Organometallics **1992,** *11,* 2863–2867 2863

chromatographed at 10 °C on alumina IV, in hexane. Elution with hexane gave a yellow band containing 0.010 g (0.012 mmol, 12%) of **10**. Further elution with a toluene/hexane mixture (1/1, v/v) gave a red band containing a mixture of **6** and $(ICH_2)(CO)_2CpMo(\mu\text{-dppm})MoCp(CO)_2I$ (**12**). Concentration in vacuo of the solution and cooling to −20 °C gave 0.030 g of orange-red crystals, which were still found to be a mixture of compounds **6** and **12**. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6, selected data): δ −18.5 (d, J_{PC} = 10 Hz, $MoCH_2I$).

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Supplementary Material Available: A listing of IR data (4000–200 cm^{-1}) for new compounds and $^{31}P\{^1H\}$ NMR spectra for **1b** and **8** and ^1H NMR spectra for **1b**, **3**, **4**, and **5** (8 pages). Ordering information is given on any current masthead page.

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2-Hetero-1λ^5,3λ^5-diphosphabenzenes as Ligands in Molybdenum Complexes

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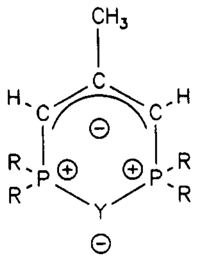
Treatment of (2,5-norbornadiene)molybdenum tetracarbonyl with 5-methyl-1,1,3,3-tetraphenyl-1λ^5-phospha-3-phosphonia-2-boratabenzene (**1**) results in the formation of a complex **1**·$Mo(CO)_4$ (**4**). Likewise, the reaction of (cycloheptatriene)molybdenum tricarbonyl with 5-methyl-1,1,3,3-tetraphenyl-1λ^5,3λ^5-diphosphabenzene (**2**) gives a complex **2**·$Mo(CO)_3$ (**5**). Complexes **4** and **5**, obtained in high yields, have been characterized on the basis of their IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, as well as by mass spectrometry and elemental analysis. Ocher-yellow crystals of composition **4**·THF were grown from tetrahydrofuran/hexane and studied by X-ray crystallography: space group $C2/m$, a = 23.343 (4) Å, b = 14.016 (1) Å, c = 13.352 (2) Å, β = 122.90 (1)°, V = 3667.83 Å^3, Z = $^8/_2$. Bright yellow crystals of composition **5**·0.5THF were obtained by crystallization from THF: space group $Pbca$, a = 16.687 (2) Å, b = 17.375 (2) Å, c = 22.929 (3) Å, V = 6647.96 Å^3, Z = 8. Compounds **4** and **5** feature zero-valent molybdenum centers in a pseudooctahedral coordination sphere with the heterocycles **1** and **2** bound as four-electron donors via their methallylic functions and the semiylidic function PCHP as an additional two-electron donor in **5**.

Introduction

According to recent structural work, 2-hetero-1λ^5,3λ^5-diphosphabenzenes **1–3** are best described as composed of carbanionic, methallylic moieties bridging the cationic triatomic units PBH_2P, PCHP, and PNP.[1,2] In agreement with theoretical work, the tetracoordinate λ^5-phosphorus centers are acting as conjugation barriers for the individual π-systems: the π-methallylic units are completely planar but tilted against the plane of the heteroatoms.



Y = BH_2 **1**
CH **2**
N **3**
R = C_6H_5

Owing to their phosphonium methallylide characters, the methallylic parts of the rings should have excellent donor properties, thus making these heterocycles powerful ligands. The low ionization energies of λ^5-phosphinines[3] and λ^5-di- and -triphosphabenzenes[4] indicate that for **2** the carbon atom bridging the two phosphorus atoms should also be able to serve as a donor site.[5,6]

Ylide coordination to metals can follow very different structural patterns depending on the nature of the ylide.[7–10] The stability of the resulting complexes is determined by the substituents at the ylidic functions, in particular, the integration of the carbanionic center into a π-system. For **1–3**, the methallylic parts of the molecules should serve as four-electron-donor groups, attached to metals mainly through the two ylidic carbon atoms. For P,P bridging BH_2 groups, any donor properties can be ruled out, and "phosphanitrilic" functions P^V–N–P^V are known to be extremely poor donor sites for low-valent metals. However, carbon atoms between the two phosphorus atoms as in **2** have been observed as donor centers previously for open-chain ligands, which therefore suggests in summary quite different ligand properties for **1** and **2**, but similar properties for **1** and **3**.

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We have therefore investigated the reactivity of one prototype each of the series 1 and 2 toward molybdenum carbonyl precursors.

Results and Discussion

Attempts to displace ligating carbonyls in $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ either by 1 or by 2 in tetrahydrofuran in a thermal reaction lead only to decomposition of the starting materials even under mild to moderate conditions (<70 °C). Photochemical activation of the carbonyl ligands also proved to be unfavorable due to the strong absorbance of the uncoordinated heterocycles 1 and 2 in the UV region. Monoactivated species like $(CO)_5Cr{\cdot}THF$ or $(CO)_5Mo{\cdot}THF$ also were of no advantage and gave only decomposition products with 1 or 2.

It was only in the reactions of 1 and 2 with molybdenum carbonyl precursors, the maximum hapticity of which matched those of the ligand, that well-defined products could be obtained (Schemes I and II).

Scheme I

$$\mathrm{NBD{\cdot}Mo(CO)_4 + 1 \rightarrow \underset{4}{1{\cdot}Mo(CO)_4} + NBD}$$

NBD = 2,5-norbornadiene

Scheme II

$$\mathrm{CHT{\cdot}Mo(CO)_3 + 2 \rightarrow \underset{5}{2{\cdot}Mo(CO)_3} + CHT}$$

CHT = cycloheptatriene

The reaction of (2,5-norbornadiene)molybdenum tetracarbonyl with equimolar quantities of 5-methyl-1,1,3,3-tetraphenyl-1λ^5-phospha-3-phosphonia-2-boratabenzene (1) in tetrahydrofuran at −60 °C yields the desired complex 4 in very good yield. The ocher-yellow complex 4 is stable as a solid in an inert atmosphere at room temperature. Its IR spectrum (in tetrahydrofuran) shows four intense low-frequency bands at $\tilde{\nu}$ = 2009, 1915, 1893, and 1875 cm^{-1}. This multiplicity suggests the presence of a *cis*-$(CO)_4ML_2$ complex with local point symmetry C_{2v}. The significant shift of the bands to lower frequency is indicative of the incorporation of a ligand with rather low π-acceptor characteristics, which induces a stronger back-donation of electrons from the molybdenum center toward the carbonyl groups.

Compound 4 is readily soluble in aromatic hydrocarbons and tetrahydrofuran but shows slow decomposition in solution to give a dark brown slurry. The product was further identified by NMR spectroscopy, electron impact mass spectrometry, and elemental analysis (Experimental Section).

Benzene solutions of 4 show a broad resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ = 8.3 ppm, with the ^{31}P–^{11}B coupling being poorly resolved and shifted to lower field as compared to the signal of the free ligand 1 (−5.2 ppm). Impurities (from decomposition) give rise to some very-low-intensity signals near −5 ppm. The ^1H NMR spectrum shows singlets for the methallylic protons and second-order multiplets for the phenyl protons. In the $^{13}C\{^1H\}$ NMR spectra, the most interesting feature is the very large shift toward lower field of the resonance of the central carbon atom of the methallylic groups: the signal at 214.95 ppm is downfield by no less than 50 ppm from the resonance of the uncoordinated ligand 1. The presence of small intensity resonances of the uncoordinated ligand 1 is again indicating a partial decomposition of 4 in benzene or tetrahydrofuran.

The molecular structure of 4 was determined by single-crystal X-ray diffraction. Compound 4 crystallizes in the monoclinic space group $C2/m$ (No. 12) with a half-molecule of the complex together with a half-molecule of tetrahydrofuran in the asymmetric unit. Molecule 4 thus obeys crystallographical mirror symmetry (point group C_s, Figure 1). The heterocycle 1 is coordinated to the metal through the π-allylic system with the two ylidic carbon atoms C(1/1′) as nearest neighbors (Figure 1). The coordination at the molybdenum center corresponds to a distorted octahedron. The atoms C(1/1′), C(30/30′), and Mo are virtually coplanar, with a maximum deviation of 0.06 Å for the atoms C(1/1′). The angle between the two axial carbonyl groups [159.8 (4)°] deviates strongly from 180° due to steric repulsion from the exocyclic methyl and the BH_2 group of the heterocycle. The equatorial carbonyls are exactly in trans positions relative to the ylide atoms (average: 180.0 (3)°).

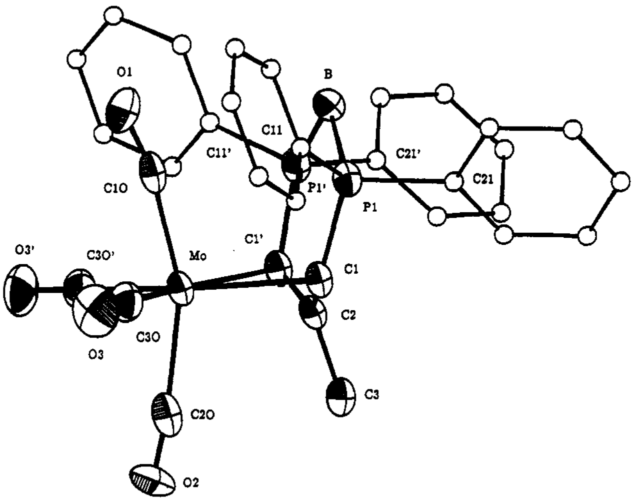

Figure 1. Molecular structure of 4 with atom numbering scheme (ORTEP, 50% probability ellipsoids for the heavier atoms; phenyl carbon atoms isotropically with arbitrary radii, hydrogen atoms omitted).

The six-membered heterocycle adopts a half-chair conformation. The methallylic fragment is almost planar with a maximum deviation from planarity for atom C(2) of 0.01 Å and a sum of angles at C(2) of 359.6 (4)°. This plane forms a dihedral angle of 147.6 (7)° with the P(1)BP(1′) plane [uncoordinated 1: 144.0 (2)°]. The relative orientation of the four phenyl rings has changed significantly in the coordinated ligand as compared to free 1 [angles between normals to planes: ring C(11) and C(11′) = 115.0°, ring C(21) and C(21′) = 90.9°, in contrast to 94.0°/78.8° in 1]. The Mo–C(1/1′) and Mo–C(2) bond lengths of 2.399 (6) and 2.321 (9) Å, respectively, are in good agreement with those found for the related (allylidenetriphenylphosphorane)molybdenum tetracarbonyl complex.[13] The ylidic bonds [P(1)–C(1), P(1′)–C(1′)] are enlarged from 1.732 (2) in 4 to 1.770 (7) Å in 2, indicating a reduction in the ylidic character upon coordination. While the distance C(allyl)–C(methyl) [C(2)–C(3)] is rather unchanged [1.49 (1) Å], the bond lengths C(2)–C(1/1′) by contrast show an increase from 1.397 (3) and 1.387 (3) Å in 1 to 1.436 (8) Å in 4. The two P/P′–B distances [1.917 (7) Å] agree with the P–B distances found in 1 and in other six-membered rings containing R_2P–BH_2–PR_2 moieties.

By treating 5-methyl-1,1,3,3-tetraphenyl-1λ^5,3λ^5-diphosphabenzene (2) with an equimolar amount of (cycloheptatriene)molybdenum tricarbonyl in tetrahydrofuran, complex 5 was obtained in good yield and high purity. The bright yellow compound 5 is stable as a solid at room

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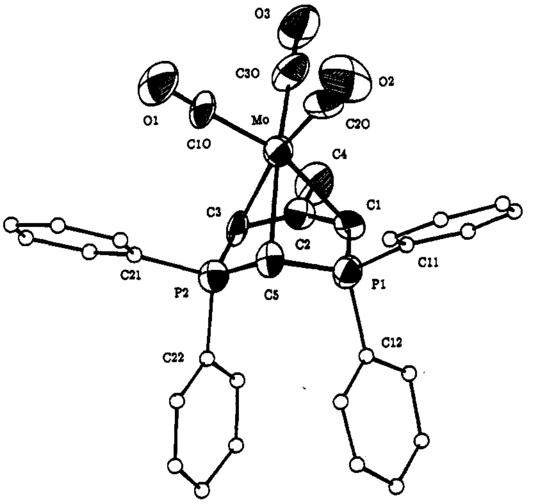

Figure 2. Molecular structure of **5** with the atom numbering scheme (ORTEP, 50% probability ellipsoids shown for the heavier atoms; phenyl carbon atoms with arbitrary radii, hydrogen atoms omitted).

temperature and starts to decompose only above 175 °C in a nitrogen atmosphere. The IR spectrum (in THF) exhibits three intense carbonyl bands at $\tilde{\nu}$ = 1925, 1837, and 1813 cm^{-1}, easily assigned to a $L_2L'M(CO)_3$ complex with local point symmetry C_{3v}. The large bathochromic shift as compared to η^6-C_7H_8-$Mo(CO)_3$ indicates low π-acceptor characteristics for the ligand **2** and hence more extensive back-donation of electrons from the metal to the carbonyl groups.

Compound **5** is appreciably soluble only in dimethyl sulfoxide and THF, where it shows no decomposition. The composition of the pure product has been confirmed by elemental analysis and electron impact mass spectroscopy. A highly symmetrical structure is evident from the results of a NMR analysis and an X-ray structural study.

Solutions of compound **5** in DMSO show a single resonance line in the $^{31}P\{^1H\}$ NMR spectrum with δ = 2.90 ppm (δ = 2.07 ppm in THF).

The ^1H NMR signals for the protons of the heterocyclic ring appear at low field as compared to those of **2** and represent spin systems of higher order. The phenyl–proton resonances appear as complex multiplets in the usual region of aromatic hydrocarbons. Compound **5** is stable against moisture (solutions in wet DMSO show a proton NMR signal at δ = 3.33 ppm) and can be stored for months under water. Decomposition is initiated only upon addition of acid.

In the $^{13}C\{^1H\}$ NMR spectrum, the resonances of all four carbon atoms of the heterocycle appear strongly shifted toward higher fields relative to **2**. Thus, the semiylidic carbon resonance moves from δ = −3.00 for **3** to δ = −19.75 ppm for **5**, and that of CHP carbons is shifted from δ = 51.8 to δ = 31.20 ppm. As for **4**, the signal for the central carbon atom is displaced most significantly from δ = 159.5 to δ = 124.85 ppm. The signals for the carbonyl groups appear at 225.06 and 226.55 ppm.

All these data reflect the strong donor properties of ligand **2**.

Compound **5** crystallizes in the orthorhombic space group *Pbca* (No. 61) with a complete molecule of the complex and a half-molecule of tetrahydrofuran in the asymmetric unit. The structure of molecule **5** approaches local mirror symmetry (point group C_s) except for an asymmetrical twist of the phenyl rings at the phosphorus centers [angle between planes of ring C(11) and C(21) = 26.12° and of ring C(12) and C(22) = 14.96°]. Heterocycle **2** is coordinated to the metal–tricarbonyl fragment via the methallylic π-system, mainly carbon atoms C(1) and C(3), and via the semiylidic carbon atom C(5) (Figure 2). The molybdenum atom is closer to the plane formed by the three carbonyl carbons than to the plane of the heterocyclic carbon atoms. These two planes are almost exactly parallel, with an interplanar angle of only 2.58°. The methallylic fragment is almost planar with a maximum deviation from planarity for atom C(2) of 0.06 Å and a sum of angles at C(2) of exactly 360.0 (2)°. The six-membered heterocycle adopts a half-chair conformation with a dihedral angle of 127.87° between the planes.

Experimental Section

All manipulations were performed under an atmosphere of pure dry nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and distilled in an inert atmosphere prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL GX400 spectrometer, with the deuterated solvents as internal and 85% H_3PO_4 (δ = 0.00) as external standards. For IR studies (compounds in THF solution), a Perkin-Elmer 1600 FTIR spectrometer was used. Mass spectra were recorded on a MAT 311A (Varian) instrument. Microanalyses were performed at the Microanalytical Laboratory of this Institute.

(5-Methyl-1,1,3,3-tetraphenyl-1λ^5-phospha-3-phosphonia-2-boratabenzene)molybdenum Tetracarbonyl (4). A solution of **1** (0.70 g, 1.60 mmol) in 10 mL of diethyl ether was treated at −60 °C with a solution of (2,5-norbornadiene)molybdenum tetracarbonyl (0.48 g, 1.60 mmol) in 40 mL of tetrahydrofuran. After warming to room temperature, the reaction mixture was stirred for 15 h. Unsoluble byproducts were separated, and the orange-red filtrate was treated carefully with hexane. The precipitate was separated, washed with hexane, and dried in vacuo: yield 0.85 g (83%), ocher-yellow powder, mp 125 °C (dec). IR (THF/KBr): $\tilde{\nu}$(CO) (cm^{-1}) 2009 (s), 1915 (s), 1893 (s), 1875 (s). ^1H NMR (C_6D_6): δ (ppm) 2.45 (s, 3 H, CH_3), 2.91 (s, 2 H, CHP), 6.91–6.97 (m, 4 H, N = 6.7 Hz, p-C_6H_5), 7.13–7.17 (m, 8 H, N = 17.7 Hz, m-C_6H_5), 7.26–7.31 (m, 4 H, N = 20.8 Hz, o-C_6H_5), 7.78–7.83 (m, 4 H, N = 18.9 Hz, o-C_6H_5). $^{13}C\{^1H\}$ NMR (THF-d_8): δ (ppm) 34.98 (t, ^3J(PC) = 5.87 Hz, CH_3), 41.02 (d, ^1J(PC) = 62.11 Hz, CHP), 129–133 (m, 4 C_6H_5), 200.98 (s, 2 CO), 214.95 (t, ^2J(PC) = 11.95 Hz, C–CH_3), 223.34 (s, 2 CO). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 8.3 (br d, ^1J(PB) = 80 Hz). MS (EI): m/e 616 (M^+ − CO). Anal. Calcd for $C_{32}H_{27}BMoO_4P_2$: C, 59.66; H, 4.22; P, 9.60. Found: C, 59.61; H, 4.64; P, 9.63.

(5-Methyl-1,1,3,3-tetraphenyl-1λ^5,5λ^5-diphosphabenzene)molybdenum Tricarbonyl (5). A solution of **2** (0.50 g, 1.15 mmol) in 20 mL of tetrahydrofuran was slowly added at room temperature to a solution of (cycloheptatriene)molybdenum tricarbonyl (0.31 g, 1.15 mmol) in 15 mL of tetrahydrofuran. The solution was stirred at room temperature for 15 h. The bright yellow precipitate was separated, washed with hexane, and dried in vacuo: yield 0.83 g (90%), bright yellow powder, mp 175 °C (dec). IR (THF, KBr): $\tilde{\nu}$(CO) (cm^{-1}) 1925 (s), 1837 (w), 1813 (w). ^1H NMR (DMSO-d_6): δ (ppm) 2.28 (pseudo tt, 1 H, N = 12.2/3.3 Hz, CHP_2, AB_2X_2), 2.52 (s, 3 H, CH_3), 3.64 (pseudo dt, 2 H, N = 12.2/2.7 Hz, CHP, ABXX′), 7.02–7.96 (complex multiplet, total 20 H, 4 C_6H_5). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ (ppm) −19.75 (t, ^1J(PC) = 49.9 Hz, CHP_2), 30.34 (t, ^3J(PC) = 12.0 Hz, CH_3), 31.20 (d, ^1J(PC) = 91.9 Hz, CHP), 124.85 (t, ^2J(PC) = 4.5 Hz, C–CH_3), 128–138 (complex multiplet, C_6H_5), 225.06 (s, CO), 226.55 (s, 2 CO). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ (ppm) 2.90 (s). $^{31}P\{^1H\}$ NMR (THF-d_8): δ (ppm) 2.07. MS (EI): m/e 616 (M^+). Anal. Calcd for $C_{32}H_{26}MoO_3P_2$: C, 62.35; H, 4.35; P, 10.05. Found: C, 62.31; H, 4.52; P, 9.83.

Crystallography. Compound 4. A small part (0.2 × 0.2 × 0.1 mm) of a cubelike crystal mounted in a glass capillary was directly examined on an Enraf-Nonius CAD4 diffractometer,[14] and the geometric and intensity data were collected. Pertinent

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[14] Calculations were performed by using a Micro-Vaxstation 3100 M76 (Micro VMS V5.3) with the programs SHELXS-86 (structure solution), SHELX-76 (structure refinement), DELOS, LEPAGE (cell reduction), and the commercial package SDP/V V3.0.

Table I. Crystallographic Data for 4 and 5

formula	$C_{32}H_{27}BMoO_4P_2(\cdot THF)$	$C_{32}H_{26}MoO_3P_2(\cdot 0.5THF)$
fw	644.27	616.45
space group	*C*2/*m* (IT No. 12)	*Pbca* (IT No. 61)
a, Å	23.343 (4)	16.687 (2)
b, Å	14.016 (1)	17.375 (2)
c, Å	13.352 (2)	22.929 (3)
α, deg	90	90
β, deg	122.90 (1)	90
γ, deg	90	90
V, Å^3	3667.83	6647.96
Z	$^8/_2$	8
d_{calc}, g cm^{-3}	1.23	1.23
μ(Mo Kα), Å	4.20	4.57
temp, °C	−50	20
radiation	Mo Kα, graphite monochromated; λ = 0.71069 Å	
R^a	0.0742	0.0723
$R_w{}^b$	0.0629	0.0562

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. Function minimized: $\sum w(|F_o| - |F_c|)^2$.

Table II. Positional Parameters, Equivalent Isotropic Thermal Parameters, and Their Estimated Standard Deviations for 4^a

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Mo	0.17363 (5)	0.00000	0.15190 (9)	0.021
P	0.32327 (9)	0.1125 (1)	0.2269 (2)	0.022
O(1)	0.2691 (4)	0.00000	0.4320 (7)	0.046
O(2)	0.0290 (4)	0.00000	−0.0912 (7)	0.038
O(3)	0.1066 (3)	0.1651 (4)	0.2106 (5)	0.056
C(10)	0.2408 (5)	0.00000	0.329 (1)	0.026
C(20)	0.0812 (6)	0.00000	−0.011 (1)	0.026
C(30)	0.1317 (4)	0.1036 (6)	0.1906 (7)	0.030
B	0.3721 (6)	0.00000	0.313 (1)	0.030
C(1)	0.2410 (3)	0.902 (5)	0.995 (6)	0.022
C(2)	0.2218 (5)	0.00000	0.0388 (9)	0.026
C(3)	0.1775 (5)	0.00000	−0.0932 (9)	0.030
C(11)	0.3160 (4)	0.2014 (6)	0.3174 (7)	0.022
C(12)	0.2727 (5)	0.2752 (8)	0.2642 (9)	0.085
C(13)	0.2666 (5)	0.3440 (9)	0.336 (1)	0.100
C(14)	0.3040 (7)	0.341 (1)	0.453 (1)	0.060
C(15)	0.3476 (7)	0.2684 (9)	0.507 (1)	0.064
C(16)	0.3553 (5)	0.1971 (7)	0.4408 (8)	0.060
C(21)	0.3690 (3)	0.1726 (5)	0.1711 (6)	0.023
C(22)	0.4181 (4)	0.2424 (6)	0.2375 (7)	0.031
C(23)	0.4545 (4)	0.2846 (6)	0.1938 (8)	0.021
C(24)	0.4440 (4)	0.2574 (7)	0.0879 (9)	0.048
C(25)	0.3946 (4)	0.1893 (7)	0.0184 (8)	0.049
C(26)	0.2581 (4)	0.1476 (7)	0.0617 (7)	0.031

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters, *U*(eq), defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor: $U(\text{eq}) = {}^1/_2 \sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i\mathbf{a}_j$.

Table III. Positional Parameters, Equivalent Isotropic Thermal Parameters, and Their Estimated Standard Deviations for 5^a

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Mo	0.27712 (8)	0.62926 (8)	0.28846 (6)	0.060
P(1)	0.1066 (2)	0.7491 (3)	0.2667 (2)	0.060
P(2)	0.0845 (2)	0.6431 (2)	0.3629 (2)	0.055
C(10)	0.2316 (9)	0.5176 (9)	0.2973 (7)	0.078
C(20)	0.2440 (9)	0.609 (1)	0.2059 (8)	0.083
C(30)	0.342 (1)	0.623 (1)	0.2939 (8)	0.080
O(1)	0.2376 (7)	0.4519 (6)	0.3023 (6)	0.130
O(2)	0.2542 (8)	0.5932 (8)	0.1572 (5)	0.123
O(3)	0.4114 (6)	0.6205 (7)	0.2997 (6)	0.130
C(1)	0.1976 (7)	0.7650 (8)	0.2989 (7)	0.064
C(2)	0.2217 (9)	0.7336 (8)	0.3538 (7)	0.054
C(3)	0.1795 (8)	0.6728 (8)	0.3827 (6)	0.055
C(4)	0.2947 (9)	0.7643 (8)	0.3847 (7)	0.080
C(5)	0.0843 (7)	0.6564 (7)	0.2883 (7)	0.047
C(11)	0.1172 (8)	0.7573 (9)	0.1868 (4)	0.096
C(111)	0.1624 (8)	0.8218 (9)	0.1681 (4)	0.108
C(112)	0.1716 (8)	0.8336 (9)	0.1109 (4)	0.146
C(113)	0.1382 (8)	0.7837 (9)	0.0712 (4)	0.166
C(114)	0.0904 (8)	0.7211 (9)	0.0916 (4)	0.165
C(115)	0.0812 (8)	0.7052 (9)	0.1513 (4)	0.082
C(12)	0.0307 (6)	0.8190 (6)	0.2848 (4)	0.070
C(121)	−0.0505 (6)	0.7988 (6)	0.2809 (4)	0.083
C(122)	−0.1073 (6)	0.8556 (6)	0.2958 (4)	0.105
C(123)	−0.0921 (6)	0.9284 (6)	0.3114 (4)	0.110
C(124)	−0.0097 (6)	0.9502 (6)	0.3175 (4)	0.119
C(125)	0.0552 (6)	0.8960 (6)	0.3018 (4)	0.071
C(21)	0.686 (6)	0.5428 (5)	0.3829 (7)	0.053
C(211)	0.0443 (6)	0.4888 (5)	0.3454 (7)	0.083
C(212)	0.0332 (6)	0.4132 (5)	0.3636 (7)	0.106
C(213)	0.0483 (6)	0.3936 (5)	0.4193 (7)	0.120
C(214)	0.0767 (6)	0.4499 (5)	0.4594 (7)	0.128
C(215)	0.0874 (6)	0.5246 (5)	0.4382 (7)	0.089
C(22)	0.0069 (6)	0.6928 (7)	0.4014 (5)	0.055
C(221)	−0.0708 (6)	0.6670 (7)	0.4006 (5)	0.076
C(222)	−0.1360 (6)	0.7066 (7)	0.4248 (5)	0.109
C(223)	−0.1203 (6)	0.7749 (7)	0.4552 (5)	0.114
C(224)	−0.0364 (6)	0.8059 (7)	0.4561 (5)	0.119
C(225)	0.0257 (6)	0.7628 (7)	0.4289 (5)	0.096

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters, *U*(eq), defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor: $U(\text{eq}) = {}^1/_2 \sum_i\sum_j a_ia_j\mathbf{a}_i\mathbf{a}_j$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 4^a

Distances			
Mo–C(10)	2.01 (1)	C(10)–O(1)	1.15 (1)
Mo–C(20)	2.07 (1)	C(20)–O(2)	1.10 (1)
Mo–C(30/30′)	1.970 (8)	C(30/30′)–O(3/3′)	1.152 (8)
Mo–C(1/1′)	2.399 (6)	Mo–C(2)	2.321 (9)
P/P′–C(1/1′)	1.770 (7)	P/P′–B	1.917 (7)
C(2)–C(1/1′)	1.436 (8)	P/P′–C(11)	1.806 (8)
C(2)–C(3)	1.49 (1)	P/P′–C(21)	1.810 (7)
Angles			
C(10)–Mo–C(20)	159.8 (4)	C(30/30′)–Mo–C(1′/1)	180.0 (3)
C(10)–Mo–C(30/30′)	82.6 (3)	C(10)–Mo–C(1/1′)	97.4 (3)
C(20)–Mo–C(30/30′)	83.8 (3)	C(20)–Mo–C(1/1′)	99.7 (3)
C(1/1′)–C(2)–C(3)	118.3 (4)	P/P′–C(1/1′)–C(2)	122.8 (6)
C(1)–C(2)–C(1′)	123 (1)		
B–P/P′–C(1/1′)	114.3 (4)	C(1/1′)–P/P′–C(11/11′)	108.5 (3)
B–P/P′–C(11/11′)	114.2 (4)	C(1/1′)–P/P′–C(21/21′)	105.1 (3)
B–P/P′–C(21/21′)	109.7 (4)	C(11/11′)–P/P′–C(21/21′)	104.2 (3)

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits. Residual atoms E′ originate from symmetry operation *x*,−*y*,*z*.

crystallographic data are given in Table I. Lattice dimensions and Laue symmetry were determined from reflections 14 ≤ θ ≤ 18°. As the molybdenum-containing complex was measured with molybdenum radiation, an absorption correction by means of ψ scans was not carried out. For systematic absences, the space group was determined as C_2 or *C*2/*m*. Intensity data (θ/2θ scan) showed a moderate decrease of 2.6% during data collection and were corrected by routine procedures.[14] The Patterson map (SHELXS-86)[14] for space group *C*2/*m* provided the positions of the atoms Mo, B, O(1), and O(2) on the crystallographic mirror plane together with the positions of P(1/1′). The remaining parts of the molecule were located in a series of least-squares refinements and difference Fourier maps. The atoms of the tetrahydrofuran molecule (one half-molecule in the asymmetric unit with the oxygen atom lying on the mirror plane with site occupancy 0.5) were found by an alternating sequence of least-squares refinements and difference Fourier maps. Of the hydrogen atoms, nine could be found, the remaining (except for those on the slightly disordered tetrahydrofuran molecule) were calculated, but none of these hydrogen atoms were refined isotropically. This resulted in residuals *R* = 0.0742 and R_w = 0.0629 and a difference Fourier map with residual contours of ca. 1 e Å^{-3} near the disordered tetrahydrofuran molecule. The atomic positional parameters for the non-hydrogen atoms are listed in Table II.

Compound 5. A small part (0.2 × 0.2 × 0.3 mm) of a crystal was mounted in a glass capillary. Unit cell dimensions were determined by precession methods and refined directly on a Syntex P2$_1$ diffractometer, and intensity data were collected. Pertinent crystallographic data are given in Table I. Lattice dimensions and Laue symmetry were determined from reflections

Organometallics 1992, 11, 2867-2873

Table V. Selected Bond Distances (Å) and Angles (deg) for 5

Distances			
Mo-C(10)	1.95 (2)	C(10)-O(1)	1.15 (1)
Mo-C(20)	1.94 (2)	C(20)-O(2)	1.16 (1)
Mo-C(30)	1.93 (2)	C(30)-O(3)	1.17 (1)
Mo-C(1)	2.42 (1)	Mo-C(3)	2.42 (1)
Mo-C(2)	2.35 (1)	Mo-C(5)	2.43 (1)
P(1)-C(1)	1.71 (1)	P(2)-C(3)	1.73 (1)
C(2)-C(1)	1.43 (2)	C(2)-C(3)	1.43 (2)
C(2)-C(4)	1.51 (2)		
P(1)-C(5)	1.73 (1)	P(2)-C(5)	1.73 (1)
P(1)-C(11)	1.85 (1)	P(2)-C(21)	1.821 (9)
P(1)-C(12)	1.804 (8)	P(2)-C(22)	1.789 (9)
Angles			
C(1)-Mo-C(10)	164.9 (6)	C(3)-Mo-C(20)	166.1 (5)
C(5)-Mo-C(30)	171.0 (6)		
P(1)-C(1)-C(2)	125 (1)	P(2)-C(3)-C(2)	123 (1)
C(1)-C(2)-C(4)	120 (1)	C(3)-C(2)-C(4)	116 (1)
C(1)-C(2)-C(3)	124 (1)		
C(5)-P(1)-C(1)	102.6 (7)	C(5)-P(2)-C(3)	102.8 (6)
C(5)-P(1)-C(11)	112.2 (7)	C(5)-P(2)-C(21)	112.1 (6)
C(5)-P(1)-C(12)	114.3 (7)	C(5)-P(2)-C(22)	115.0 (6)
P(1)-C(5)-P(2)	114.1 (7)		
C(1)-P(1)-C(11)	109.3 (7)	C(3)-P(2)-C(21)	110.7 (6)
C(1)-P(1)-C(12)	114.5 (6)	C(3)-P(2)-C(22)	113.0 (6)
C(11)-P(1)-C(12)	104.1 (5)	C(21)-P(2)-C(22)	103.4 (5)

$10 \leq \theta \leq 13°$. From systematic absences, the space group was determined as *Pbca*. Intensity data showed only a small decrease of 2% during data collection. For the same reasons as for compound 2, no absorption correction was carried out. The Mo atom was located by the Patterson map (SHELXS-86),[14] the remaining parts of the molecule in a series of least-squares refinements and difference Fourier maps. The atoms of the solvent tetrahydrofuran molecule (one half-molecule in the asymmetric unit—site occupancy 0.5 for the oxygen atom—with two carbon atoms showing a distinct disorder and site occupancy 0.25) were found by an alternating sequency of least-squares refinements and Fourier maps. The four phenyl rings were refined as rigid groups, and all hydrogen atoms were calculated in fixed positions. This resulted in residuals $R = 0.0723$ and $R_w = 0.0562$ and a satisfactory difference Fourier map with residual contours well below 1 e Å^{-3} near the disordered solvent molecule. The atomic positional parameters for the non-hydrogen atoms are listed in Table III. Selected bond distances and angles for 4 and 5 are listed in Tables IV and V, respectively.

Supplementary material for both structures has been deposited.

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Registry No. 1, 132749-41-8; 2, 125995-74-6; 4, 142131-40-6; 4·THF, 142131-41-7; 5, 142159-55-5; 5·$^1/_2$THF, 142159-56-6; (2,5-norbornadiene)molybdenum tetracarbonyl, 12146-37-1; (cycloheptatriene)molybdenum tricarbonyl, 12083-34-0.

Supplementary Material Available: Tables of hydrogen atom positions, bond distances, interbond angles, anisotropic thermal parameters, and root-mean-square amplitudes of anisotropic displacement (20 pages). Ordering information is given on any current masthead page.

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Syntheses and Molecular Structures of Hexasilylbenzenes and Disilylacetylenes

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For the preparation of bis(phenylsilyl)acetylene (2), Li_2C_2 has been obtained from $Br_2CHCHBr_2$ (or ClCHCHCl) and alkyllithium reagents and reacted with $ClSiH_2Ph$. HC_2Na and $BrSiH_2Ph$ afford the primary product HC_2SiH_2Ph (4), from which, via metalation and treatment with H_3SiBr, $H_3SiC_2SiH_2Ph$ (5) can be generated. 2 could not be trimerized when treated with various transition metal catalysts. Hexakis(phenylsilyl)benzene (1) is available from the reaction of $PhSiH_2Cl$ and C_6Br_6 with Mg in tetrahydrofuran, and the *p*-tolyl analogue 3 has been prepared similarly using *p*-$TolSiH_2Cl$. The crystal and molecular structures of 1–3 have been determined by single-crystal X-ray diffraction. 2 has standard disilylalkyne dimensions. In contrast to the hexakis(trimethylsilyl) analogue, 1 and 3 feature planar central benzene rings with the arylsilyl groups at opposite corners above and below the plane. 1 crystallizes from CCl_4 with two independent molecules and three solvent molecules of CCl_4 in the asymmetric unit (rhombohedral, space group $R\bar{3}$). Both 1 and 3 crystallize from ethyl acetate without solvent, but only the structure of 3 has been determined (rhombohedral, space group $R\bar{3}$). 2 crystallizes from the melt (monoclinic, space group $P2_1/a$).

Introduction

Phenylsilane, $H_3SiC_6H_5$ (or silylbenzene), and one of the three possible isomeric disilylbenzenes, *p*-$(H_3Si)_2C_6H_4$, are the only silylbenzenes described in the literature with no further substituents at silicon but hydrogen.[1-3] For the synthetic chemist, the fully substituted derivative hexasilylbenzene (A), the hexasilyl analogue of hexamethylbenzene (B), remains a challenge.

While many of the fully *methylated* silylbenzenes, mostly poly(trimethylsilyl)benzenes, are well represented in the organosilicon literature,[4-6] it was not until the work

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