

Complexes of P(III)-phosphocavitands with Groups VI and VII transition metal carbonyls

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Abstract

A study has been made of the interaction between the new type of cavitands, P(III)-phosphocavitands, and the Cr, Mo, W, and Mn carbonyl complexes. The possibility has been shown for the directed coordination of all or some phosphorus atoms of the cavitand molecules with metals. The effect of the substituents at the phosphorus atoms in the macrocycles on the process selectivity has been revealed. The first metallocomplexes of phosphocavitands containing trivalent phosphorus atoms have been obtained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphocavitands; Groups VI and VII transition metals; Complexation

1. Introduction

Rigid cup-shaped macrocyclic systems constructed on the base of a calix[4]resorcinolarene matrix have been introduced into chemical studies by Cram [1]. He called them cavitands for the reasons of structural analogy. The main line of investigation in the chemistry of cavitands is concerned with the design and study of their phosphorus derivatives (phosphocavitands) [2–4]. The present work is devoted to this topic and involves the data on the synthesis and chemical features of phosphito- and amidophosphitocavitand complexes with carbonyls of Groups VI and VII transition metals; for preliminary communication on this problem see Ref. [5].

In the molecules of these tetradentate ligands, the exocyclic substituents at the phosphorus atoms are strictly equatorial. Hence, the lone electron pairs of the phosphorus atoms are oriented axially with a slight incline toward the central axis of the system. This structure of the initial macrocyclic system favors the stereospecificity of processes involving the lone electron pairs of phosphorus. At the same time, the volume and nature of the groups added to the phosphorus atoms

should significantly affect the course of the reaction as well as the composition and structure of resulting products because of the rigidity of the cavitand skeleton.

Note that reactions involving the addition of di- or monoatomic groups readily held within the cavitand cavity to phosphorus atom (oxidation [6,7], sulfurization [7,8], selenization [7,8], and complexation with Ag, Au, and Cu halogenides [9–11]) are generally stereoregular. In the molecules of resulting symmetric stereoisomers the substituents at the phosphorus atoms are oriented axially, and all phosphorus sites are functionalized without structural modification of the macrocyclic skeleton.

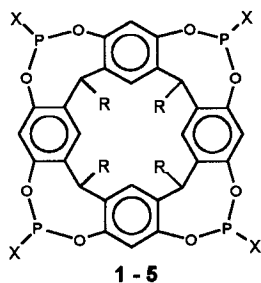
The insertion of bulky polyatomic functional groups to the phosphorus atoms in the cavitand molecules proceeds in a different way. The interaction between amidophosphocavitands and phenylazide does not result in the oxidative imination of all phosphorus atoms: one of them remains trivalent [12]. In the ligand exchange between phosphocavitands and $\text{acacRh}(\text{CO})_2$, the complete functionalization of phosphorus sites occurs, but the conformation of a phosphocine cycle in the formed tetranuclear complex changes that results in a distortion of the cavitand skeleton [13].

In order to further elucidate the peculiarities of interaction between P(III)-phosphocavitands and poly-

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atomic metallocomplexes, we studied the reaction of amidophosphito- and phosphitocavitands (**1–5**) with reagents having large molecules: hexacarbonyls of Group VI metals (Cr, Mo, and W) and Mn cyclopentadienyltricarbonyl.



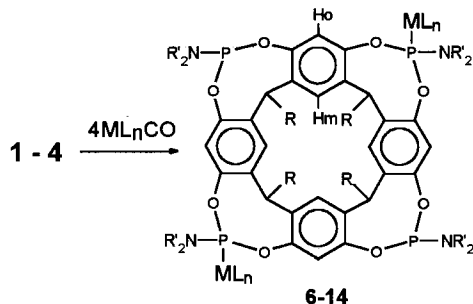
R=CH₃, X=NMe₂ (1); R=CH₃, X=NEt₂ (2); R=C₃H₇, X=NMe₂ (3); R=C₃H₇, X=NEt₂ (4); R=CH₃, X=OPr-i (5).

2. Results and discussion

All reactions were carried out in dioxane with varying reagent ratios and activation methods. We found that the reactions of cavitands **1–5** with Mo(CO)₆ and Cr(CO)₆ could be induced by both thermal and photochemical activation, but the process was less selective under ultraviolet irradiation. At the same time, the ligand exchange between amidophosphocavitands and W(CO)₆ or C₅H₅Mn(CO)₃ proceeded only under photochemical activation. It should be noted that the complexation products of amidophosphito- and phosphitocavitands could differ in the degree of modification, in spite of similar reaction conditions.

2.1. Binuclear metallocomplexes of amidophosphitocavitands **1–4**

The reaction of amidophosphitocavitands **1–4** with the carbonyl complexes of metals results in the formation of binuclear complexes **6–14** even in the presence



ML_n=Cr(CO)₅ (6-8): R=Me, R'=Me(6); R=Me, R'=Et(7); R=Pr, R'=Et(8);
 ML_n=Mo(CO)₅ (9-11): R=Me, R'=Me(9); R=Me, R'=Et(10); R=Pr, R'=Et(11);
 ML_n=W(CO)₅, R=Me, R'=Et (12);
 ML_n=MnC₅H₅(CO)₂ (13, 14): R=Me, R'=Et(13); R=Pr, R'=Me(14)

of double excess of the complexing agent under durable heating or irradiation.

Binuclear metallocomplexes of cavitands **6–14** were isolated as individual compounds with yields of 56–

79%. Their structures were supported by NMR spectroscopy and X-ray diffraction analysis. The ³¹P-NMR spectra of complexes **6–11**, **13**, and **14** in the temperature range from –80 to +40°C exhibited two singlets of similar intensities corresponding to the coordinated (the downfield signal) and uncoordinated (the upfield signal) phosphorus atoms (Table 1). In the ¹H-NMR spectra, singlets from both the *o*- and *m*-protons of benzene nuclei, respectively, are observed, as well as the doubling of proton signals from the amide groups at the phosphorus atoms, radicals (R), and internuclear bridges. These ¹H-NMR spectra of binuclear complexes of phosphocavitands suggest the diagonal arrangement of metal-containing units with respect to the macrocycle cavity and the retained symmetry of its molecular skeleton. The more involved NMR spectra of the tungsten complex **12** can be due to the increased discrepancy between the arrangements of metal units in the cavitand cavity.

In order to investigate the effect of the metal complexation on the phosphocavitand geometry, the X-ray analysis of a crystal of **11** has been carried out. Similar

to the molecules studied previously [7,8,13–15], phosphocavitand **11** has a 'bowl' shape with the hydrocarbon substituents in the 'bottom' (the C(5), C(12), C(19) and C(26) atoms) and the metallophosphorus P–Mo–(CO)₅ fragments at the 'cover' (C(2), C(9), C(16) and C(23) atoms) (Fig. 1). It is noteworthy that, although the Mo(CO)₅ fragments are attached only to two phosphorus centers (atoms P(1) and P(3)), they fully shield the phosphocavitand by the CO ligands with the shortest CO⋯P intramolecular distances equal to 3.48 and 3.62 Å. The presence of the metal-containing fragments causes significant distortions of the bowl resulting in the inequivalence of the both cover and bottom rim diameters (C⋯C distances) **11**. The distortion of the cover rim is much more pronounced: its

diameters differ by 0.42 Å (the C(2)⋯C(16) and C(9)⋯C(23) distances are 8.052(5) and 8.471(5) Å, respectively), while the difference in diameters of the bottom rim is only 0.11 Å (the C(5)⋯C(19) and C(12)⋯C(26) distances are 5.147(5) and 5.260(5) Å, respectively). For comparison, the corresponding distances in the uncoordinated phosphocavitand **4** are 8.291(5) and 5.236(5) Å, respectively [7].

The molecular geometry of coordinated phosphocavitand **11** is similar to that of tetrapropylamidophosphitocavitand **4** studied previously [7] (Table 2). All phosphocine cycles have chair–boat conformations with the axial Mo atoms and propyl groups and the equatorial NEt₂ groups. The presence of the Mo(CO)₅ moieties results in the significant elongation of the

Table 1
¹H- and ³¹P-NMR spectral parameters of metal complexes 6–19 (CDCl₃)

No.	δ ³¹ P (ppm)	δ ¹ H (ppm)					
		Hm	Ho	CH	R	X	
6	141.9, s, 189.9, s	7.28, s, 4H	6.70, s, 4H	4.90, q, 2H, 4.61, q, 2H	1.77, d, 6H, 1.69, d, 6H (CH ₃)	2.94, d, 12H, 2.78, d, 12H (NCH ₃)	
7	144.2, s, 188.3, s	7.33, s, 4H	6.76, s, 4H	4.92, q, 2H, 4.65, q, 2H	1.75, d, 6H, 1.73, d, 6H (CH ₃)	3.43, m, 8H, 3.27, m, 8H (NCH ₂); 1.26, t, 12H, 1.17, t, 12H (CH ₃)	
8	143.8, s, 188.2, s	7.27, s, 4H	6.74, s, 4H	4.73, q, 2H, 4.52, q, 2H	2.23, m, 8H, 1.40, m, 8H, 1.03, t, 6H, 1.01, t, 6H (CH ₂ CH ₂ CH ₃)	3.44, m, 8H, 3.27, m, 8H (NCH ₂); 1.26, t, 12H, 1.18, t, 12H (CH ₃)	
9	143.4, s, 168.1, s	7.33, s, 4H	6.65, s, 4H	4.91, q, 2H, 4.68, q, 2H	1.79, d, 6H, 1.75, d, 6H (CH ₃)	2.98, d, 12H, 2.80, d, 12H (NCH ₃)	
10	143.1, s, 168.9, s	7.31, s, 4H	6.66, s, 4H	4.91, q, 2H, 4.68, q, 2H	1.77, d, 6H, 1.75, d, 6H (CH ₃)	3.48, m, 8H, 3.26, m, 8H (NCH ₂); 1.25, t, 12H, 1.17, t, 12H (CH ₃)	
11	143.2, s, 168.9, s	7.19, s, 4H	6.67, s, 4H	4.74, t, 2H, 4.51, t, 2H	2.22, m, 8H, 1.40, m, 8H, 1.03, t, 6H, 0.99, t, 6H (CH ₂ CH ₂ CH ₃)	3.47, m, 8H, 3.25, m, 8H (NCH ₂); 1.26, t, 12H, 1.17, t, 12H (CH ₃)	
12	143.4, s, 147.4, s, 148.5, s	7.31, s, 2H, 7.30, s, 2H	6.76, s, 2H, 6.69, s, 2H	4.91, q, 2H, 4.71, q, 2H	1.78, d, 6H, 1.75, d, 6H (CH ₃)	3.46, m, 8H, 3.28, m, 8H (NCH ₂); 1.28, t, 12H, 1.18, t, 12H (CH ₃)	
13	143.1, s, 207.9, s	7.29, s, 4H	6.47, s, 4H	4.82, b.s, 4H	1.75, b.s, 12H (CH ₃)	3.47, m, 8H, 3.29, m, 8H (NCH ₂); 1.22, b.s, 24H (CH ₃)	
14	143.2, s, 208.5, s	7.18, s, 4H	6.47, s, 4H	4.63, t, 2H, 4.47, t, 2H	2.21, b.s, 8H, 1.37, b.s, 8H, 1.00, b.s, 12H (CH ₂ CH ₂ CH ₃)	2.89, d, 12H, 2.76, d, 12H (NCH ₃)	
15	149.2, s	7.13, s, 4H	6.66, s, 4H	5.02, q, 4H	1.71, d, 12H (CH ₃)	5.02, m, 4H (OCH); 1.31, d, 24H (CH ₃)	
16	171.6, s	7.17, s, 4H	6.85, s, 4H	5.06, q, 4H	1.77, d, 12H (CH ₃)	5.06, m, 4H (OCH); 1.31, d, 24H (CH ₃)	
17	144.9, s, 172.6, s	7.32, s, 2H, 7.26, s, 2H	6.65, s, 2H, 6.51, s, 2H	4.89, q, 2H, 4.75, q, 1H, 4.67, q, 1H	1.78, d, 3H, 1.74, d, 6H, 1.70, d, 3H (CH ₃)	3.46, q, 4H, 3.31, q, 4H, 3.26, q, 8H (NCH ₂); 1.23, t, 6H, 1.21, t, 6H, 1.18, t, 12H (CH ₃)	
18	143.7, s, 174.2, s	7.29, s, 2H, 7.22, s, 2H	6.61, s, 2H, 6.47, s, 2H	4.84, q, 2H, 4.70, q, 1H, 4.62, q, 1H	1.74, d, 3H, 1.66, d, 6H, 1.59, d, 3H (CH ₃)	2.93, d, 12H, 2.90, d, 6H, 2.76, d, 6H (NCH ₃)	
19	144.8, s, 172.3, s	7.19, s, 2H, 7.13, s, 2H	6.66, s, 2H, 6.51, s, 2H	4.69, t, 2H, 4.54, t, 1H, 4.47, t, 1H	2.21, m, 8H, 1.61, m, 8H, 1.03, t, 3H, 0.98, t, 3H, 0.89, t, 3H (CH ₂ CH ₂ CH ₃)	3.43, q, 4H, 3.39, q, 4H, 3.27, q, 8H (NCH ₂); 1.26, t, 6H, 1.20, t, 6H, 1.17, t, 12H (CH ₃)	

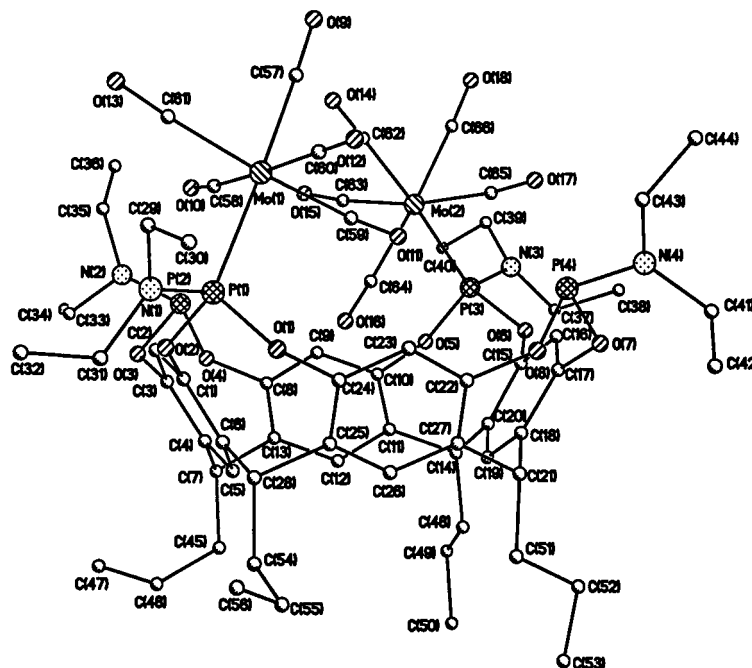
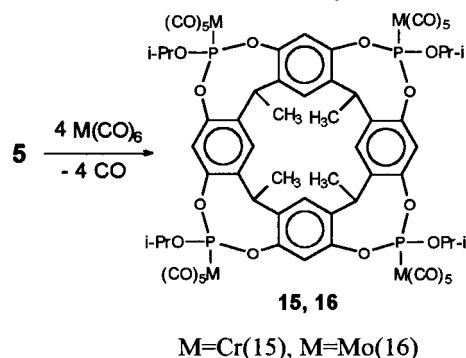


Fig. 1. The general view of phosphocavitand 11.

P(1)⋯O and P(3)⋯O distances up to 1.677 Å, in comparison with the P(2)–O and P(4)–O bonds (1.633(3)–1.654(3) Å). The Mo–P bonds are equal to 2.510 and 2.518(1) Å for P(1) and P(3), respectively. The mutual arrangement of the Mo(CO)₅ moieties in the phosphocavitand is slightly different, which leads to the formation of the unusual CO⋯Ph contact (Fig. 2) with the shortest C(10)⋯C(64) distance equal to 3.200(5) Å and the parallel orientation of the CO and Ph (2.1°). This contact probably results from the iteration of the π-system of Ph and the C=O ligand and leads to the significant elongation of the Mo(2)⋯C(64) distance up to 2.094(4) Å.

2.2. Tetranuclear metallocomplexes of phosphocavitand 5

The reaction of phosphocavitand **5** with Cr and Mo hexacarbonyls resulted in formation of tetranuclear complexes **15** and **16** isolated with yields of 46–55%.



We could not obtain analogous complexes with tungsten and manganese, because the macrocyclic system of phosphocavitand **5** is subjected to decomposition under ultraviolet irradiation to a greater extent than amidophosphitocavitands **1–4**.

The compositions and structures of complexes **15** and **16** were supported by the elemental analysis and NMR spectroscopy (Table 1). The ³¹P-NMR spectra of **15** and **16** at 25°C exhibit a singlet at 150 ppm; their ¹H-NMR spectra have a set of signals from all groups of protons. These facts suggest the chemical and structural identity of all four phosphocine cycles in the molecules of cavitands **15** and **16** [4]. However, the study of complex **16** by means of ³¹P-NMR spectroscopy at lower temperature shows that the chemically equivalent phosphorus nuclei became magnetically inequivalent even at 0°C, and four singlets with similar chemical shifts and equal integral intensities (δ_P 149.4, 149.5, 155.0, and 155.8 ppm) are observed at –60°C. These data indicate that similar to the rhodium complexes of phosphocavitands [8], the tetranuclear complexes of phosphocavitands **15** and **16** are conformationally labile systems.

2.3. Mononuclear metallocomplexes of amidophosphitocavitands 1, 2, and 4

In order to study the reactivity of the synthesized metallocomplexes, we attempted to execute a further ligand exchange of these compounds with P(III)-phosphocavitands. It was intended to elucidate the possibil-

ity for the displacement of the carbonyl ligands in the metallo-pentacarbonyl fragments of the complexes by the phosphoric ones. The reactions were conducted in dioxane at 95–105°C. It was shown that no ligand exchange took place in the tetranuclear complexes of phosphocavitands **15** and **16**, but their uncontrolled decomposition was observed.

Interesting results were obtained in the study of binuclear complexes of amidophosphitocavitands. When the equimolar amounts of complex **10** and the corresponding P(III)-phosphocavitand **2** were used, the signal of the coordinated phosphorus atom in the ^{31}P -NMR spectrum was shifted downfield, as compared to that in the binuclear complex **10** ($\Delta\delta \sim -6$ ppm). In addition, the integral intensity ratio between the signals of coordinated and uncoordinated phosphorus atoms changed from 1:1 to 1:3 in the resulting compounds. The order of reagent mixing did not affect the ^{31}P -NMR spectra.

Table 2
Selected bond lengths (Å) and bond angles (°) for **11**

<i>Bond lengths</i>			
Mo(1)–P(1)	2.518(1)	P(1)–O(1)	1.646(2)
Mo(2)–P(3)	2.510(1)	P(1)–O(2)	1.633(2)
Mo(1)–C(57)	2.012(4)	P(1)–N(1)	1.642(3)
Mo(1)–C(58)	2.043(4)	P(2)–O(3)	1.671(3)
Mo(1)–C(59)	2.056(4)	P(2)–O(4)	1.673(2)
Mo(1)–C(60)	2.060(4)	P(2)–N(2)	1.648(3)
Mo(1)–C(61)	2.041(4)	P(3)–O(5)	1.654(2)
Mo(2)–C(62)	2.019(4)	P(3)–O(6)	1.628(3)
Mo(2)–C(63)	2.036(4)	P(3)–N(3)	1.651(3)
Mo(2)–C(64)	2.094(4)	P(4)–O(7)	1.662(3)
Mo(2)–C(65)	2.054(4)	P(4)–O(8)	1.677(3)
Mo(2)–C(66)	2.021(4)	P(4)–N(4)	1.649(3)
<i>Bond angles</i>			
C(57)–Mo(1)–C(61)	85.9(2)	C(65)–Mo(2)–C(64)	92.9(2)
C(57)–Mo(1)–C(58)	87.1(1)	C(62)–Mo(2)–P(3)	176.5(1)
C(61)–Mo(1)–C(58)	87.3(1)	C(66)–Mo(2)–P(3)	97.4(1)
C(57)–Mo(1)–C(59)	87.9(2)	C(63)–Mo(2)–P(3)	92.7(1)
C(61)–Mo(1)–C(59)	171.7(1)	C(65)–Mo(2)–P(3)	92.9(1)
C(58)–Mo(1)–C(59)	87.0(1)	C(64)–Mo(2)–P(3)	88.8(1)
C(57)–Mo(1)–C(60)	88.7(1)	O(2)–P(1)–N(1)	95.8(1)
C(61)–Mo(1)–C(60)	94.4(2)	O(2)–P(1)–O(1)	103.3(1)
C(58)–Mo(1)–C(60)	175.4(1)	N(1)–P(1)–O(1)	100.4(1)
C(59)–Mo(1)–C(60)	90.9(2)	O(2)–P(1)–Mo(1)	119.78(9)
C(57)–Mo(1)–P(1)	174.5(1)	N(1)–P(1)–Mo(1)	118.3(10)
C(61)–Mo(1)–P(1)	90.7(1)	O(1)–P(1)–Mo(1)	115.80(8)
C(58)–Mo(1)–P(1)	97.1(1)	N(2)–P(2)–O(3)	99.1(1)
C(59)–Mo(1)–P(1)	95.9(1)	N(2)–P(2)–O(4)	98.7(1)
C(60)–Mo(1)–P(1)	87.2(1)	O(3)–P(2)–O(4)	98.7(1)
C(62)–Mo(2)–C(66)	86.1(1)	O(6)–P(3)–N(3)	96.3(1)
C(62)–Mo(2)–C(63)	86.8(2)	O(6)–P(3)–O(5)	102.6(1)
C(66)–Mo(2)–C(63)	87.8(2)	N(3)–P(3)–O(5)	99.7(1)
C(62)–Mo(2)–C(65)	88.1(2)	O(6)–P(3)–Mo(2)	117.28(9)
C(66)–Mo(2)–C(65)	84.8(2)	N(3)–P(3)–Mo(2)	121.5(1)
C(63)–Mo(2)–C(65)	171.3(1)	O(5)–P(3)–Mo(2)	115.8(1)
C(62)–Mo(2)–C(64)	87.8(1)	N(4)–P(4)–O(7)	97.0(1)
C(66)–Mo(2)–C(64)	173.6(1)	N(4)–P(4)–O(8)	99.9(1)
C(63)–Mo(2)–C(64)	93.8(2)	O(7)–P(4)–O(8)	99.8(1)

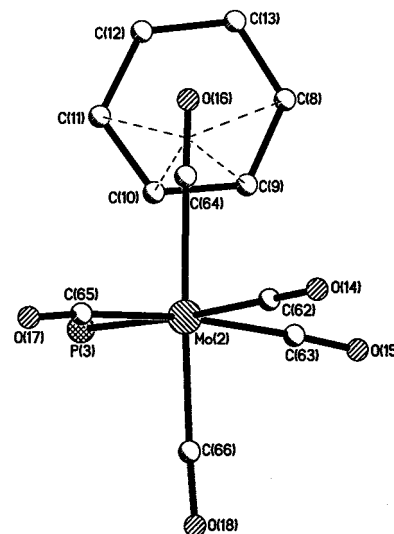
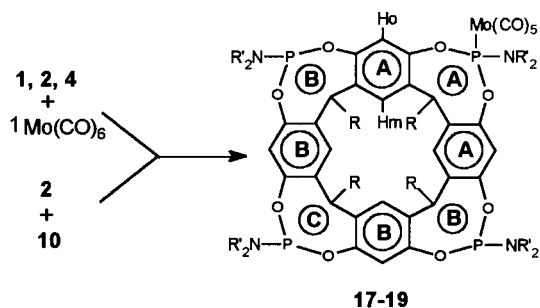


Fig. 2. The scheme illustrating the formation of the intramolecular CO...Ph contact in **11**.

The reaction product was isolated; its composition and structure were supported by the elemental analysis as well as by ^1H - and ^{31}P -NMR spectroscopy. The obtained data imply that the resulting compound **17** includes only one metal-containing fragment. In the ^{31}P -NMR spectra of the mononuclear complex **17**, two singlets were observed in the temperature range from -80 to $+40^\circ\text{C}$: a downfield signal (δ 172.6 ppm) from the coordinated phosphorus atom and an upfield averaged signal (δ 144.9 ppm) from three uncoordinated phosphorus atoms (Table 1). Doubling of the signals from the *m*- and *o*-protons of the aromatic nuclei and trebling of the signals from the other groups of protons were observed in its ^1H -NMR spectra, which was due to the nonequivalence of protons from benzene cycles **A** and **B** and phosphocine cycles **A**, **B**, and **C** (Table 1). The integral signal intensities corresponded to their theoretical values.



R=Me, R'=Et(**17**); R=Me, R'=Me(**18**); R=Pr, R'=Et(**19**)

Thus, a redistribution of metal-containing fragments between binuclear complex **10** and unfunctionalized phosphocavitand **2** with the formation of mononuclear complex **17** proceeds in this case.

In order to confirm the obtained results, we performed the counter-synthesis of **17** from the equimolar amounts of amidophosphitocavitand **2** and $\text{Mo}(\text{CO})_6$. The reaction was conducted in dioxane at 95–105°C. The physicochemical parameters of the isolated product were identical to those of complex **17**. Mononuclear metal complexes **18** and **19** were also synthesized by this method.

3. Experimental

$^1\text{H-NMR}$ spectra were recorded on a Bruker WM-200 spectrometer with TMS as an internal standard. $^{31}\text{P-NMR}$ spectra (at 32.4 MHz, 85% H_3PO_4 as an external standard) were recorded on a Bruker WP-80 spectrometer.

Crystal data for **11**· $\text{C}_4\text{H}_8\text{O}_2$: $\text{C}_{75}\text{H}_{68}\text{Mo}_2\text{N}_4\text{O}_{20}\text{P}_4$, $M = 1661.09$, monoclinic, space group $P2_1/c$, $a = 25.183(7)$, $b = 13.544(4)$, $c = 23.409(8)$ Å, $\beta = 103.89(2)^\circ$, $V = 7751(4)$ Å³, $\rho_{\text{calc}} = 1.423\text{g cm}^{-3}$, $\mu = 4.79\text{ cm}^{-1}$, for $Z = 4$. Intensities of 21 240 reflections ($R_{\text{int}} = 0.0419$) were measured at 213 K with a Syntex $P2_1$ automated diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å, $\theta/2\theta$ scan, $\theta \leq 30^\circ$). The structure was solved by the direct method and refined by full-matrix least-squares against F^2 in the anisotropic (H-atoms isotropic) approximation. All hydrogen atoms, with the exception of the dioxane solvate molecule, were located from the electron density difference synthesis and were included in the refinement in the isotropic approximation. The analysis of the difference in electron densities has revealed that both oxygens in the dioxane molecule are disordered by two positions, which were refined with the occupancies of 0.5. The refinement for **11** converged to $wR_2 = 0.1335$ and $\text{GOF} = 0.853$ for 20 733 independent reflections ($R_1 = 0.0520$ was calculated against F for the 11 753 observed reflections with $I > 2\sigma(I)$). The number of the refined parameters was 1120. All calculations were performed using SHELXTL PLUS 5.1 on an IBM PC/AT.

All syntheses were performed in dry solvents under argon. P(III)-phosphocavitands **1**, **2**, **5** and **3**, **4** were synthesized in accordance with the methods described previously (Refs. [15] and [7], respectively).

3.1. Binuclear metal complexes of amidophosphitocavitands

3.1.1. Complexes **6–11**

A solution of the corresponding cavitand and $\text{M}(\text{CO})_6$ in 0.8 ml of dioxane was exposed at 100–105°C for 18 h ($M = \text{Cr}$) or 4 h ($M = \text{Mo}$). The formed precipitate was filtered; the solvent was partially evaporated; the precipitated product was filtered off, washed with cold dioxane, and dried at 40–50°C under vacuum.

3.1.1.1. Complex 6. This complex was obtained by the reaction of cavitand **1** (0.0585 g, 0.699 mmol) with $\text{Cr}(\text{CO})_6$ (0.0615 g, 0.279 mmol). Yield: 0.0631 g (74%). M.p. 182–185°C (dec.). Anal. Found: C, 49.02; H, 4.13; N, 4.52; P, 10.31. Calc. for $\text{C}_{50}\text{H}_{48}\text{Cr}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 49.19; H, 3.96; N, 4.59; P, 10.15%.

3.1.1.2. Complex 7. This complex was obtained by the reaction of cavitand **2** (0.0556 g, 0.0586 mmol) with $\text{Cr}(\text{CO})_6$ (0.0516 g, 0.234 mmol). Yield: 0.0617 g (79%). M.p. 169–172°C (dec.). Anal. Found: C, 52.13; H, 4.82; N, 4.09; P, 9.21. Calc. for $\text{C}_{58}\text{H}_{64}\text{Cr}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 52.26; H, 4.84; N, 4.20; P, 9.30%.

3.1.1.3. Complex 8. This complex was obtained by the reaction of cavitand **4** (0.0716 g, 0.0675 mmol) with $\text{Cr}(\text{CO})_6$ (0.0594 g, 0.27 mmol). Yield: 0.0579 g (59%). M.p. 156–160°C. Anal. Found: C, 55.36; H, 5.49; N, 3.58; P, 8.72. Calc. for $\text{C}_{66}\text{H}_{80}\text{Cr}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 54.85; H, 5.58; N, 3.88; P, 8.57%.

3.1.1.4. Complex 9. This complex was obtained by the reaction of cavitand **1** (0.056 g, 0.067 mmol) with $\text{Mo}(\text{CO})_6$ (0.0707 g, 0.268 mmol). Yield: 0.0591 g (56%). M.p. 139–140°C. Anal. Found: C, 45.43; H, 3.98; N, 4.05; P, 9.27. Calc. for $\text{C}_{50}\text{H}_{48}\text{Mo}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 45.89; H, 3.69; N, 4.28; P, 9.47%.

3.1.1.5. Complex 10. This complex was obtained by the reaction of cavitand **2** (0.1031 g, 0.109 mmol) with $\text{Mo}(\text{CO})_6$ (0.1148 g, 0.435 mmol). Yield: 0.1214 g (79%). M.p. 129–130°C. Anal. Found: C, 48.82; H, 4.67; N, 3.63; P, 8.53. Calc. for $\text{C}_{58}\text{H}_{64}\text{Mo}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 49.03; H, 4.54; N, 3.94; P, 8.72%.

3.1.1.6. Complex 11. This complex was obtained by the reaction of cavitand **4** (0.0606 g, 0.0572 mmol) with $\text{Mo}(\text{CO})_6$ (0.0604 g, 0.2288 mmol). Yield: 0.0526 g (60%). M.p. 148–150°C. Anal. Found: C, 51.56; H, 5.29; N, 3.38; P, 7.82. Calc. for $\text{C}_{66}\text{H}_{80}\text{Mo}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 51.71; H, 5.26; N, 3.65; P, 8.08%.

3.1.2. Complex **12**

A suspension of cavitand **2** (0.043 g, 0.045 mmol) and $\text{W}(\text{CO})_6$ (0.0638 g, 0.18 mmol) in 1.5 ml of dioxane was exposed to UV radiation at 25°C for 12 h. The solvent was partially evaporated; the formed precipitate was filtered off, washed with cold dioxane, and dried at 40–50°C under vacuum. Yield: 0.0525 g, (73%). M.p. 239–242°C (dec.). Anal. Found: C, 43.81; H, 3.96; N, 3.48; P, 7.83. Calc. for $\text{C}_{58}\text{H}_{64}\text{W}_2\text{N}_4\text{O}_{18}\text{P}_4$: C, 43.63; H, 4.04; N, 3.51; P, 7.76%.

3.1.3. Complexes **13** and **14**

A suspension of the corresponding cavitand and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ in 1.5 ml of dioxane was exposed to UV

radiation at 25°C for 15 h. The solvent was partially evaporated; the formed precipitate was filtered off, washed with cold hexane, and dried at 40–50°C under vacuum.

3.1.3.1. Complex 13. This complex was obtained by the reaction of cavitand **2** (0.0588 g, 0.062 mmol) with $C_5H_5Mn(CO)_3$ (0.0506 g, 0.248 mmol). Yield: 0.0507 g, (63%). M.p. 201–204°C (dec.). Anal. Found: C, 57.48; H, 5.69; N, 4.41; P, 9.61. Calc. for $C_{62}H_{74}Mn_2N_4O_{12}P_4$: C, 57.23; H, 5.73; N, 4.30; P, 9.52%.

3.1.3.2. Complex 14. This complex was obtained by the reaction of cavitand **3** (0.0673 g, 0.071 mmol) with $C_5H_5Mn(CO)_3$ (0.0579 g, 0.284 mmol). Yield: 0.0618 g (67%). M.p. 195–198°C (dec.). Anal. Found: C, 57.52; H, 5.70; N, 4.38; P, 9.59. Calc. for $C_{62}H_{74}Mn_2N_4O_{12}P_4$: C, 57.23; H, 5.73; N, 4.30; P, 9.52%.

3.2. Tetranuclear metallocomplexes of phosphocavitand **5**

A solution of cavitand **5** and $M(CO)_6$ in 0.8 ml of dioxane was exposed at 100–105°C for 4 h. The formed precipitate was filtered off, washed with hexane, and dried at 40–50°C under vacuum.

3.2.1. Complex 15

This complex was obtained by the reaction of cavitand **5** (0.0557 g, 0.0621 mmol) with $Cr(CO)_6$ (0.0546 g, 0.248 mmol). Yield: 0.0564 g (55%). M.p. 162–164°C (dec.). Anal. Found: C, 46.38; H, 3.03; P, 7.61. Calc. for $C_{64}H_{52}Cr_4O_{32}P_4$: C, 46.17; H, 3.15; P, 7.44%.

3.2.2. Complex 16

This complex was obtained by the reaction of cavitand **5** (0.0544 g, 0.0607 mmol) with $Mo(CO)_6$ (0.0641 g, 0.243 mmol). Yield: 0.0512 g (46%). M.p. 136–139°C (dec.). Anal. Found: C, 41.69; H, 2.85; P, 6.95. Calc. for $C_{64}H_{52}Mo_4O_{32}P_4$: C, 41.76; H, 2.85; P, 6.73%.

3.3. Mononuclear metallocomplexes of amidophosphitocavitands

3.3.1. Complex 17

Method A. A solution of the binuclear complex **10** (0.1138 g, 0.087 mmol) and cavitand **2** (0.0825 g, 0.087 mmol) in 1 ml of dioxane was exposed at 95–100°C for 6 h. The precipitate was filtered off. The solvent was partially evaporated. The formed precipitate was filtered off and dried at 40–50°C under vacuum. Yield: 0.0577 g (56%). M.p. 149–153°C (dec.). Anal. Found: C, 54.01; H, 5.35; N, 4.80; P, 10.40. Calc. for $C_{53}H_{64}MoN_4O_{13}P_4$: C, 53.72; H, 5.44; N, 4.73; P, 10.46%.

3.3.2. Complexes 17–19

Method B. A solution of the corresponding cavitand and $Mo(CO)_6$ in 0.8 ml of dioxane was exposed at 100–105°C for 4 h. The solvent was partially evaporated. The precipitated product was filtered off and dried at 40–50°C under vacuum.

3.3.2.1. Complex 17. This complex was obtained by the reaction of cavitand **2** (0.0634 g, 0.067 mmol) with $Mo(CO)_6$ (0.0176 g, 0.067 mmol). Yield: 0.0492 (62%). M.p. 149–153°C (dec.). Anal. Found: C, 53.90; H, 5.38; N, 4.75; P, 10.42. Calc. for $C_{53}H_{64}MoN_4O_{13}P_4$: C, 53.72; H, 5.44; N, 4.73; P, 10.46%.

3.3.2.2. Complex 18. This complex was obtained by the reaction of cavitand **1** (0.0572 g, 0.0684 mmol) with $Mo(CO)_6$ (0.0181 g, 0.0684 mmol). Yield: 0.0535 g (73%). M.p. 145–149°C (dec.). Anal. Found: C, 50.45; H, 4.89; N, 5.34; P, 11.49. Calc. for $C_{45}H_{48}MoN_4O_{13}P_4$: C, 50.34; H, 4.51; N, 5.23; P, 11.56%.

3.3.2.3. Complex 19. This complex was obtained by the reaction of cavitand **4** (0.0634 g, 0.0597 mmol) with $Mo(CO)_6$ (0.0158 g, 0.0597 mmol). Yield: 0.0634 g (82%). M.p. 142–144°C (dec.). Anal. Found: C, 56.61; H, 6.33; N, 4.29; P, 10.07. Calc. for $C_{61}H_{80}MoN_4O_{13}P_4$: C, 56.48; H, 6.22; N, 4.32; P, 9.55%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147210 for compound **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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