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LETTERS TO THE EDITOR

Bimetallic Complexes of Phosphoramidite Cavitands

V. I. Maslennikova, S. E. Goryukhina, O. S. Serkova, L. K. Vasyanina, and E. E. Nifant'ev

Moscow State Pedagogical University, Moscow, Russia

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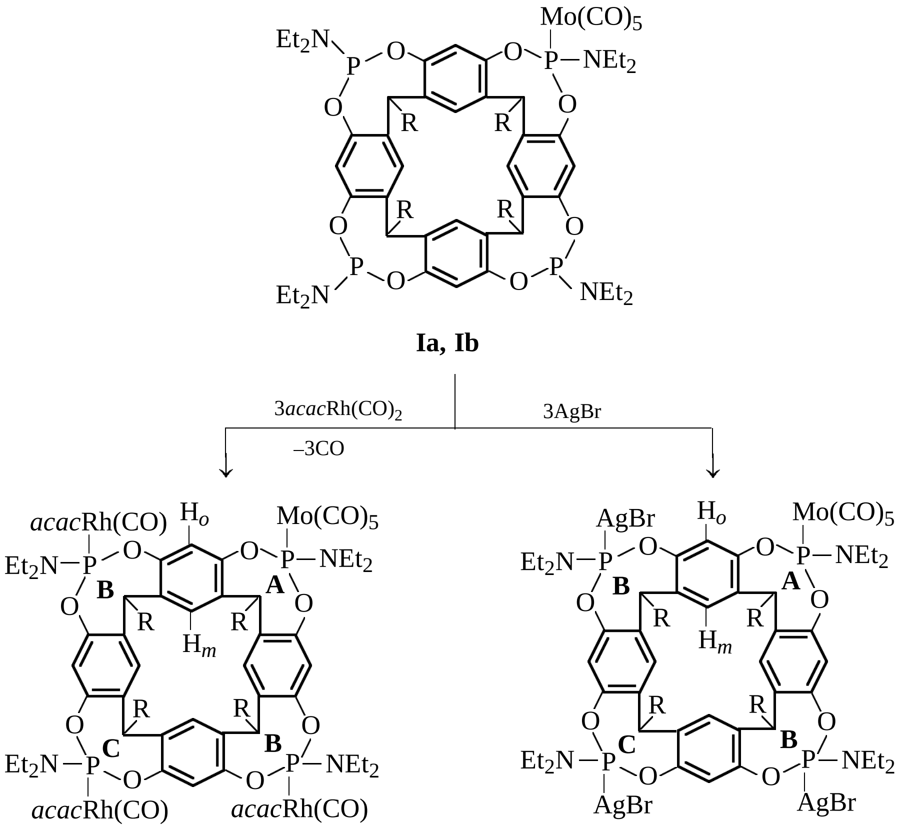
Phosphoramidite cavitands exhibit a high ligating ability which arises from the presence of unshared electron pairs on phosphorus. On the basis of these compounds, a series of complex coordination systems containing up to four identical metal fragments specifically arranged in relation to each other and the cavity have been obtained [1–5]. In this contribution we report the synthesis of complexes of phosphoramidite cavitands containing different metal fragments in one molecule. Mononuclear molybdenum complexes **I** we obtained previously were used as ligands and *acac*Rh$(CO)_2$ or AgBr as complex-forming agents.

The reactions were carried out at room temperature and a 1 : 3 ratio of the ligand to complex-forming agent. As a result, bimetallic phosphocavitand derivatives **II** and **III** were obtained.



Ia, Ib

IIa, IIb

IIIa, IIIb

R = Me (**Ia, IIa, IIIa**), Pr (**Ib, IIb, IIIb**).

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The composition and structure of complexes **II** and **III** were established by means of elemental analysis, mass spectrometry, and NMR spectrometry. The ^{31}P NMR spectra of complexes **II** show a singlet of the phosphorus atom coordinated with molybdenum, and two doublet signals with coupling constants characteristic of phosphorus coordinated with rhodium. The integral intensity ratio of the doublets is 2 : 1, which is caused by the nonequivalence of phosphocine rings **B** and **C**. The ^{31}P NMR spectra of compounds **III** contain a signal of phosphorus bound with molybdenum, as well as two broadened doublets of phosphorus coordinated with silver, with equal intensities and close chemical shifts and $^1J_{PAg}$ coupling constants. The phosphorus signals of phosphocine rings **B** and **C** are overlapping, and the presence of two doublets is explained by the presence of two magnetic isotopes of silver in close concentrations. In the ^1H NMR spectra of compounds **II** and **III** display signals of all groups of protons of the macrocyclic ligand with slightly altered chemical shifts. The integral intensity ratio of the signals agrees with theory.

Complex IIa. A solution of mononuclear complex **Ia** and 0.234 mmol of *acac*Rh(CO)$_2$ in 1 ml of chloroform was kept for 15 h at 20°C. The solvent was partially removed by distillation, and the residue was treated with hexane. The resulting precipitate was filtered off and dried in a vacuum (1 mm) at 40–50°C. Yield 83%, mp 167–169°C (decomp.). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.14 t (6H, NCH_2CH_3), 1.17 t (18H, NCH_2CH_3), 1.73 d (3H, CH_3, $^3J_{HH}$ 7.2 Hz), 1.78 d (9H, $CHCH_3$, $^3J_{HH}$ 7.3 Hz), 2.03 s (12H, *acac* CH_3), 2.06 s (6H, *acac* CH_3), 3.38 m (4H, NCH_2, $^3J_{PH}$ 12.4 Hz), 3.67 m (8H, NCH_2, $^3J_{PH}$ 14.1 Hz), 3.81 m (4H, NCH_2, $^3J_{PH}$ 14.1 Hz), 4.84–4.91 m (4H, $CHCH_3$), 5.16 s (2H, *acac* CH), 5.50 s (1H, *acac* CH), 6.86 s (2H, H_o), 7.07 s (2H, H_o), 7.18 s (2H, H_m), 7.20 s (2H, H_m). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 164.83 s (1P, P–Mo), 133.7 d (2P, P–Ph, $^1J_{PRh}$ 270.7 Hz), 126.7 d (1P, P–Rh, $^1J_{PRh}$ 251.6 Hz). Found, %: C 45.46, H 4.54, N 2.99, P 6.62. $C_{71}H_{85}MoN_4 \cdot O_{22}P_4Rh_3$. Calculated, %: C 45.64; H 4.59; N 3.27; P 6.38.

Complex IIIb. A solution of 0.0425 mmol of mononuclear complex **Ia** in 0.8 ml of methylene chloride was added to 0.13 mmol of AgBr, and the resulting mixture was kept for 10 days at 20°C. The solvent was removed by distillation, and the residue was treated with dioxane. The resulting precipitate was filtered off, the filtrate was evaporated, and the residue was dried in a vacuum (1 mm) at 20°C. Yield 56%, mp 201–204°C (decomp). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 t (12H, $CH_2CH_2CH_3$), 1.17 t (6H, NCH_2CH_3), 1.25 t (18H, NCH_2CH_3), 1.39 m (8H, $CH_2CH_2CH_3$), 2.22 m (8H, $CH_2CH_2CH_3$), 3.27 m (4H, NCH_2, J_{PH} 10.2 Hz), 3.40 m (12H, NCH_2, $^3J_{PH}$ 13.2 Hz), 4.50 t (1H, CHPr), 4.58 t (2H, CHPr), 4.72 t (1H, CHPr), 6.65 s (2H, H_o), 6.75 s (2H, H_o), 7.18 s (2H, H_m), 7.20 s (2H, H_m). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 168.31 s (1P, PMo), 135.43 d, 133.86 d (3P, PAg, $^1J_{PAg}$ 724.1 Hz, $^1J_{PAg}$ 727.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 1927.3 (100) M^+ $[C_{61}H_{80}Ag_3Br_3MoN_4O_{13}P_4]^+ \cdot NaCl$.

All experiments were carried out in anhydrous solvents under argon. The ^1H NMR spectra were obtained on a WM-200 spectrometer against internal TMS. The ^{31}P NMR spectra were measured on a WP-80 instrument against external 85% phosphoric acid. The mass spectra were obtained on a Kratos PC-Kompact MALDI spectrometer.

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