-0; 15-¹/₃C₆H₅CH₃, 90508-10-4; 16-C₆H₅CH₃, 90508-11-5; 17-²/₃C₆H₅CH₃, 90508-13-7; 18-C₆H₆, 90508-15-9; 19-C₆H₆, 90508-17-1; 20-C₆H₆, 90508-19-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters for the structures shown in Figure 1 (13 pages). Ordering information is given on any current masthead page.¹²

(7) Most of the hosts are new compounds. Their synthesis, spectra, and other properties will be described in a full account.

(8) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried.

(9) Host/guest ratios are 3:1, 1:1, and 3:2, respectively.

(10) Compounds of the type Ph₂P(=X)(CH₂)_nP(=X)Ph₂ ($n = 2, 3$; X = S, Se) with structures analogous to **18** form complexes with aromatic hydrocarbons (Brown, D. H.; Cross, R. J.; Mallinson, P. R.; MacNicol, D. D. *J. Chem. Soc., Perkin Trans. 2* 1980, 993), possibly for similar reasons.

(11) These complexes are very different from the weak, layered complex of benzene with triphenylmethane: Allemand, A.; Gerdil, R. *Acta Crystallogr., Sect. A* 1975, *A31*, S 130.

(12) Publication of complete crystallographic details of these and other complexes is planned.