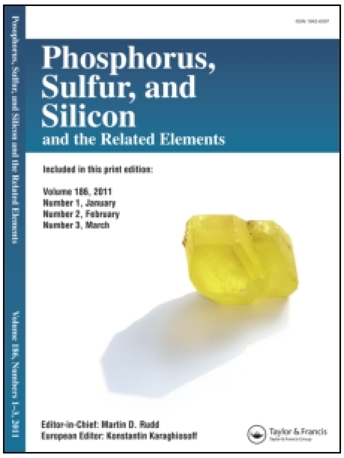

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COMPLEXES OF PHOSPHOCAVITANDS WITH GROUP VI METALS

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COMPLEXES OF PHOSPHOCAVITANDS WITH GROUP VI METALS

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The first complexes of amidophosphito- and phosphitocavitands with the group VI transition metal hexacarbonyls have been obtained. It was shown that the liganding ability of P(III)-phosphocavitands depended on the nature of exocyclic substituents at the phosphorus atoms.

Keywords: phosphocavitands; group VI transition metals; complexation

INTRODUCTION

The previous study of liganding ability of P(III)-phosphocavitands showed that the interaction between phenylphosphonitocavitands and Ag, Au and Cu halides resulted in formation of symmetric tetranuclear complexes, where each phosphorus atom was bound to the metal atom[1–3]. Religanding (ligand exchange) of *acac*Rh(CO)$_2$ with amidophosphito- and phosphitocavitands also proceeds with formation of tetrameric complexes, but in this case the molecular skeleton of cavitand is distorted and the macrocyclic matrix becomes unsymmetrical, which can be due to both the impact of metal-containing fragments on the macrocycle and the effect of substituents at the phosphorus atoms on the process. In order to elucidate the complexation peculiarities of P(III)-phosphocavitands and to expand the new class of metallocomplexes, we studied the reaction of amidophos-

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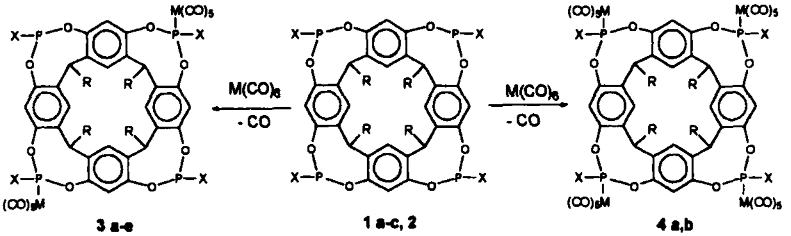
phito- and phosphitocavitands with hexacarbonyls of the group VI transition metals (Cr, Mo, W). The first results of this study are presented below.

RESULTS AND DISCUSSION

The reactions of cavitands **1** and **2** with Cr, Mo, and W hexacarbonyls run in dioxane. It should be noted that the religanding of $Cr(CO)_6$ and $Mo(CO)_6$ proceeds at both thermal (95–105°C) and ultraviolet activation (at 25°C) of metal hexacarbonyl, while the reaction of cavitand **1b** with $W(CO)_6$ proceeds only at the photochemical activation.

In spite of similar reaction conditions, the complexation products of amidophosphito- and phosphitocavitands differ in the number of functionalized phosphorus centres.



1a, 3a: R=Me, X=NMe$_2$; 1b, 3b,c,e: R=Me, X=NEt$_2$; 1c, 3d: R=Pr, X=NEt$_2$; 2, 4a,b: R=Me, X=OPr-i

M=Cr (3a, 3b, 4a); M=Mo (3c, 3d, 4b); M=W (3e)

So, the interaction between amidophosphocavitands **1a-c** and metal hexacarbonyls results in formation of binuclear complexes **3a-e**, even when the twofold excess of $M(CO)_6$ and durable heating or irradiation are used. Using NMR spectroscopy, we showed that the cavitand skeleton remains unchanged and the phosphorus atoms, arranged along a diagonal of molecular cup, coordinate with the metal (Table I). The ^{31}P NMR spectra of complexes **3a-d** exhibit two singlets with equal intensities corresponding to the coordinated (downfield signal) and non-coordinated (upfield signal) phosphorus atoms. In the ^{1}H NMR spectra, the protons of all four benzene nuclei are equivalent and the protons of phosphocin cycles are nonequivalent, which is manifested in the doubling of protons of amide groups at the phosphorus atoms, radicals (R), and internuclear bridges in the calixarene matrix. This view of ^{1}H NMR spectra is possible only due to the diagonal arrangement of metal-containing fragments.

At the same time, the religanding of Cr and Mo hexacarbonyls with phosphocavitand **2** yields tetranuclear complexes **4a,b**, whose composition and structure were supported by the elemental analysis and NMR spectroscopy. The ^{31}P NMR spectra of these compounds display a singlet at 25°C and the ^{1}H NMR spectra – a set of signals from all proton groups (Table I). This attests the chemical and structural identity of all four phosphocin cycles in the molecules of cavitand **4**. However, the study of complex **4a** using the ^{31}P NMR spectroscopy at low temperatures showed that the phosphorus nuclei in the molecule of cavitand **4a** became magnetically nonequivalent even at 0°C, but four singlets with similar chemical shifts and equal integral intensities (δ_P 149.4, 149.5, 155.0, and 155.8) were observed at –60°C. These data indicate that, similarly to the rhodium complexes of phosphocavitands[5], the tetranuclear complexes of phosphocavitands **4a,b** are conformationally labile systems.

EXPERIMENTAL

All syntheses were performed in dry deoxygenated solvents under argon. ^{1}H NMR spectra were recorded on a Bruker WM-200 spectrometer with TMS as an internal standard. ^{31}P NMR spectra (at 32.4 MHz, 85% H_3PO_4 as an external standard) were recorded on a Bruker WP-80 spectrometer.

Complexes 3a-d

A solution of the corresponding cavitand 1 (0.065 mmol) and $M(CO)_6$ (0.261 mmol) in dioxane (0.8 ml) was kept at 100–105°C for 18 h (M = Cr) and 4 h (M = Mo). The precipitate was filtered off; the solvent was evaporated in part; the formed precipitate was filtered, washed with cold dioxane, and dried at 40–50°C *in vacuo*.

Complex 3a (stereoisomer)

Was obtained from cavitand 1a. Yield 74%; m.p. 182-185°C (decomp.). $C_{50}H_{48}Cr_2N_4O_{18}P_4$, *M* 1220.83 Calcd. C 49.19, H 3.96, N 4.59, P 10.15. Found C 49.02, H 4.13, N 4.52, P 10.31.

TABLE I ^{1}H and ^{31}P NMR spectral parameters of complexes **3, 4** ($CDCl_3$)

δ ^{31}*P ppm.*	δ ^{1}*H, ppm*				
	Hm	*Ho*	*CH*	*R*	*X*
1.9, 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)
4.2, 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, 1.1 12H (CH_3)
3.1, 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, 1.1 12H (CH_3)
3.2, 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 ($CH_2CH_2CH_3$)	3.47, m, 8H, 3.25, m, 8H (NCH_2); 1.26, t, 12H, 1.1 12H (CH_3)
3.4, s 147.4, s 3.5, 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, 1.1 12H (CH_3)
1.6, s	7.17, s. 4H	6.85, s, 4H	5.06, q, 4H	1.77, d, 12H (CH_3)	5.06, q, 4H (OCH) 1.31, (CH_3)
9.2, s	7.13, s, 4H	6.66, s, 4H	5.02, q, 4H	1.71, d, 12H (CH_3)	5.02, q, 4H (OCH) 1.31, (CH_3)

Complex 3b (stereoisomer)

Was obtained from cavitand 1b. Yield 78%; m.p. 169-172°C (decomp.). $C_{58}H_{64}Cr_2N_4O_{18}P_4$, *M* 1333.05. Calcd. C 52.26, H 4.84, N 4.20, P 9.30. Found C 52.13, H 4.82, N 4.09, P 9.21.

Complex 3c (stereoisomer)

Was obtained from cavitand 1b. Yield 79%; m.p. 129-130°C (decomp.). $C_{58}H_{64}Mo_2N_4O_{18}P_4$, *M* 1420.94. Calcd. C 49.03, H 4.54, N 3.94, P 8.72. Found C 48.82, H 4.67, N 3.63, P 8.53.

Complex 3d (stereoisomer)

Was obtained from cavitand 1c. Yield 60%; m.p. 148-150°C. $C_{66}H_{80}Mo_2N_4O_{18}P_4$, *M* 1533.16. Calcd. C 51.71, H 5.26, N 3.65, P 8.08. Found C 51.56, H 5.29, N 3.38, P 7.82.

Complex 3e

A suspension of cavitand 1b (0.045 mmol) and $W(CO)_6$ (0.18 mmol) in dioxane (1.5 ml) was UV irradiated at 25°C for 12 h. The solvent was evaporated in part; the formed precipitate was filtered, washed with cold dioxane, and dried at 40–50°C *in vacuo*. Yield 73%; m.p. 239–242°C (decomp.). $C_{58}H_{64}W_2N_4O_{18}P_4$, *M*1596.76. Calcd. C 43.63, H 4.04, N 3.51, P 7.76. Found C 43.81, H 3.96, N 3.48, P 7.83.

Complexes 4a, b

A solution of cavitand 2 (0.065 mmol) and the corresponding $M(CO)_6$ (0.26 mmol) in dioxane (0.8 ml) was kept at 100–105°C for 19 h (M = Cr) and 4 h (M = Mo). The precipitate formed was filtered, washed with cold dioxane, and dried at 40–50°C *in vacuo*.

Complex 4a

Yield 54%; m.p. 162–164°C (decomp.). $C_{64}H_{52}Cr_4O_{32}P_4$, M 1664.97. Calcd. C 46.17, H 3.15, P 7.44. Found C 46.38, H 3.03, P 7.61.

Complex 4b

Yield 46%; m.p. 136–139°C (decomp.). $C_{64}H_{52}Mo_4O_{32}P_4$, M 1840.75. Calcd. C 41.76, H 2.85, P 6.73. Found C 41.69, H 2.85, P 6.95.

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