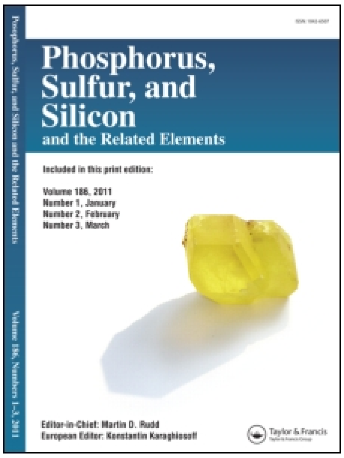


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Tripodal Triphosphines and Their Derivatives

Jerry L. Mills[a]; David E. Harwell[a]; Virginia K. De Marquis[a]; John N. Marx[a]
[a] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX

To cite this Article Mills, Jerry L. , Harwell, David E. , De Marquis, Virginia K. and Marx, John N.(1994) 'Synthesis of Tripodal Triphosphines and Their Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 87: 1, 149 — 156

To link to this Article: DOI: 10.1080/10426509408037449
URL: http://dx.doi.org/10.1080/10426509408037449

Phosphorus, Sulfur, and Silicon, 1994, Vol. 87, pp. 149–156

SYNTHESIS OF TRIPODAL TRIPHOSPHINES AND THEIR DERIVATIVES

JERRY L. MILLS, DAVID E. HARWELL, VIRGINIA K. DE MARQUIS,
AND JOHN N. MARX
Department of Chemistry and Biochemistry, Texas Tech University,
Lubbock, TX 79409-1061

Dedicated to Dr. Alan H. Cowley on the occasion of his 60th birthday.

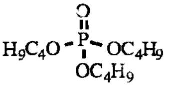
A general strategy for the synthesis of a series of tripodal triphosphines $XC[(CH_2)_nPR_2]_3$ (where X = H or Me, n = 1-4) has been sought. Particular emphasis has been placed on attempts to synthesize a series member $XC[(CH_2)_{n+1}PR_2]_3$ from its precursor $XC[(CH_2)_nPR_2]_3$. We will present the results of our synthetic efforts, together with the characterization of a number of new tripodal triphosphines and their derivative oxides. Some "ether-legged" tripodal triphosphines have also been synthesized.

Key Words: tripod, ligand, phosphine oxide, extraction

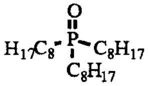
INTRODUCTION

Many of the radioisotopes which remain after the reprocessing of nuclear fuel from commercial and military reactors are of great commercial or scientific value. Others, such as ^{237}Np, ^{241}Am, ^{234}Am, and ^{241}Cm, are excellent candidates for muon-induced fission[1], as a means of disposal, but they must be isolated from each other to facilitate processing. A cheap, efficient way to selectively extract and separate the elements of the lanthanide and actinide families is needed.

The organophosphorus ligands which have previously been developed generally can be classified in one of six categories: phosphonates, phosphine oxides, diphosphine oxides, diphosphonates, carbamoylphosphonates, and carbamoylphosphine oxides. Phosphonates, such as TBP, and phosphine oxides, such as TOPO, are monodentate, neutral ligands.[2-5]


$H_9C_4O-\overset{\overset{O}{\|}}{\underset{OC_4H_9}{P}}-OC_4H_9$

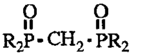
Tributylphosphonate
(TBP)


$H_{17}C_8-\overset{\overset{O}{\|}}{\underset{C_8H_{17}}{P}}-C_8H_{17}$

Trioctylphosphine oxide
(TOPO)

The diphosphine oxides (DPO), diphosphonates (DP), carbamoylphosphonates (CMP), and carbamoylphosphine oxides (CMPO) are all neutral bidentate ligands .[6-10]

TBP is the most common extractant (the PUREX process). It effectively extracts U(VI), Np(IV), and Pu(IV) from highly acidic solutions; however, it does not extract Am(III), Cm(III) or other actinides under these conditions.[3-5] The bifunctional organophosphorus extractants offer some hope, but their limited solubility in the organic diluents used in biphasal separations restrict their usefulness. CMP was found to extract Ln(III) ions, An(III) ions, Th(IV), and U(VI) effectively from highly acidic (>2M) nitric acid solutions.[11-18] Substitution of alkyl or phenyl groups for the OR groups, as in

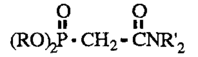


$R_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{P}}R_2$

Diphosphine oxide
(DPO)

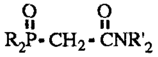
$R_2P\text{-}CH_2\text{-}P(OR')_2$

Diphosphonate
(DP)



$(RO)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}NR'_2$

Carbamoylphosphonate
(CMP)



$R_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}NR'_2$

Carbamoylphosphine oxide
(CMPO)

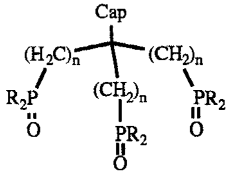
CMPO, was found to increase the extractant's capacity, but decreased its selectablity and solubility in the organic phase.[19,20] Carbamoylmethylphosphine oxides of the type $R(Ph)P(O)CH_2C(O)NR'_2$ were found to be the most effective extractants and led to the first implementation of the TRUEX process for the extraction of generic actinides.

As promising and effective as these extractants are, they fail to offer the ability to selectively extract one or two Ln/An ions in a series. They also involve biphasal liquid-liquid separations which are labor intensive and require large volumes of organic solvents.

The ideal extractant should coordinate in a tridentate fashion to take maximum advantage of the chelation effect. It should also be able to separate radionuclides into small groups of like characteristics, and contain a mechanism to fine tune the ligand's chelating ability so that, preferentially, only one radionuclide is targeted at a time. The extraction process should also allow for the maximum amount of automation so that human exposure to radiation would be limited. This could be accomplished by attaching the ligand to a solid support such as polystyrene through a covalently bonded alkyl tether so that effluent flows could be directed through a series of heterogeneous extraction columns. Attaching the ligand to a solid support would eliminate the need for the tedious and expensive back-extractions involved in biphasal liquid-liquid separations.

RESULTS AND DISCUSSION

In an attempt to provide a new series of ligands to meet the above criteria (based on derivative chemistry), a series of tripodal triphosphine oxides with the structure depicted below have been developed.



The ligands are tridentate to allow for coordination with lanthanides and actinides. The length of the legs can also be varied so that the ligand's bite-size can be changed to match to the size of the species being extracted. Coordination might also be non-chelating as was found in the structure of $[Ni_3Cl_6\{(CH_2CH_2PPh_2)_3\}_2]$.[21] Ligands can be attached to a solid support by substituting an organic tether group in place of the cap. It is hoped that by using tripods of increasing bite-size in series, it will be possible to obtain effective separation of cations on the basis of size (see Figure 1). Analogs were synthesized with n values of one, two, and three corresponding to methyl, ethyl, and propyl legs, respectively. Lanthanide and actinide cations are characteristically hard acids; however, they do vary slightly with respect to hardness and softness. By substituting either electron-withdrawing or electron-donating groups for R on the phosphorus atom,

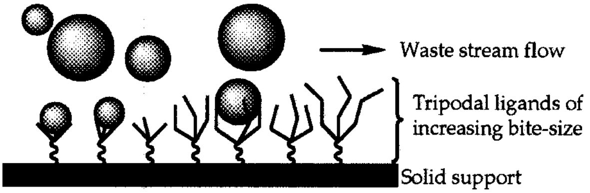


Figure 1 Cartoon depiction of tripods of increasing bite-size in series.

further selectivity of the ligand for a specific radionuclide can be provided. Electron-withdrawing groups should cause the phosphine oxide to be a harder ligand while, conversely, electron-donating groups should cause the phosphine oxide to become a softer ligand. Compounds of this type offer the promise of superior coordination properties with respect to Ln/An (III) ions.

"Methyl-legged" Tripod

The first tripodal triphosphine oxide in the proposed synthetic series is 1,1,1-tris(diphenylphosphorylmethyl)ethane. Hewertson and Watson first synthesized 1,1,1-tris(diphenylphosphorylmethyl)ethane in 1962.[22] In the preparation they reacted 1,1,1-tris(hydroxy-methyl)ethane with thionyl chloride or phosphorus tribromide to generate the corresponding trichloro- or tribromo-tripod, respectively. The resulting halogenated compound was then reacted with lithium diphenylphosphide to produce the tripod triphosphine, triphos. Triphos is now commercially available and has become one of

$$CH_3C(CH_2OH)_3 + 3\ SOCl_2 \xrightarrow[\text{[N}_2\text{]}]{0°C,\ pyridine} \xrightarrow[50°C]{oil\ bath} CH_3C(CH_2Cl)_3$$

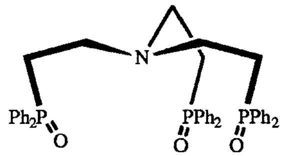
$$CH_3C(CH_2OH)_3 + PBr_3 \xrightarrow[\text{[N}_2\text{]}]{170°C} CH_3C(CH_2Br)_3$$

$$CH_3C(CH_2X)_3 + 3\ LiPPh_2 \xrightarrow{\text{[N}_2\text{]}} CH_3C(CH_2PPh_2)_3 + 3\ LiX$$

today's most popular tridentate ligands.[23] Very little research, however, has been reported with regard to the coordination ability of the trioxide, 1,1,1-tris(diphenylphosphoryl-methyl)ethane.

Triphos was oxidized in an aqueous solution of hydrogen peroxide to produce 1,1,1-tris(diphenylphosphorylmethyl)ethane in near quantitative yield. Samples of the resulting oxide were then submitted to Los Alamos National Laboratory for testing. Surprisingly the ligand was not found to effectively chelate any of the trivalent actinides or lanthanides, even at significant concentration levels (3 M ligand). This was a very unexpected result, because bis(diphenylphosphoryl)methane has been found to be very effective at coordinating lanthanide and actinide ions under similar conditions.[24] Computer simulations of 1,1,1-tris(diphenylphosphorylmethyl)ethane both at Texas Tech and at Los Alamos suggested that the cause for the lack of coordination was steric in nature.[25] It was felt that the bite-size of the ligand was too small to provide optimum binding conditions, because the legs of the ligand were too short to wrap around the metal ion. Similar simulations with 1,1,1-tris-(diphenylphosphorylethyl)ethane, the next prototype in the synthetic series, indicated that it should be able to effectively coordinate to the metal ion.

The amine analog of 1,1,1-tris(diphenylphosphorylethyl)ethane, tris(diphenylphosphorylethyl)amine was synthesized at Los Alamos and performed well in extraction studies; however, the substitution of nitrogen for carbon at the apical position presented new synthetic challenges with respect to attachment to a solid support.



"Ethyl-legged" Tripods

Upon first inspection of the structure of 1,1,1-tris(diphenylphosphorylmethyl)ethane, it would seem that the easiest route to lengthening the tripodal legs would be a simple homologation reaction. Several reactions were tried including:

$$CH_3C(CH_2Br)_3 \quad + \quad KC{\equiv}N \xrightarrow{DMSO}$$

$$+ \quad KC{\equiv}N \xrightarrow{H_2O,\ THF}$$

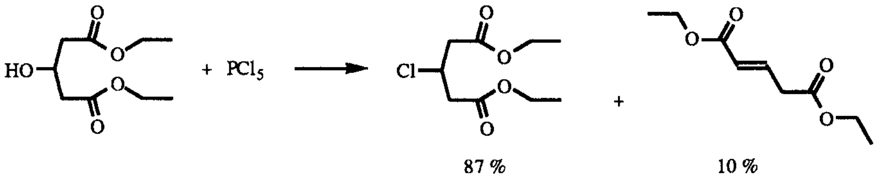
$$+ \quad LiC{\equiv}CH \xrightarrow{THF}$$

$$+ \quad LiCH_2P(O)Ph_2 \xrightarrow{THF}$$

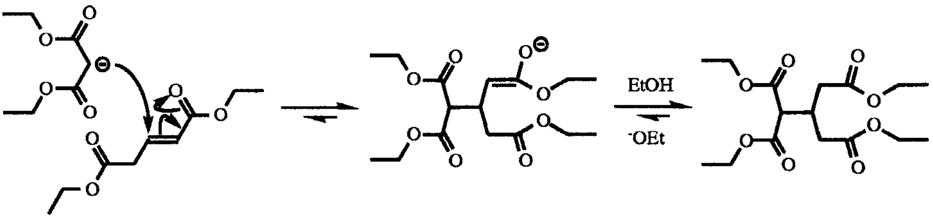
$$+ \quad NaCH(CO_2CH_2CH_3)_2 \xrightarrow{CH_3CH_2OH}$$

However, none was successful. When these homologation efforts failed, it was obvious that a total synthesis would be necessary.

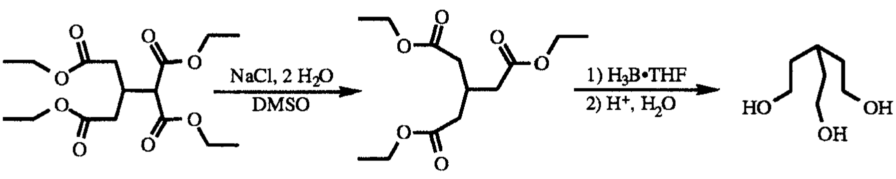
Diethyl-3-hydroxygluterate was reacted with phosphorus pentachloride to produce both diethyl-3-chlorogluterate and its corresponding elimination product.



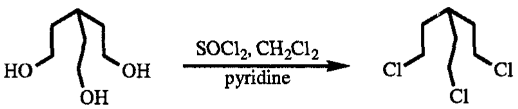
Diethyl-3-chlorogluterate was coupled with the enolate of diethyl malonate through an S_N2 reaction.[26] The coupling of the diethyl malonate anion to diethyl-3-chloroglutarate proceeds through the same elimination intermediate followed by a 1,4 or Michael addition.



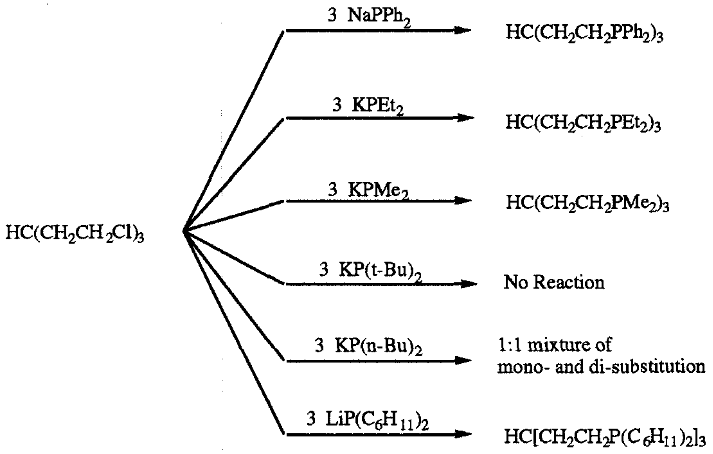
Decarboalkoxylation of the tetraester was achieved utilizing sodium chloride in DMSO. The chloride ion readily displaces the carbonyl group to yield the trisester.[27]



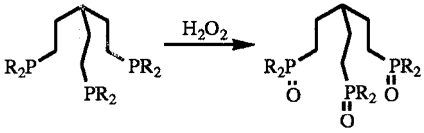
The trisester was then reduced with borane to produce the corresponding triol. Substitution of chloro groups for the hydroxyl groups was accomplished with thionyl chloride. The cyclization byproduct, 4-(2-chloroethyl)tetrahydropyran, was also formed.



Substitution of the chloro groups with either the lithium, sodium, or potassium phosphide results in the formation of the respective tripod triphosphine.



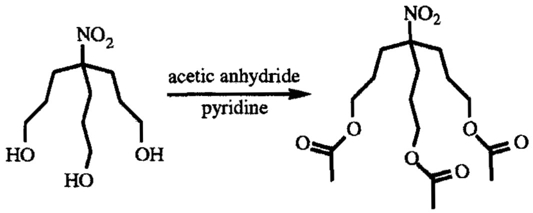
Subsequent oxidation of the phosphine with aqueous hydrogen peroxide proceeded cleanly to produce the oxides. Purification was achieved by column chromatography.

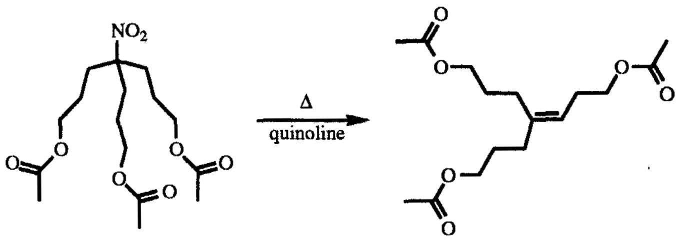


Samples of 1,1,1-tris(diphenylphosphorylethyl)methane were shipped to Los Alamos National Laboratory where analytical tests on the extraction and separation characteristics of the ligand were performed. The compound was found to extract both Eu (III) and Am (III) from aqueous solution in very high efficiency.[24] Extraction studies have not yet been performed for the other ligands mentioned above.

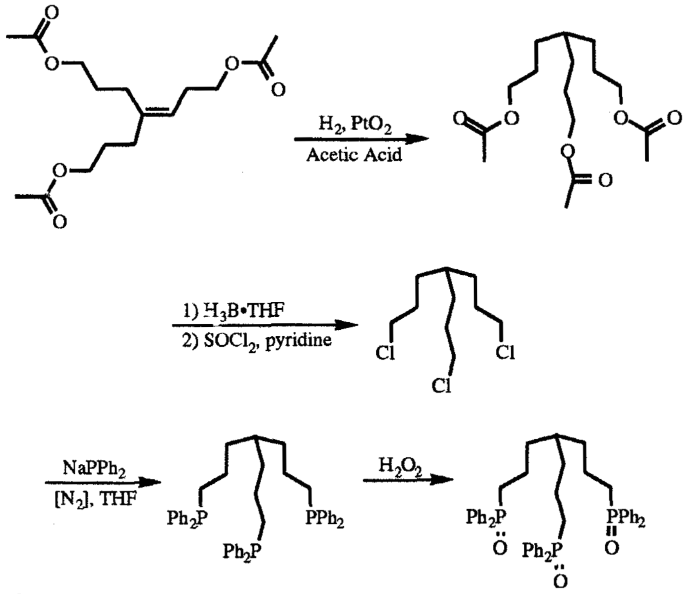
"Propyl-legged" Tripod

Synthesis of 1,1,1-tris-(diphenylphosphorylpropyl)methane began with the commercially available compound nitromethanetrispropanol. The hydroxyl groups were first protected by acylation. The nitro group of the resulting trisester was then eliminated by refluxing the tripod overnight in quinoline.



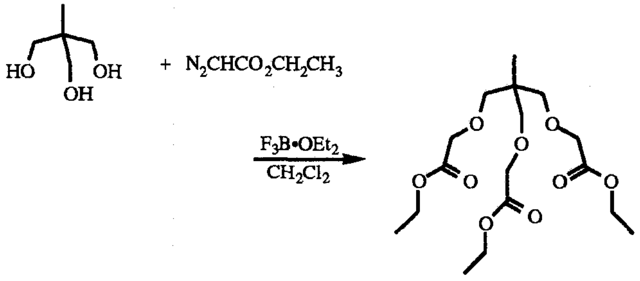


The double bond was then hydrogenated using Adam's catalyst (PtO_2) under 50 psi pressure of hydrogen. Reduction with borane followed by substitution with thionyl chloride resulted in 1,1,1-tris(chloroethyl)methane. Just as with the "ether-legged" tripod, phosphination was achieved using sodium diphenylphosphide. Oxidation with aqueous hydrogen peroxide resulted in 1,1,1-tris(diphenylphosphorylpropyl)methane.

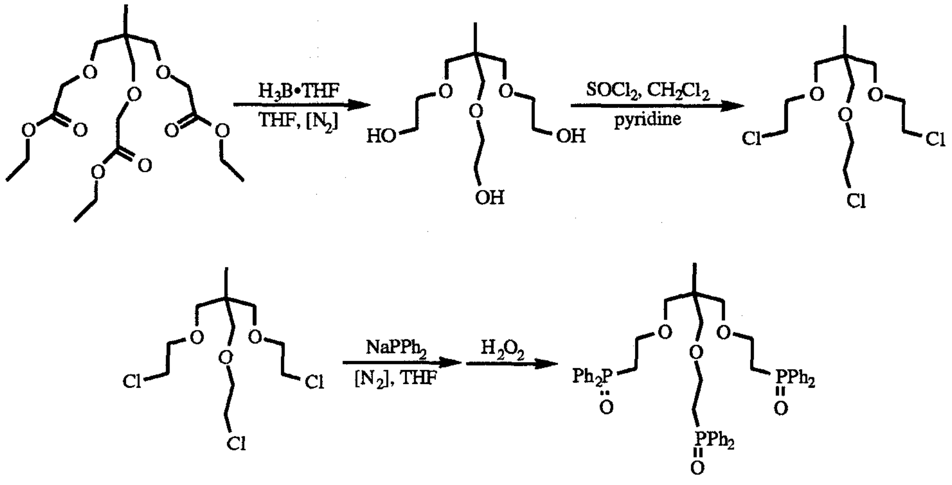


"Ether-legged" Tripod

Finally the "ether-legged" tripod, 1,1,1-tris(diphenylphosphorylethoxymethyl)-ethane, was produced in the reaction of 1,1,1-tris(hydroxymethyl)ethane with diazoethyl acetate to form 1,1,1-tris(3'-ethoxycarbonyl-2'-oxapropyl)ethane.[28]



It was found that the trisalcohol had to be completely dry prior to reaction with diazoethyl acetate to prevent unwanted side reactions. Borane reduction of the trisester followed by reaction with thionyl chloride produced 1,1,1-tris(chloroethoxy-methyl)ethane. Phosphination with sodium diphenylphosphide followed by oxidation with aqueous hydrogen peroxide resulted in the desired product.



Evaluation of the remaining tripodal triphosphines is currently underway at Los Alamos National Laboratory.

ACKNOWLEDGMENTS

We would like to thank Los Alamos National Laboratory and the Department of Energy for their financial support.

We would also like to thank B. F. Smith, M. M. Jones, and G. D Jarvinen of Los Alamos National Laboratory for performing the coordination studies.

REFERENCES

1. Y. Ronen, *Ann. Nucl. Energy*, **20**, 225-226 (1993).
2. J. C. Warf, *J. Amer. Chem. Soc.*, **71**, 3257 (1949).
3. E. Hesford, E. E. Jackson and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **9**, 279 (1959).
4. T. H. Siddall, *J. Inorg. Nucl. Chem*, **13**, 151 (1960).
5. J. O. Liljenzin, G. Persson, I. Svantesson and S. Wingefors, *Radiochem. Acta.*, **35**, 155 (1984).
6. T. H. Siddall, *J. Inorg. Nucl. Chem.*, **25**, 883 (1963).
7. T. H. Siddall, *J. Inorg. Nucl. Chem.*, **26**, 1991 (1964).
8. W. E. Stewart and T. H. Siddall, *J. Inorg. Nucl. Chem.*, **30**, 3281 (1968).
9. W. E. Stewart and T. H. Siddall, *J. Inorg. Nucl. Chem.*, **32**, 3599 (1970).
10. M. L. Good and T. H. Siddall, *J. Inorg. Nucl. Chem.*, **2**, 337 (1966).
11. W. W. Schultz and L. D. McIsaac in. *Book* , , W. Muiler and R. Linder, Eds., North Holland Publishing Co., Amsterdam, 1976, pp 433-447.
12. *Transplutonium Elements-Production and Recovery* , , American Chemical Society, Washington, D. C., 1981, pp 109-129.
13. *Actinide Separations* , , American Chemical Society, Washington, D. C., 1980, pp 395-410.
14. D. G. Kalina, E. P. Horwitz, L. Kaplan and A. C. Muscatello, *Sep. Sci. Tech.*, **16**, 1127 (1981).
15. E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason and H. Diamond, *Sep.Sci. Tech.*, **17**, 1261 (1982).
16. E. P. Horwitz, A. C. Muscatello, D. G. Kalina and L. Kaplan, *Sep. Sci. Tech.*, **16**, 417 (1981).
17. E. P. Horwitz, D. G. Kalina and A. C. Muskatello, *Sep. Sci. Tech.*, **16**, 403 (1981).
18. A. C. Muscatello, E. P. Horwitz, D. G. Kalina and L. Kaplan, *Sep. Sci. Tech.*, **17**, 859 (1982).
19. R. R. Shoun and W. J. McDowell, *Radiochim. Acta.*, **29**, 143 (1981).
20. B. F. Myasoedov, M. K. Chmutova, N. E. Kochetkova, D. E. Koiro, G. A. Pribylova, N. P. Mesterova, T. Y. Medved and M. I. Kabachnik, *Extr. Ion Exch.*, **4**, 61 (1986).
21. F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orlandini, *J. Chem. Soc. Dalton Trans.*, **1992**, 33-35 (1992).
22. W. Hewertson and H. R. Watson, *Chem. Soc. J.*, 1490-1494 (1962).
23. F. A. Cotton and B. Hong in. *Book* , 40, S. J. Lippard, Eds., John Wiley & Sons, Inc., New York, 1992, pp 179-289.
24. G. Jarvenin.
25. B. F. Smith, M. M. Jones and G. D. Jarvinen "Extractive Evaluation of Tripodyl Phosphoryl Containing Neutral Ligands for the Extraction of Trivalent Actinides and Lanthanides," Los Alamos National Laboratory, 1991.
26. Dreifuss and Ingold, *J. Chem. Soc.*, **123**, 2964-2967 (1923).
27. A. P. Krapcho and A. J. Lovey, *Tet. Lett.*, 957-960 (1973).
28. M. Güggi, M. Oehme, E. Pretch and W. Simon, *Helv. Chim. Acta.*, **59**, 2417-2420 (1976).