Carbamoylmethylphosphine oxide derivatives of adamantane as extracting agents of americium and europium

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Adamantane di-1,3-carbamoylmethylphosphine oxide derivatives were synthesized. Their efficiency in extraction of americium(III) and europium(III) from nitric acid solutions was shown.

Key words: adamantane carbamoylmethylphosphine oxide derivatives, americium, europium, extraction.

Preparation of efficient and selective ligands for extraction of radionuclides is of considerable interest due to intensive development of nuclear power engineering and necessity of processing spent nuclear fuel. Mono- and bidentate neutral organophosphorus compounds are among the most efficient extracting agents for actinides and lanthanides and are used presently for processing the spent nuclear fuel. For instance, *N,N*-di-*iso*-butyl(carbamoylmethyl)octylphenylphosphine oxide **1a** is used[1] as an extracting agent for isolation of highly toxic transplutonium actinides from high-acidity saline solutions in the known TRUEX process (transuranium extraction). Compound **1a** belongs to the class of carbamoylmethylphosphine oxides (CMPO), whose representatives (**1—5**) are considered in the present work.

Since several bidentate CMPO molecules coordinate with one trivalent actinide cation upon complex formation,[1a] it seems reasonable to synthesize such ligands in which several CMPO groups are pre-organized on the common molecular platform. Indeed, the introduction of four CMPO groups to the upper rim of calix[4]arenes produced[2] ligands **2a**, which are much more efficient (by at least 1000 times) than ligand **1a**. Poly-CMPO derivatives on the triphenylmethane molecular platform **2b** also exhibit high ionophoric ability toward actinides,[3] although the extraction ability decreases considerably, unlike that of compounds **2a**, with an increase in the concentration of HNO_3.

We have recently shown[4] that *p*-adamantylcalix[4]arenes with the CMPO groups in the adamantane moieties (**3a—c**) extract americium(III) and europium(III) to dichloromethane in 3 *M* HNO_3 solutions much more efficiently that their monomeric analogs *N*-(1-adamantyl)- and *N*-(1-adamantylmethyl)carbamoylmethyldiphenylphosphine oxides (**4a,b**) and model *N,N*-dibutyl(carbamoylmethyl)diphenylphosphine oxide (**1b**). Ligand **3b** demonstrated better extraction properties; the binding center in this ligand is remote from adamantane by one C atom. Shortening or elongation of the linker worsens the extraction properties (compounds **3a** and **3c**). Probably, the direct attachment of the CMPO groups to the bulky adamantane moiety in molecule **3a** impedes cation coordination, and the removal of them by two C atoms in molecule **3c** makes the ligand too mobile.

Available data indicate that the presence of several CMPO groups in a molecule is not the only factor determining the complexation ability. Probably, mutual orientation of linking centers, flexibility of linkers, and appropriate balance between rigidity and flexibility of the molecular platform also affect the ionophoric ability of the ligand.

In the present work, we have studied for the first time dicarbamoylmethylphosphine oxide derivatives of adamantane **5** in which the CMPO groups are bound to the 1,3-positions of the rigid adamantane platform through methylene or ethylene bridges and studied their ionophoric

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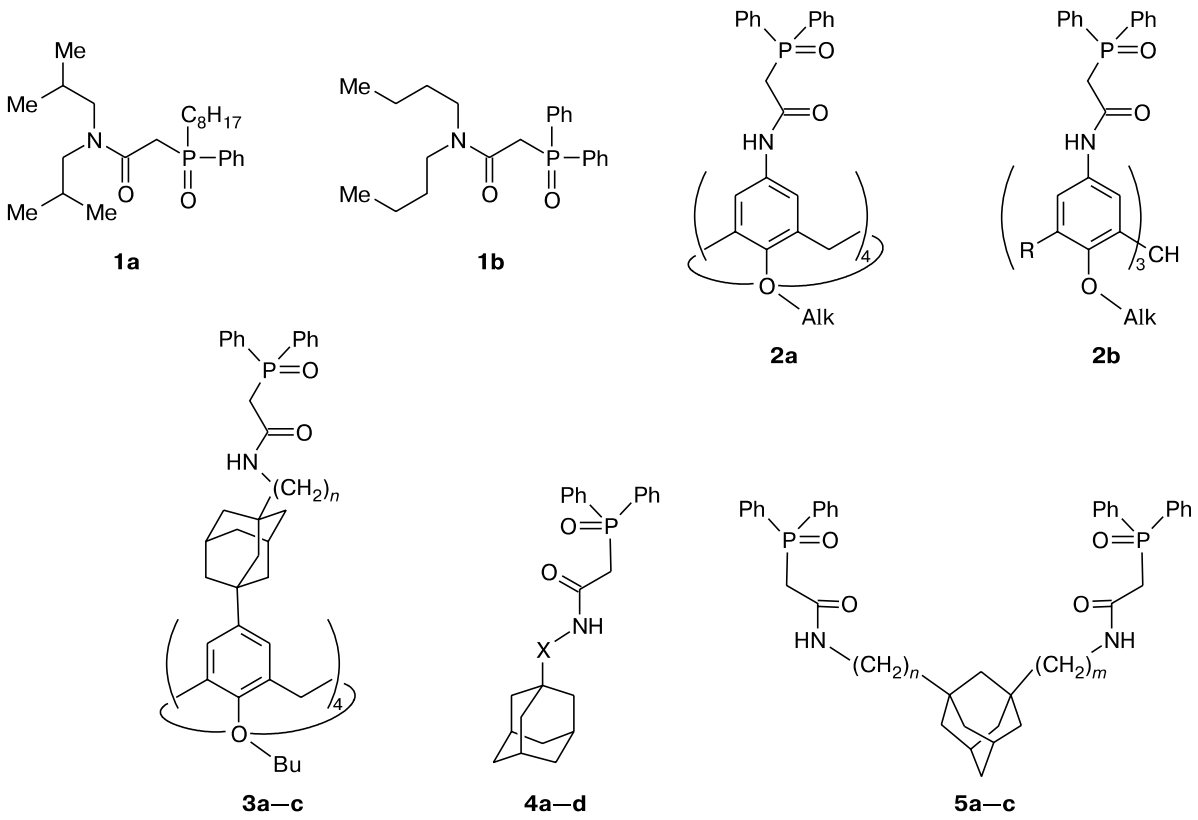


3: n = 0 (**a**), 1 (**b**), 2 (**c**); **4:** X = 0 (**a**), CH_2 (**b**), CH(Ph) (**c**), CH_2CH(Et) (**d**); **5:** $n = m = 1$ (**a**), $n = 1$, $m = 2$ (**b**), $n = m = 2$ (**c**)

ability toward americium(III) and europium(III). Compounds **1b** and mono-CMPO derivatives of adamantane **4a—d** were used as models for a comparison of the extraction properties.

Results and Discussion

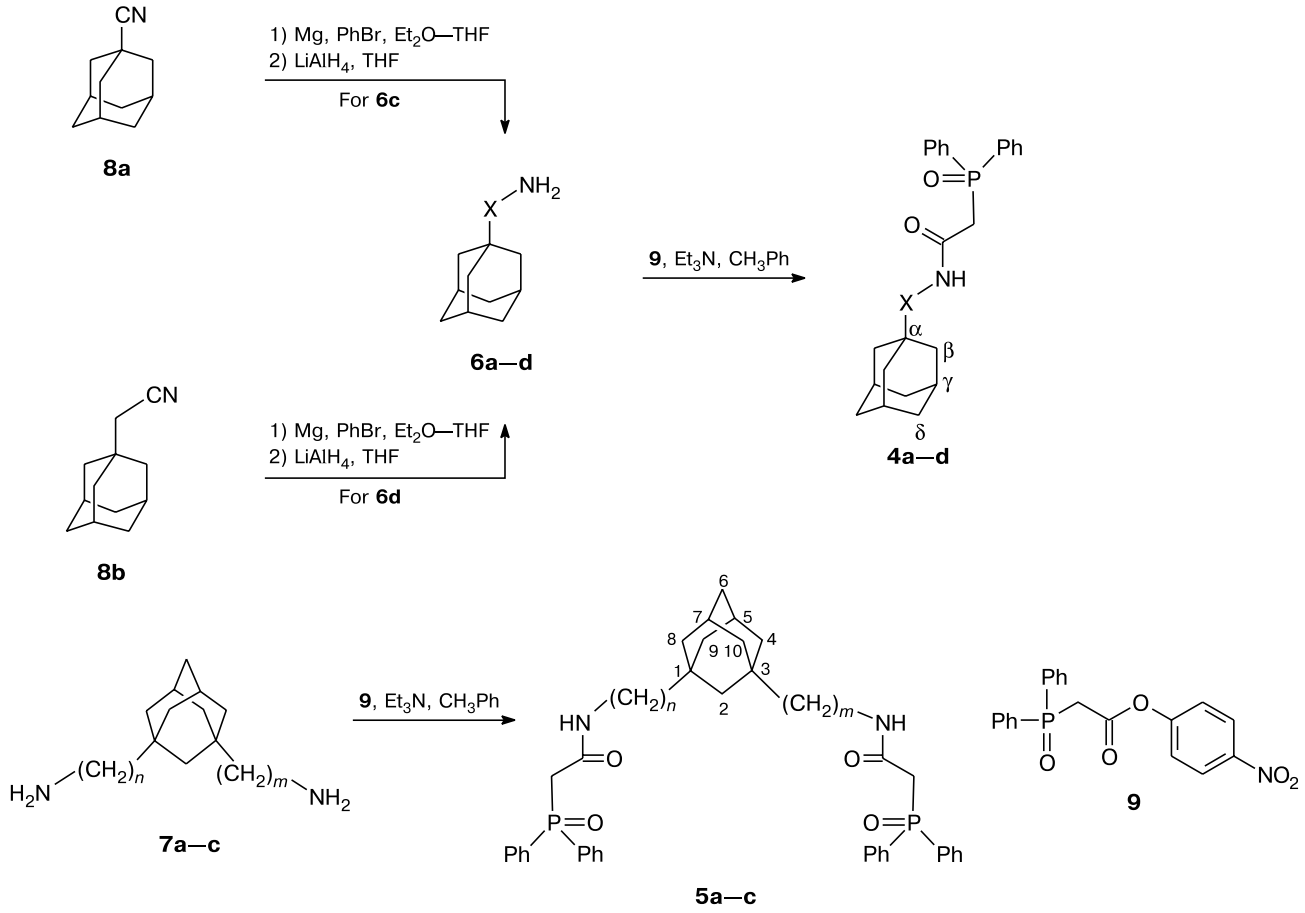
Adamantane carbamoylmethylphosphine oxide ligands **4** and **5** are derivatives of the corresponding 1-mono- and 1,3-diamino-containing adamantanes **6a—d** and **7a—c** (Scheme 1). 1-Aminoadamantane (**6a**),[5] 1-aminomethyladamantane (**6b**),[6] 1,3-diaminomethyladamantane (**7a**),[7] 1-aminomethyl-3-(2-aminoethyl)adamantane (**7b**),[8] and 1,3-di(2-aminoethyl)adamantane (**7c**)[9] were prepared according to earlier described procedures. 1-(α-Aminobenzyl)adamantane (**6c**) and 1-(2-aminobutyl)adamantane (**6d**) were synthesized from 1-cyanoadamantane (**8a**)[7] and 1-cyanomethyladamantane (**8b**),[7] respectively, by the reaction with phenylmagnesium bromide or ethylmagnesium iodide followed by the reduction of the obtained *N*-magnesiumhaloketimines with lithium aluminum hydride in THF. The carbamoylmethylphosphine oxide functions were introduced to nodal positions of the adamantane cycle by the acylation of the corresponding amines **6a—d** or **7a—c** with *p*-nitrophenyl diphenylphosphorylacetate (**9**) similarly to the method proposed previously[2a] for CMPO-derivatives of calixarenes.

The extraction ability of adamantane CMPO ligands **4** and **5** was studied by the example of extraction of americium(III) and europium(III) from acidic aqueous solutions to the organic phase. CMPO **1b** was used as standard.

When studying the extraction properties of the new extracting agents, the distribution coefficients (D) of Am^{3+} and Eu^{3+} between 3 M HNO_3 aqueous solution and dichloromethane solution of each ligand were measured as a function of ligand concentration (c_L). The nitric acid concentration (3 mol L^{-1}) in the initial aqueous phase corresponded to the acidity of solutions in real industrial processes. To determine the number of ligand molecules per metal cation in the extracted complexes (so-called solvate number, SN), we measured the slope ratio of the plots $\log D = f(\log c_L)$. The obtained results are given in Table 1 as distribution coefficients D determined by the radiometric method from γ-radiation of the ^{241}Am and ^{152}Eu isotopes and are illustrated in Figs 1—3.

As can be seen from the data in Table 1, monosubstituted CMPO derivatives **4a** and **4b** with the ionophoric group directly attached to the adamantane cycle or remote by one methylene unit extract americium(III) and europium(III) cations from HNO_3 solutions approximately

Scheme 1



4, 6: X = 0 (**a**), CH_2 (**b**), CH(Ph) (**c**), $CH_2CH(Et)$ (**d**); **5, 7:** $n = m = 1$ (**a**), $n = 1$, $m = 2$ (**b**), $n = m = 2$ (**c**)

to the same extent and much worse than standard CMPO ligand **1b**. The introduction of the Ph substituent to the adamantylmethyl moiety in ligand **4c** or removal of the CMPO group by two C atoms from adamantane in ligand **4d** much decreases the extraction ability of the ligands. This is related, most likely, to an increase in the screening effect of the substituent at the linking center in the first case and to a less ligand pre-organization in the second case.

On the contrary, all CMPO ligands **5** with two binding groups extract Am^{3+} and Eu^{3+} more efficiently than model compound **1b** and much more efficiently than their mono-substituted analogs **4** (see Table 1). At the same time, they are strongly inferior to *p*-adamantylcalix[4]calixarene

Table 1. Distribution coefficients (D) for the extraction of Am^{3+} and Eu^{3+} from 3 M HNO_3 to dichloromethane at different ligand concentrations (c_L)

c_L /mol L^{-1}	**1b**		**3b***		**4a**		**4b**		**4c**		**4d**		**5a**	**5b**	**5c**	
	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}		D_{Am}	D_{Eu}
0.005	0.01	0	32	26	—	—	—	—	—	—	—	—	0.15	0.13	0.10	0.07
0.010	0.03	0.02	240	125	—	—	—	—	—	—	—	—	0.81	0.66	0.59	0.37
0.020	0.14	0.05	920	570	—	—	0	0.01	—	—	—	—	3.7	3.9	3.2	2.0
0.040	0.5	0.27	—	—	0.08	0.04	0.05	0.03	0.005	0.005	0.01	0.01	25.0	38.0	27.0	16.0
0.060	1.2	0.64	—	—	0.23	0.14	—	—	—	—	—	—	—	—	—	—
0.080	—	—	—	—	0.4	0.21	0.29	0.17	0.01	0.01	0.05	0.04	—	—	190.0	230.0

* See Ref. 4.

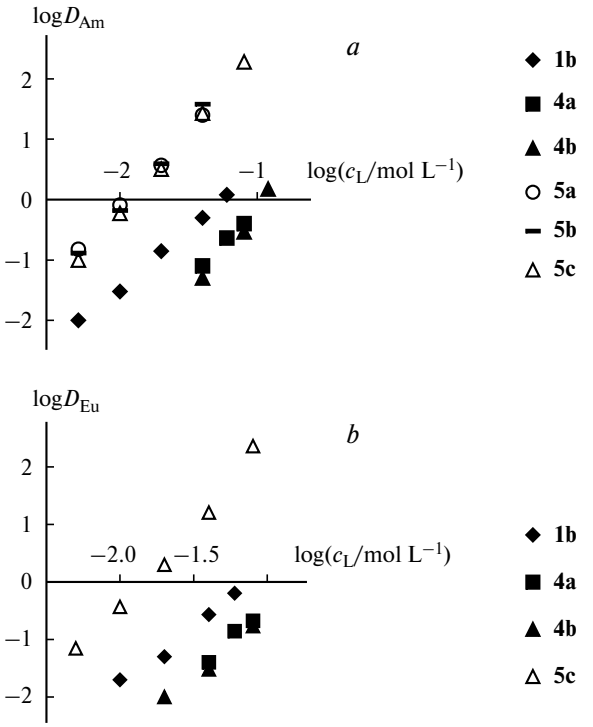


Fig. 1. Distribution coefficients (D) for Am^{3+} (a) and Eu^{3+} (b) as functions of the ligand concentration c_L (double logarithmic dependence) for extraction by ligands **1b**, **4**, and **5** from 3 M HNO_3 to dichloromethane.

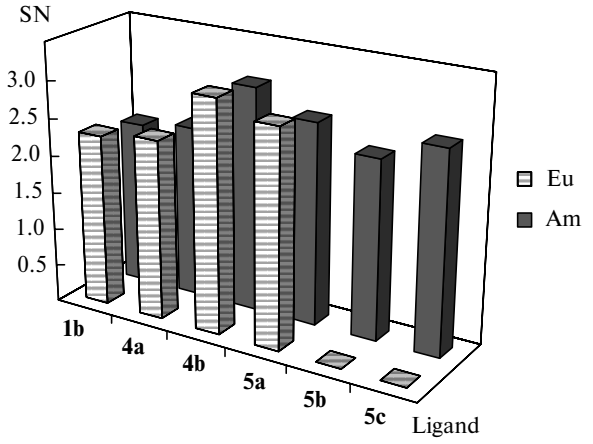


Fig. 2. Solvate numbers (SN) for the extraction of Am^{3+} and Eu^{3+} from 3 M HNO_3 solutions to dichloromethane by ligands **1b**, **4**, and **5**.

ligand **3b**. It turned out that the linker length (one or two methylene groups) exerts no substantial effect on the extraction efficiency of adamantane derivatives **5a,c**. Ligand **5b** demonstrated virtually the same efficiency.

The cooperative effect, *viz.*, increase in the distribution coefficient for the poly-CMPO derivatives compared to the monoanalogs at the same concentration of the reaction centers, is a measure of non-additive increasing

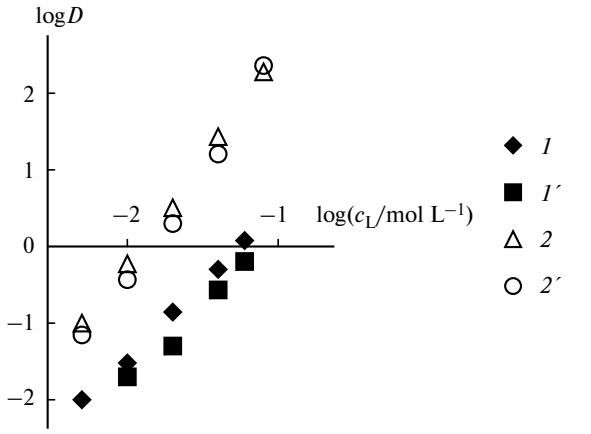


Fig. 3. Comparison of the distribution coefficients (D) for Am^{3+} (*1*, *2*) and Eu^{3+} (*1′*, *2′*) for extraction by ligands **1b** (*1*, *1′*) and **5c** (*2*, *2′*) from 3 M HNO_3 to dichloromethane.

the extraction ability in the polysubstituted ligands. To determine the cooperative effect of the CMPO groups attached to the adamantane platform in derivatives **5**, the distribution coefficients D for **5** at a certain ligand concentration were compared to similar D values of ligands **4** at a doubled concentration. It turned out that for pair **5a/4b** the effect of adamantane platform pre-organization is ~15, whereas for pair **5b/4d** it increases to ~$3 \cdot 10^2$. Since the D values for **5a** and **5c** are close, we can conclude that the cooperative effect increases with linker elongation.

An important characteristic of extraction is the solvate number that characterizes the composition of the formed complexes. We determined the solvate numbers for ligands **4a,b** and **5a—c** for extraction of Am^{3+} and Eu^{3+} by the slope method.[10] The logarithmic plots of the distribution coefficients *vs.* ligand concentration for extraction of americium and europium by ligands **1b**, **4**, and **5** are shown in Fig. 1.

The slope ratios of the lines are rather close in all cases. According to the results of analysis of the slope ratios of the lines (see Fig. 2), the typical solvate numbers for all CMPO-adamantanes **4** and **5** for americium and europium extraction range from 2 to 3. This means that the solvates containing two or three molecules in the complex are most stable. These data contradict the assumption that two CMPO groups of the disubstituted ligand are involved in coordination with one metal ion. However, the increase in the extraction ability indicates an additional stabilization of the complex by the second CMPO group of the extracting agent.

The influence of the nitric acid concentration on the extraction of Eu^{3+} by ligands **5a** and **5b** is illustrated in Fig. 4. As for model compound **1b**, the extraction maximum is achieved at medium concentrations of nitric acid (3—5 mol L^{-1}), indicating that these compounds can be used under real conditions of radionuclide separation.

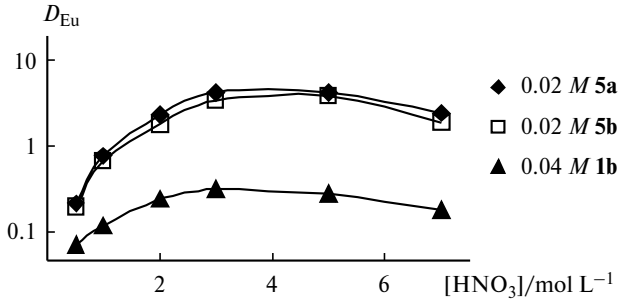


Fig 4. Distribution coefficients (D) for the extraction of Eu^{3+} by ligands **1b**, **5a**, and **5b** at different nitric acid concentrations (solvent dichloromethane).

One of the most important problems of spent nuclear fuel processing remains the separation of trivalent actinides, which is difficult due to their similar chemical properties. It is known[11] that CMPO-calixarenes **2a** are highly selective toward actinides and their D_{Am}/D_{Eu} is ~5. In our case, americium is extracted by ligand **5c** only slightly more efficiently than europium, and the D_{Am}/D_{Eu} does not exceed 2 (see Table 1, Fig. 3): its extraction properties are almost the same as those for compound **1b**. Probably, this is caused by relatively weak pre-organization of the binding centers in positions 1 and 3 of the adamantane platform of ligands **5**.

Thus, all newly synthesized adamantane 1,3-dicarbamoylmethylphosphine oxide derivatives **5** much more efficiently extract americium(III) and europium(III) from 3 *M* HNO_3 to dichloromethane than their monosubstituted analogs **4** and standard ligand **1b**. In mono-CMPO adamantanes **4**, the removal of the binding center from the adamantane cycle or an increase in the screening effect of the substituent decreases the extraction efficiency. Di-CMPO derivatives **5a** and **5c**, whose binding groups are separated from adamantane by one or two C atoms, extract Am^{3+} and Eu^{3+} with close efficiency. The synthesis of compound **5b** with linkers of different length (—CH_2— and —$(CH_2)_2$—) produced no extracting agents, whose extraction ability (D) or selectivity (D_{Am}/D_{Eu}) would be higher. The maximum of the extraction ability for derivatives **5** is observed in 3 *M* HNO_3, which is typical of the CMPO derivatives. The synthesized ligands are not selective, and their distribution coefficient D_{Am}/D_{Eu} is at most 2.

Experimental

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz) in $CDCl_3$ with operation frequencies 400, 100, and 162 MHz, respectively. In the ^1H and ^{13}C NMR spectra the chemical shifts are given relative to residual $CHCl_3$ (δ 7.25) and $CDCl_3$ (δ 76.92), and those in the ^{31}P NMR spectra are relative to 85% H_3PO_4 (external standard). The C atoms of the adamantane cycle are enumerated for the ^{13}C NMR spectra in Scheme 1. Preparative column chromatography were carried out on Kieselgel 40/60 (Merck), and TLC analysis was performed on DC Alufolien Kieselgel 60 F_{254} plates (Merck) with UV development. All solvents were purified according to known procedures.

1-Aminoadamantane (**6a**),[5] 1-aminomethyladamantane (**6b**),[6] 1,3-diaminomethyladamantane (**7a**),[7] 1-aminomethyl-3-(2-aminoethyl)adamantane (**7b**),[8] 1,3-di(2-aminoethyl)adamantane (**7c**),[9] 1-cyanoadamantane (**8a**),[7] 1-cyanomethyladamantane (**8b**),[7] *p*-nitrophenyl diphenylphosphorylacetate (**9**)[2a], 1-[(diphenylphosphoryl)acetamido]adamantane (**4a**),[4] and 1-[(diphenylphosphorylacetamido)methyl]adamantane (**4b**)[4] were synthesized according to known procedures.

Synthesis of CMPO ligands 4 and 5 (general procedure). Aminoadamantane **6a—d** or **7a—c** (1 mmol) and *p*-nitrophenyl ester **9** (1.25 equiv. per NH_2 group) was suspended in toluene (5—10 mL) containing triethylamine (1.25 equiv. per NH_2 group or 2—2.5 equiv. per $NH_2 \cdot HCl$ group). The reaction mixture was stirred 5—8 h with heating to 80 °C under argon (TLC monitoring). The solvent was distilled off under reduced pressure, and the residue was dissolved in chloroform (20 mL). The organic extract was washed successively with 5% Na_2CO_3 (4×10 mL) and water (4×10 mL) and dried over $MgSO_4$, and the solvent was distilled off. The residue was triturated with hexane and filtered or reprecipitated from a $CHCl_3$—hexane mixture (since compound **4c** is soluble in hexane, it was isolated by column chromatography on SiO_2 using $CHCl_3$—hexane as eluent).

1-[α-(Diphenylphosphorylacetamido)benzyl]adamantane (4c) was synthesized from **6c** (0.24 g, 1.0 mmol), compound **9** (0.48 g, 1.25 mmol), and triethylamine (0.17 mL, 1.25 mmol) in toluene (5 mL) at 80 °C for 5 h. The yield was 0.4 g (83%), m.p. 97—99 °C. Found (%): C, 77.12; H, 6.98; N, 2.71; P, 6.52. $C_{31}H_{34}NO_2P$. Calculated (%): C, 77.00; H, 7.09; N, 2.90; P, 6.40. ^1H NMR, δ: 8.34 (d, 1 H, NH, J = 9.3 Hz); 7.90—7.05 (m, 15 H, CH_{Ph}); 4.54 (d, 1 H, C<u>H</u>NH, J = 9.3 Hz); 3.40—3.20 (m, 2 H, CH_2PO); 1.84 (br.s, 3 H, CH_{Ad}); 1.60—1.32 (m, 12 H, $(CH_2)_{Ad}$). ^{13}C NMR, δ: 163.71 (d, CO, J = 3.8); 138.62 (C_{Ph}); 132.24 (dd, C_{Ph}, J_1 = 13.9 Hz, J_2 = 2.5 Hz); 131.57 (dd, C_{Ph}, J_1 = 95.5 Hz, J_2 = 19.0 Hz); 130.50 (dd, C_{Ph}, J_1 = 25.2 Hz, J_2 = 10.1 Hz); 128.77 (dd, C_{Ph}, J_1 = 12.0 Hz, J_2 = 8.2 Hz); 128.34, 127.34, 126.57 (all C_{Ph}); 63.03 (CHNH); 38.44 (C^{β}_{Ad}); 37.88 (d, CH_2PO, J = 59.4 Hz); 36.56 (C^{δ}_{Ad}); 36.23 (C^{α}_{Ad}); 28.14 (C^{γ}_{Ad}). ^{31}P NMR, δ: 30.03 (P=O).

1-[2-(Diphenylphosphorylacetamido)butyl]adamantane (4d) was synthesized from amine hydrochloride **6d** (0.24 g, 1.0 mmol), compound **9** (0.48 g, 1.25 mmol), and triethylamine (0.56 mL, 4 mmol) in toluene (10 mL) at 75 °C for 5 h. The yield was 0.4 g (89%), m.p. 148—150 °C. Found (%): C, 74.65; H, 8.19; N, 3.01; P, 6.68. $C_{28}H_{36}NO_2P$. Calculated (%): C, 74.81; H, 8.07; N, 3.12; P, 6.89. ^1H NMR, δ: 8.15—7.10 (m, 11 H, CH_{Ph} + NH); 3.95 (m, 1 H, C<u>H</u>NH); 3.49 (d, 2 H, CH_2PO, J = 15.1 Hz); 1.80—0.95 (m, 19 H, CH_{Ad} + $(CH_2)_{Ad}$ + AdC<u>H</u>$_2$ + C<u>H</u>$_2$$CH_3$); 0.46 (br.s, 3 H, Me). ^{31}P NMR, δ: 34.15 (P=O).

1,3-Di[(diphenylphosphorylacetamido)methyladamantane (5a) was synthesized from amine **7a** (0.19 g, 1.0 mmol), compound **9** (0.84 g, 2.2 mmol), and triethylamine (0.30 mL, 2.2 mmol) in toluene (20 mL) at 75 °C for 5.5 h. The yield was 0.54 g (80%), m.p. 175—176 °C. Found (%): C, 70.95; H, 6.33; N, 4.01; P, 8.89. $C_{40}H_{44}N_2O_4P_2$. Calculated (%): C, 70.78; H, 6.53; N, 4.13; P, 9.13. ^1H NMR, δ: 7.85—7.70 (m, 8 H,

CH_{Ph}); 7.40—7.55 (m, 14 H, CH_{Ph} + NH); 3.33 (d, 4 H, CH_2PO, J = 12.4 Hz); 2.79 (d, 4 H, $C\underline{H}_2NH$, J = 6 Hz); 1.75 (s, 2 H, $(CH_2)_{Ad}$); 1.00—1.40 (m, 12 H, $(CH_2)_{Ad}$). ^{13}C NMR, δ: 164.61 (d, CO, J = 4.4 Hz); 132.37 (d, C_{Ph}, J = 2.2 Hz); 131.74 (d, C_{Ph}, J = 102.4 Hz); 130.65 (d, C_{Ph}, J = 9.9 Hz); 128.92 (d, C_{Ph}, J = 12.2 Hz); 50.77 (CH_2NH); 42.20 $(C(2)_{Ad})$; 39.04 $(C(4)_{Ad}$, $C(8)_{Ad}$, $C(9)_{Ad}$, $C(10)_{Ad})$; 38.39 (d, C_{CH_2PO}, J = 60.4 Hz); 35.80 $(C(6)_{Ad})$; 34.72 $(AdCH_2)$*; 34.28 $(C(1)_{Ad}$, $C(3)_{Ad})$*; 28.07 $(C(5)_{Ad}$, $C(7)_{Ad})$. ^{31}P NMR, δ: 29.76.

1-[(Diphenylphosphorylacetamido)methyl]-3-[2-(diphenylphosphorylacetamido)ethyl]adamantane (5b) was synthesized from amine **7b** (0.21 g, 1.0 mmol), compound **9** (0.84 g, 2.2 mmol), and triethylamine (0.3 mL, 2.2 mmol) in toluene (20 mL) at 80 °C for 5 h. The yield was 0.42 g (61%), m.p. 236—237 °C. Found (%): C, 71.22; H, 6.48; N, 3.92; P, 8.68. $C_{41}H_{46}N_2O_4P_2$. Calculated (%): C, 71.08; H, 6.69; N, 4.04; P, 8.94. ^1H NMR, δ: 7.85—7.65 (m, 8 H, CH_{Ph}); 7.45—7.55 (m, 14 H, CH_{Ph} + NH); 3.33 (d, 2 H, CH_2PO, J = 12.8 Hz); 3.31 (d, 2 H, CH_2PO, J = 12.9 Hz); 3.11 (m, 2 H, $C\underline{H}_2NH$); 2.85 (d, 2 H, $C\underline{H}_2NH$, J = 6.0 Hz); 1.82 (br.s, 2 H, CH_{Ad}); 1.45—1.02 (m, 14 H, $(CH_2)_{Ad}$ + $AdC\underline{H}_2$). ^{13}C NMR, δ: 164.41 (d, CO, J = 5.1 Hz); 164.21 (d, CO, J = 4.4 Hz); 132.24 (br.s, C_{Ph}); 131.43 (dd, C_{Ph}, J = 102.6 Hz); 130.72 (dd, C_{Ph}, J = 9.5 Hz); 130.65 (dd, C_{Ph}, J = 9.5 Hz); 128.78 (d, C_{Ph}, J = 12.4 Hz); 128.75 (d, C_{Ph}, J = 12.2 Hz); 50.81 (CH_2NH); 44.81 $(C(2)_{Ad})$; 42.72 (CH_2NH); 41.42 $(C(4)_{Ad}$, $C(10)_{Ad})$; 39.29 $(C(8)_{Ad}$, $C(9)_{Ad})$; 38.76 (d, C_{CH_2PO}, J = 58.1 Hz); 38.26 (d, C_{CH_2PO}, J = 59.7 Hz); 36.14 $(C(6)_{Ad})$; 34.93 $(C(1)_{Ad})$*; 34.51 $(C(3)_{Ad})$*; 32.23 $(AdCH_2)$; 28.39 $(C(5)_{Ad}$, $C(7)_{Ad})$. ^{31}P NMR, δ: 29.58, 29.54.

1,3-Di[2-(diphenylphosphorylacetamido)ethyl]adamantane (5c) was synthesized from amine **7c** (0.22 g, 1.0 mmol), compound **9** (0.95 g, 2.5 mmol), and triethylamine (0.3 mL, 2.2 mmol) in toluene (10 mL) at 75 °C for 5.5 h. The yield was 0.53 g (75%), m.p. 193—195 °C. Found (%): C, 72.17; H, 8.00; N, 6.75; P, 8.77. $C_{42}H_{48}N_2O_4P_2$. Calculated (%): C, 72.39; H, 8.03; N, 6.03; P, 8.94. ^1H NMR, δ: 7.85—7.70 (m, 8 H, CH_{Ph}); 7.61—7.55 (m, 4 H, CH_{Ph}); 7.53—7.45 (m, 10 H, CH_{Ph} + NH); 3.35 (d, 4 H, CH_2PO, J = 12.8 Hz); 3.19 (m, 4 H, $C\underline{H}_2NH$); 1.95 (br.s, 2 H, CH_{Ad}); 1.54—1.12 (m, 16 H, $(CH_2)_{Ad}$ + $AdC\underline{H}_2$). ^{13}C NMR, δ: 164.16 (d, CO, J = 4.4 Hz); 132.17 (br.s, C_{Ph}); 131.43 (d, C_{Ph}, J = 102.4 Hz); 130.53 (d, C_{Ph}, J = 9.9 Hz); 128.64 (d, C_{Ph}, J = 12.2 Hz); 46.81 $(C(2)_{Ad})$; 42.72 (CH_2NH); 41.36 $(C(4)_{Ad}$, $C(8)_{Ad}$, $C(9)_{Ad}$, $C(10)_{Ad})$; 38.47 (d, C_{CH_2PO}, J = 60.4 Hz); 36.08 $(C(6)_{Ad})$; 34.72* $(AdCH_2)$; 32.25* $(C(1)$, $C(3)_{Ad})$; 28.52 $(C(5)_{Ad}$, $C(7)_{Ad})$. ^{31}P NMR, δ: 26.63 (P=O).

1-(α-Aminobenzyl)adamantane (6c). Manganese (3.6 g, 0.15 mol) and anhydrous Et_2O (100 mL) were placed in a reactor with a stirrer, a reflux condenser, a drying tube, and a dropping funnel, and bromobenzene (15.75 mL, 0.15 mol) dissolved in Et_2O (300 mL) was added dropwise for 0.5 h. The reaction mixture was stirred for 1 h until Mg was dissolved and 1-cyanoadamantane (**8a**) (16.1 g, 0.1 mol) in THF (300 mL) was added. The resulting mixture was stored for 8 h. A suspension of previously prepared *N*-magnesiumhaloketimine was added dropwise to a suspension of lithium aluminum hydride (7.8 g, 0.21 mol) in THF (300 mL). The reaction mixture was stirred under reflux for 40 h and cooled, and water (11 mL), 12% sodium hydroxide (20 mL), and more water (30 mL) were added. The precipitate was filtered and extracted with ether (3×150 mL). The mother liquors were combined and concentrated. The residue after evaporation was distilled *in vacuo*. The yield was 15.7 g (65%), b.p. 159—163 °C (4 Torr), m.p. 68 °C. Found (%): C, 84.65; H, 9.54; N, 5.81. $C_{17}H_{23}N$. Calculated (%): C, 84.48; H, 9.05; N, 5.71. ^1H NMR (DMSO-d_6), δ: 7.02 (m, 5 H, CH_{Ph}); 3.37 (br.s, 1 H, $C\underline{H}NH_2$); 1.88 (br.s, 3 H + 2 H, CH_{Ad} + $N\underline{H}_2$); 1.38—1.60 (m, 12 H, $(CH_2)_{Ad}$). ^{13}C NMR, (DMSO-d_6), δ: 143.35, 128.23, 126.93, 126.08 (all C_{Ph}); 65.31 (CHPh); 38.19 (C^{β}_{Ad}); 36.68 (C^{δ}_{Ad}); 35.98 (C^{α}_{Ad}); 27.87 (C^{γ}_{Ad}).

1-(2-Aminobutyl)adamantane (6d) was synthesized similarly to compound **6c** from 1-cyanomethyladamantane **8b** (17.5 g, 0.1 mol), ethyl iodide (11.3 mL, 0.14 mol), and lithium aluminum hydride (5.63 g, 0.15 mol). The duration of the synthesis of *N*-magnesiumhaloketimine was 3 h, and it was reduced for 20 h. The yield of compound **6d** was 16.6 g (80%), b.p. 98—102 °C (4 Torr). Found (%): C, 81.16; H, 12.08; N, 6.66. $C_{14}H_{25}N$. Calculated (%): C, 81.00; H, 12.01; N, 6.76. ^1H NMR (CD_3OD), δ: 2.45—2.35 (m, 1 H, $C\underline{H}NH_2$); 2.10 (br.s, 3 H, CH_{Ad}); 1.90—1.30 (m, 12 H, $(CH_2)_{Ad}$ + $AdC\underline{H}_2CHC\underline{H}_2$); 1.13 (t, 3 H, Me). ^{13}C NMR (CD_3OD), δ: 49.95 ($CHNH_2$); 48.08 ($AdCH_2$); 43.39 (C^{β}_{Ad}); 37.83 (C^{δ}_{Ad}); 33.18 (C^{α}_{Ad}); 29.94 (C^{γ}_{Ad}); 29.11 ($\underline{C}H_2CH_3$); 9.76 ($CH_2\underline{C}H_3$).

Extraction experiment. A nitric acid solution of europium nitrate (~10^{-5} mol L^{-1}, 1 mL) labeled with ^{152}Eu or ^{241}Am to an activity of ~5 kBq mL^{-1} was placed in a cell, an equal volume of the extracting agent in CH_2Cl_2 was added, and the cell was closed and automatically shaken for 1 h. Extraction equilibrium was achieved within several minutes. The phases were separated by centrifuging, and the aqueous and organic phases (0.4 mL each) were sampled. The distribution coefficient was measured radiometrically on a DeskTop InSpector 1270 scintillation γ-spectrometer (Canberra Co).

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* Ambiguous assignment.

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