Synthesis and lanthanide coordination chemistry of trifluoromethyl derivatives of phosphinoylmethyl pyridine N-oxides[†]

Sylvie Pailloux,^{*a*} Cornel Edicome Shirima,^{*a*} Alisha D. Ray,^{*a*} Eileen N. Duesler,^{*a*} Karen Ann Smith,^{*a*} Robert T. Paine,^{**a*} John R. Klaehn,^{*b*} Michael E. McIlwain^{*b*} and Benjamin P. Hay^{*c*}

Received 25th March 2009, Accepted 18th June 2009 First published as an Advance Article on the web 24th July 2009 DOI: 10.1039/b905947d

A synthetic route for the formation of 2-[bis(2-trifluoromethylphenyl)phosphinoylmethyl]pyridine N-oxide (1c) and 2-[bis(3,5-trifluoromethylphenyl)phosphinoylmethyl]pyridine N-oxide (1d) was developed and the new ligands characterized by spectroscopic methods and single-crystal X-ray diffraction analyses. The coordination chemistry of 1c was examined with Yb(NO₃)₃ and the molecular structure of one complex, [Yb(1c)(NO₃)₃(DMF)]·DMF·0.5H₂O, was determined by single-crystal X-ray diffraction methods. The ligand is found to coordinate in a bidentate fashion, and this is compared against lanthanide coordination chemistry observed for the related ligand, [Ph₂P(O)CH₂] C₅H₄NO.

Introduction

The ligation behavior of the NOPO-class ligand 2-[(diphenyl)phosphinoylmethyl]pyridine N-oxide (1a) toward lanthanide ions, Ln(III), has been examined in our group and found to produce stable 1 : 1, 2 : 1 and 4 : 1 ligand-metal (L : M) complexes.¹ Although the ligand resting state structure has the P=O and N-O bond dipoles rotated away from each other, in all cases examined to date, the ligand is able to rearrange and bind to Ln(III) ions with a relatively strain-free seven-membered bidentate chelate coordination mode. The ready formation of 4:1 L:M complexes suggests that examples of 1 might serve as useful liquid-liquid extractants for f-element ions.² Unfortunately 1a only shows significant solubility in chlorocarbon solvents that are inappropriate for practical solvent extraction purposes. Therefore, a general synthesis for derivatives with aliphatic substituents was sought.³ One such compound with 2-ethylhexyl substituents, [(2- $EtHx)_2P(O)CH_2C_5H_4NO$ (1b), was prepared and found to be soluble in aromatic and aliphatic solvents.⁴ Initial extraction studies with 1b in dodecane revealed undesirable formation of a third phase during extractions. However, toluene solutions of 1b showed sharp phase separation and extractions of Eu(III) and Am(III) with 0.05 M 1b in toluene gave favorable performance.⁴ Although distribution ratios for 1b are not as large as found for the two-armed tridentate analog, [(EtHx)₂P(O)CH₂]₂C₅H₃NO (2b), interest in one-armed ligands 1 as practical liquid-liquid extraction reagents has remained strong.

In this regard, new multi-component extraction processes (UNEX) are under study in a number of programs. These typically address separations of Cs, Sr, and actinide ions from acidic

^cOak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, USA



aqueous solutions obtained from nitric acid dissolution of solid nuclear materials.⁵⁻⁸ In a current option the process employs a carbamoylmethyl phosphine oxide (CMPO), Ph₂P(O)CH₂C(O)N(*n*-Bu)₂ as the actinide ion extractant and phenyl trifluoromethyl sulfone (FS-13) as the organic diluent. As formulated, good partitioning of low concentrations of Ln and An ions is observed; however, reduced performance is found when high metal ion concentrations are encountered. In part this is a result of low organic phase solubility of the CMPO/metal complexes in FS-13.

In the present contribution, we describe the synthesis of new NOPO ligands $\{[2-(CF_3)C_6H_4]]_2P(O)CH_2]\}C_5H_4NO$ (1c) and $\{[3,5-(CF_3)_2C_6H_3)]_2P(O)CH_2]\}C_5H_4NO$ (1d) that carry CF₃ substituted aryl substituents. It was anticipated that the CF₃ functionalized aryl ligands would be more easily prepared and purified relative to 1b and that they might display improved solubility in FS-13 compared to CMPO ligands. It was also of interest to determine if the CF₃ groups would noticeably alter the coordination ability of the NOPO fragment due to greater steric demands or increased electron withdrawal from the P=O donor center.

Results and discussion

The new CF₃ derivatized phosphinoylmethyl pyridine compounds { $[2-(CF_3)C_6H_4]_2P(O)CH_2$ }C₅H₄N, **3c**, and { $[3,5-(CF_3)_2C_6H_3]_2P(O)CH_2$ }C₅H₄N, **3d** were isolated in good yield (86 and 60%, respectively) from the combination of the required phosphinoyl Grignard reagents [$2-(CF_3)C_6H_4$]₂P(O)MgBr and [$3,5-(CF_3)_2C_6H_3$]₂P(O)MgBr as summarized in Scheme 1.

Following work-up and chromatographic purification, the compounds were obtained as white (3c) and brown (3d) solids. The

^aDepartment of Chemistry, University of New Mexico, Albuquerque, NM 87131, USA. E-mail: rtpaine@unm.edu

^bIdaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA

[†] Electronic supplementary information (ESI) available: Crystallographic and computational data. CCDC reference numbers 715682–715686. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b905947d



isolated intermediates were then N-oxidized with *m*-CPBA and the target ligands **1c** and **1d** were isolated as analytically pure crystalline solids in 60 and 58% yields, respectively. The ligands are soluble in acetone, ethyl acetate, chloroform, methylene chloride, acetonitrile, alcohols and DMF and insoluble in benzene and hexane. Further, and most importantly, they are soluble in FS-13 (**1c**, 0.26 M; **1d**, 0.07 M) while the derivatives **1a** and **1b** have solubilities < 0.001 M in FS-13.

The identities of the phosphinoylmethyl pyridines and phosphinoylmethyl pyridine N-oxides have been confirmed by spectroscopic analyses. Each of 3c, 3d, 1c and 1d display intense $[M + H^+]$ and [M + Na⁺] ions in high-resolution electrospray ionization mass spectra. Based upon earlier studies of NPO and NOPO ligands having any substituents,^{1,3} it was expected that the v_{PO} infrared stretching frequency would appear in the region 1150–1200 cm⁻¹. In particular, the parent compounds $[Ph_2P(O)CH_2]C_5H_4N$ (3a) and $[Ph_2P(O)CH_2]C_5H_4NO(1a)$ show bands assigned to v_{PO} modes at 1190 cm⁻¹ (3a) and 1186 cm⁻¹ (1a), respectively. It might be expected that placement of electron-withdrawing CF₃ groups on the aryl rings would result in a significant up-frequency shift of v_{PO} . However, in the new CF_3 substituted analogs, the v_{PO} frequencies are assigned to strong bands at 1177 cm⁻¹ (3c), 1186 cm⁻¹ (3d), 1190 cm⁻¹ (1c) and 1186 cm⁻¹ (1d). These values are shifted little from the v_{PO} for 3a and 1a, and they are comparable to v_{PO} for Ph₃PO (1191 cm⁻¹)⁹ and (4-CF₃C₆H₄)₃PO (1199 cm⁻¹).⁹ The lack of a clear trend in the observed data suggest that neither N-oxidation or CF₃-substitution on the aryl substituents dramatically alter the electron density in the P=O donor groups.

In order to support the band assignments and to test the conclusions drawn from the spectra, Gaussian calculations for each molecule were performed. The computed v_{PO} values are 1194 cm⁻¹ (**3a**), 1233 cm⁻¹ (**3c**), 1215 cm⁻¹ (**3d**), 1191 cm⁻¹ (**1a**), 1239 cm⁻¹ (**1c**) and 1201 cm⁻¹ (**1d**) that are little shifted from v_{PO} for **3a** and **1a**. Given the expected computational error for v_{PO} (±30 cm⁻¹), these calculated frequencies can be considered to be the same, and comparable to the computed value of 1187 cm⁻¹ for Ph₃PO.¹⁰

Strong CF₃ stretching modes for **3c**, **3d**, **1c** and **1d** seriously complicate the fingerprint region,⁹ 1350–1120 cm⁻¹, where the N–O stretching vibration also would be expected to appear.¹¹ In the measured spectra several bands appear in this region for both pyridine and N-oxidized compounds and a confident assignment of v_{NO} for **1c** and **1d** can not be made. Gaussian

calculations suggest the appearance of a strong, low frequency N–O stretching vibration and a weaker, higher frequency N–O stretching vibration: **1a** 1275, 1320; **1c** 1273, 1329; **1d** 1274, 1314 cm⁻¹. These also can be compared against the measured (1265 cm⁻¹)¹¹ and computed (1322 cm⁻¹) v_{NO} frequency for pyridine *N*-oxide. Given the larger error associated with computed v_{NO} frequencies (±50 cm⁻¹), the small differences should not be ascribed to electronic shifts in the pyridine N–O band due to the addition of one or two CF₃ groups to each aryl group.

The ³¹P NMR spectra for 3c, 3d, 1c and 1d all display a single resonance that appears at δ 30.7, 27.2, 33.0 and 28.7, respectively. These can be compared against the values for 3a, δ 30.2 and 1a, δ 31.7. In each case, N-oxidation leads to a small downfield shift (1-3 ppm) and a similar effect appears with N-oxidation of the two-armed NPOPO ligands.^{1,3,4} It is interesting to note that the resonances for $3,5-(CF_3)_2C_6H_3$ derivatives 3d and 1d appear slightly upfield of the resonances for the 2-(CF_3)C₆H₄ 3c and 1c and the unsubstituted aryl 3a and 1a derivatives. A clear rational for this observation is not apparent at this time but a similar observation is found with related dithiophosphinic acids.¹² The ¹H and ¹³C{¹H} NMR spectra are dominated by overlapping resonances from the substituted aryl and pyridine rings and only partial assignments have been made. The exo-CH₂P(O) group provides a signature doublet resonance due to coupling with the P-atom: ¹H δ 4.10 (J = 14.5 Hz) (3c), 4.09 (J = 15.5 Hz) (3d), 4.35 (J = 14.3 Hz) (1c), 4.30 (J = 15.3 Hz) (1d); ¹³C{¹H} δ 41.6 (J =68.1 Hz) (**3c**), 41.6 (J = 66.6 Hz) (**3d**), 33.4 (J = 92.3 Hz) (**1c**) and 33.9 (J = 68.7 Hz) (1d). These data can be compared with data for **3a**: ¹H δ 3.88 (J = 14.2 Hz), ¹³C{¹H} δ 40.7 (J = 64 Hz) and **1a**: ¹H δ 4.22 (J = 14 Hz), ¹³C{¹H} δ 30.7 (J = 66 Hz). Additional assignments for aryl and pyridine ring resonances provided in the Experimental section were aided by assignments for related secondary phosphine oxides.13

The recent observation by one of us^{12} of short intramolecular non-bonded $P(v) \cdots F$ interactions between two fluorine atoms and the phosphorus atom in $[2-(CF_3)C_6H_4]_2P(S)(SH)$ of 2.968 and 3.165 Å led here to determinations of the molecular structures of **3c**, **3d**, **1c** and **1d**. In general, the molecular structures are similar and views are shown in Figs. 1–4. A summary of selected



Fig. 1 Molecular structure and atom labeling scheme for $\{[2-(CF_3)C_6H_4]_2P(O)CH_2\}C_3H_4N, 3c.$



Fig. 2 Molecular structure and atom labeling scheme for $\{[3,5-(CF_3)_2-C_6H_3]_2P(O)CH_2\}C_5H_4N, 3d$.



Fig. 3 Molecular structure and atom labeling scheme for {[2-(CF₃)- C_6H_4]₂P(O)CH₂} C_5H_4 NO, 1c.

bond lengths is given in Table 1. The structure of each molecule consists of a planar pyridine or pyridine *N*-oxide ring with a



Fig. 4 Molecular structure and atom labeling scheme for $\{[3,5-(CF_3)_2-C_6H_3]_2P(O)CH_2\}C_5H_4NO, 1d$.

pendent [2-(CF₃)C₆H₄]₂P(O)CH₂- or [3,5-(CF₃)₂C₆H₃]₂P(O)CH₂arm attached at the 2-position of the pyridine ring. The P=O bond vector is rotated away from the plane of the pyridine or pyridine N-oxide by 50.7° (3c), 61.0° (3d), 44.2° (1c) and 69.4° (1d).¹⁴ The twist of these planes originates from P=O/N-lone pair or P=O/N-bond pair non-bonded repulsions and the twist angles are similar to those observed for [Ph₂P(O)CH₂]₂C₆H₃N (73.3 and -65.9°).¹⁵ It is noted that the 2-CF₃ groups in 3c and 1c appear to constrain the orientation of the P=O group relative to the pyridine/pyridine N-oxide ring to a greater degree as evidenced by the smaller twist angle. The P=O bond lengths in 3d, 1c and 1d are the same (av. 1.484 Å) while the value in 3c is slightly shorter, 1.4734(2) Å. Although the CF_3 groups in 3d and 1d are disordered, there appear to be no close non-bonded interactions between the F-atoms and the P-atom in these two molecules. This is to be expected given the 3,5-positions of the CF₃ substituents on the aryl rings. However, in 3c and 1c several F atoms make close approaches to the backside of the P-atom. The non-bonded $P \cdots F$ distances in **3c**, $P \cdots F4$, 2.889 Å, and $P \cdots F2$, 3.147 Å, and in 1c, $P \cdots F1$, 2.908 Å and 1c $P \cdots F5$, 3.191 Å are shorter than the sum of covalent radii, 3.27 Å.¹⁶ These values compare well against short non-bonded distances in $[2-(CF_3)C_6H_4]_2P(S)(SH)$ (2.968 and 3.165 Å).12

Before undertaking detailed extraction analyses with 1c and 1d and performance comparisons against 1a, it was important

Table 1 Selected bond lengths (Å) for 3c, 1c, 3d, 1d and [Yb(1c)(NO₃)₃(DMF)]·DMF·0.5H₂O

Bond	3c		1c		3d		1d		$[Yb(1c)(NO_3)_3(DMF)] \cdot DMF \cdot 0.5H_2O$	
P=O	P–O	1.4734(2)	P1O2	1.4822(9)	P101	1.4874(14)	P–O2	1.4825(12)	P-01	1.5016(11)
P–C	P–C6	1.8262(15)	P1-C6	1.8180(13)	P1-C6	1.8077(18)	P–C6	1.8325(17)	P-C6	1.8123(14)
	P-C12	1.8396(15)	P1-C7	1.8177(12)	P1-C7	1.8178(17)	P–C7	1.8165(17)	P–C7	1.8236(16)
	P-C19	1.8175(15)	P1-C14	1.8180(13)	P1-C15	1.8070(15)	P-C15	1.8052(17)	P-C14	1.8127(17)
N–O			N1-01	1.3064(14)			N–O1	1.303(2)	N1-O2	1.3318(16)
N–C	N–C1	1.339(2)	N1-C1	1.3591(17)	N1-C1	1.344(3)	N–C1	1.359(3)	N1-C1	1.351(2)
	N–C5	1.342(2)	N1-C5	1.3682(17)	N1-C5	1.334(3)	N–C5	1.364(3)	N1-C5	1.353(2)
C–C	C5–C6	1.507(2)	C5–C6	1.4885(17)	C5–C6	1.510(2)	C5–C6	1.488(2)	C5–C6	1.489(2)
Yb–O t	ond lengths	for [Yb(1c)(NC	0 ₃) ₃ (DMF)]·I	DMF-0.5H ₂ O						
	Yb–O1	2.2499(11)	Yb–O3	2.2575(11)	Yb–O5	2.3997(13)	Yb–O8	2.4055(12)	Yb-O11	2.4362(13)
	Yb–O2	2.2660(11)	Yb–O4	2.4079(14)	Yb–O7	2.4908(13)	Yb-O10	2.3831(13)		

to examine the coordination behavior of 1c toward Ln(III) ions. If differences are to appear, they should come with a small lanthanide ion and 1c where the 2-CF₃ substituents might be expected to produce steric congestion in the neighborhood of the coordinated Ln(III) ion. Initially, 1c and Yb(NO₃)₃ were combined in a 1:1 ratio in MeOH. The mixture produced a solid that was recrystallized from DMF. Infrared spectra for the complex show numerous overlapping bands in the region 1500–1000 cm⁻¹ and assignments of $v_{\rm NO}$ and $v_{\rm PO}$ and hence coordination shifts could not be confidently made. However, X-ray diffraction quality crystals were obtained and the molecular structure of the complex was determined. A view of the molecule is shown in Fig. 5 and selected bond lengths are listed in Table 1. The asymmetric unit consists of one molecule of $[Yb(1c)(NO_3)_3(DMF)]$ and an outer-sphere DMF molecule hydrogen bonded to a partially occupied (50%) water molecule. The inner sphere around the Yb(III) contains one molecule of 1c and three NO₃⁻ ions all coordinated in a bidentate fashion and an O-bonded DMF. The resulting nine-coordinate coordination polyhedron approximates a mono-capped square antiprism. The Yb-O1(P) bond length, 2.2499(11) Å, and the Yb-O2(N) bond length, 2.2660(11) Å, can be compared to the related bond lengths, 2.252(5) and 2.2354 Å [Yb-O(P)] and 2.260(4) Å [Yb-O(N)] in $Yb(2a)_2(NO_3)_3$ where $2a = [Ph_2P(O)CH_2]_2C_5H_3NO$. There, 2a acts as a tridentate ligand.¹ Structural data also have been reported for 2 : 1 and 4 : 1 inner-sphere complexes involving the bidentate parent ligand 1a:³ Pr(1a)₂(NO₃) Pr–O(P) 2.439(6), 2.474(6) Å and Pr–O(N) 2.467(7), 2.426(7) Å; Tb(1a)₄³⁺ Tb–O(P) 2.335(5), 2.379(5), 2.399(5), 2.338(5) Å and Tb-O(N) 2.398(6), 2.420(6), 2.411(6), 2.395(6) Å. The majority of the comparable (*i.e.*, M-O(P) or M-O(N)) differences between the Pr-O, Tb-O and Yb-O bond lengths result from the differences in lanthanide ionic radii. However, in most case, in the same molecule, the M-O(P) bond length is shorter than the M–O(N) bond length consistent with the P=O donor group acting as the stronger donor. The phosphoryl group bond length P-O1, 1.5016(11) Å also shows



Fig. 5 Molecular structure and atom labeling scheme for $[Yb(1c)(NO_3)_3(DMF)]$ ·DMF·0.5H₂O (outer-sphere DMF and 0.5 H₂O omitted for clarity).

significant bond lengthening relative to the bond length in the free ligand **1c**, 1.4822(9) Å and the N-oxide bond length, 1.3318(16) Å, is elongated relative to that in **1c**, 1.3064(14) Å consistent with strong ligand–Yb(III) ion interactions. It is also noteworthy that the twist angle between the coordinated P=O and N–O groups is 66.8° which is larger than in the free ligand. Lastly, it is found that both CF₃ groups of the coordinated ligand are disordered over two positions.¹⁷ Nonetheless, two F-atom positions on each group result in non-bonded separations, F2…P 3.109 Å, F5…P 3.069 Å, F8…P 2.929 Å and F12…P 2.881 Å, that are shorter than the sum of van der Waals radii. This is consistent with the retention of backside P(v)…F interactions in the complex.

Given that our prior work with the related bidentate ligand **1a** led to isolation and structure determinations for 2 : 1 and 4 : 1 ligand–lanthanide complexes,¹ efforts were also made in the present study to prepare 2 : 1 and 4 : 1 complexes using the new ligand **1c**, several lanthanide nitrates and a wide range of reaction solvents. In each case, complexation was indicated by very rapid formation of precipitates that resisted dissolution and crystal growth. Hence, the identity of these complexes remains undefined. The apparent low solubility of the complexes under synthesis conditions could complicate the potential use of the ligand as a solvent extractant since the extraction complexes must remain soluble in the organic process solvent. However, we note here that under extraction conditions (~0.1 M **1c** in FS-13 and low [Ln(III)]), the complexes are soluble in the organic phase.

Initially it was thought that the CF₃ groups of 1c might reduce the effective donor strength of the ligand through electron withdrawal from the P=O donor group. It was also considered that 2-CF₃ substitution on the phosphoryl aryl rings might impose steric hindrance to formation of complexes with Ln(III) ions. However, these factors apparently do not impact the ability of 1c to form at least the 1 : 1 complex isolated and structurally characterized here. The next question then becomes: can one or both of these factors be responsible for the inability to isolate 2:1 and 4:1 complexes which are formed with the parent bidentate ligand 1a? In an attempt to address, at the least, the steric issue, we have completed molecular modeling calculations for 2 : 1 (Fig. 6) and 4:1 (Fig. 7) compositions. The starting structures were those found from the crystal structure determinations for $Pr(1a)_2(NO_3)_3$ and $Tb(1a)_{4^{3+}}$. These structures were optimized with an extended MM3 force field to obtain minimum energy gas-phase structures. At this point, CF₃ groups were added at the 2-position of each phenyl ring and the structures re-optimized. The calculations, as summarized in Table 2, indicate that there is no steric reason for the 2:1 or 4:1 complexes not to form. In fact, the calculations suggest that the CF₃ substituted ligands provide slightly more sterically favorable structures.

 Table 2
 Computed molecular mechanics strain energies (kcal mol⁻¹)

Complex	$U_{ m complex}$	$nU_{ m ligand}$	$\Delta U = U_{ m complex} - n U_{ m ligand}$
$Ln(1a)_2(NO_3)_3$	45.63	29.26	16.4
$Ln(1c)_2(NO_3)_3$	76.53	63.66	12.9
$Ln(1a)_4[(NO_3)_3$	81.89	58.52	23.4
$Ln(1c)_4](NO_3)_3$	144.89	127.32	17.6



Fig. 6 Computed, energy minimized structure for the 2 : 1 complex, $Pr(1c)_2(NO_3)_3$.



Fig. 7 Computed, energy minimized structure for the 4 : 1 complex, $Tb(\mathbf{1c})_4^{3+}$.

Conclusion

The objectives of this study centered on decoration of the aryl substituents on phosphorus in ligand **1a** with CF_3 groups in order to enhance the solubility of this ligand type in the fluorocarbon solvent FS-13. It was also of interest to determine if CF_3 decoration would adversely impact the coordination ability of the NOPOclass ligand. The results of the study show that both **1c** and **1d** are more soluble in FS-13 than is **1a** with the greater solubility found in the 2-substituted derivative **1c**. In addition, both of the new ligands are solids and they are more easily purified than **1a**. Despite the presence of the electron-withdrawing CF₃ substituents, the CF₃ decorated ligands form complexes with Ln(NO₃)₃. One complex, [Yb(1c)(NO₃)₃(DMF)](DMF)(H₂O)_{1/2}, was isolated, structurally characterized and the ligand confirmed to act as a bidentate chelate. These results suggest additional modifications to the parent structure 1c that should further enhance ligand solubility and complexation behavior. These modified systems currently under development will be the focus of detailed extraction analyses in the future.

Experimental

The organic reagents and solvents were obtained from Aldrich Chemical Co. or VWR and they were used as received. Solvents were dried by standard procedures and stored under dry nitrogen. NMR spectra were recorded on a Bruker FX-250 spectrometer using H₃PO₄ (³¹P) and Me₄Si (¹H, ¹³C) as external standards. Downfield shifts from the reference were designated as + δ . Mass spectra were obtained from the University of New Mexico Mass Spectrometry Facility. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental analyses were determined by Galbraith Laboratories.

Ligand syntheses

2-(Bromomethyl)pyridine was prepared by neutralization of 2-(bromomethyl)pyridine hydrobromide with a saturated aqueous solution of NaHCO₃¹. **CAUTION**: This reagent and its solutions should be handled in a well ventilated fume hood. The compound is an aggressive skin irritant and contact should be avoided. The compound has a small vapor pressure at 23 °C making it a potential bronchial irritant as well. The HBr neutralized ligand should be used immediately as it has a short shelf-life.

2-[Bis(2-(trifluoromethylphenyl))phosphinoylmethyl]pyridine (3c)

A solution of 2-bromobenzotrifluoride (8.03 mL, 59.0 mmol) in dry THF (10 mL) was added dropwise to a stirred suspension of Mg turnings (1.43 g, 59.0 mmol) in dry THF (10 mL) and stirred (1 h). The temperature rose during the addition and the mixture was then cooled (23 °C). A solution of diethyl phosphite (2.01 mL, 15.7 mmol) in dry THF (10 mL) was added dropwise and this mixture was first refluxed (1 h) and then cooled (23 °C). A solution of 2-(bromomethyl)pyridine (1.0 g, 7.8 mmol) in dry THF (10 mL) was added dropwise (23 °C) and the resulting mixture stirred and refluxed (12 h). The mixture was quenched with saturated aqueous NH₄Cl solution (100 mL) and the aqueous phase extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried (Na₂SO₄) and vacuum evaporated. The resulting colorless oil was purified by flash chromatography (silica gel, 70-230 mesh, elution MeOH–CH₂Cl₂ 1 : 99). The compound 3c was obtained as a white powder (2.9 g, 86%) mp 108-110 °C. Crystals of 3c were grown from EtOAc (Found: C, 55.92; H, 3.45; N, 3.31%). C₂₀H₁₄NOF₆P requires C, 55.96; H, 3.29; N, 3.26%. HRMS (ESI): m/z 430.0805 $[M + H^+]$, 452.0609 $[M + Na^+]$: C₂₀H₁₅NOF₆P requires 430.0795. IR (KBr, cm⁻¹): 3075 (m), 3029 (sh, w), 2924 (sh, w), 2854 (m), 2785 (w), 2612 (w), 2091 (w), 1998 (w), 1960 (vw), 1924 (vw), 1888 (vw), 1850 (w), 1780 (vw), 1738 (m), 1657 (m), 1586 (s), 1474 (s), 1439 (s), 1402 (m), 1311 (vs), 1265 (vs), 1227 (vs), 1177 (sh, s), 1128 (vs), 1034 (vs), 888 (m), 824 (s), 776 (vs), 707 (s), 636 (m), 592 (s). ³¹P NMR (CDCl₃): δ 30.7. ¹H NMR (CDCl₃): δ 8.30 (d, $J_{\rm HH} = 5.0$ Hz, 1 H, py), 8.16 (dm, $J_{\rm HP} = 14.0$ Hz, 2 H), 7.75 (m, 2 H), 7.62–7.49 (m, 6 H), 7.06 (m, 1 H), 4.09 (d, ² $J_{\rm HP} =$ 14.5 Hz, 2 H). ¹³C{¹H} NMR (CDCl₃): δ 152.4 (d, ² $J_{\rm CP} = 7.2$ Hz, py), 149.4 (py), 136.6 (py), 134.6 (d, $J_{\rm CP} = 8.2$ Hz), 132.2 (d, $J_{\rm CP} =$ 10.7 Hz), 131.9 (d, ¹ $J_{\rm CP} = 77.4$ Hz), 131.5 (d, $J_{\rm CP} = 11.6$ Hz), 131.5 (m), 127.8 (m), 126.0 (py), 124.2 (d, ¹ $J_{\rm CF} = 258$ Hz, CF₃), 41.6 (d, $J_{\rm CP} = 68.1$ Hz, CH₂).

2-[Bis(3,5-bis(trifluoromethylphenyl))phosphinoylmethyl]pyridine (3d)

A solution of 3,5-bis(trifluoromethyl)bromobenzene (5.0 mL, 29.0 mmol) in dry THF (10 mL) was combined dropwise with Mg turnings (0.7 g, 29.0 mmol) in dry THF (10 mL). The temperature rose during the addition and the mixture was stirred (1 h). The mixture was cooled (23 °C), a solution of diethyl phosphite (1.0 mL, 7.8 mmol) in dry THF (10 mL) was added dropwise and then refluxed (1 h). To the resulting mixture, a solution of 2-(bromomethyl)pyridine (1.0 g, 7.8 mmol) in dry THF (10 mL) was added dropwise (23 °C), the mixture stirred and then refluxed (12 h). The mixture was quenched with saturated aqueous NH₄Cl solution (100 mL), the aqueous phase separated, extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phases dried (Na₂SO₄). The solvent was evaporated leaving a dark oil that was purified by flash chromatography (silica gel, 70-230 mesh, elution MeOH–CH₂Cl₂ 1 : 99). The compound 3d was obtained as a brown solid (2.6 g, 60%) mp; 132–134 °C. X-Ray quality crystals were obtained by recrystallization from EtOAc. HRMS (ESI): m/z566.0536 [M + H⁺], 588.0352 [M + Na⁺]: C₂₂H₁₃NOF₁₂P requires 566.0543. IR (KBr, cm⁻¹): 3074 (m), 3020 (m), 2962 (m), 2922 (m), 2854 (m), 2789 (vw), 2644 (vw), 2557 (vw), 2273 (w), 2225 (w), 2118 (vw), 1933 (w), 1843 (w), 1619 (s), 1473 (s), 1437 (s), 1369 (vs), 1284 (vs), 1186 (vs), 1134 (vs), 1000 (w), 847 (m), 787 (m), 739 (m), 691 (m), 616 (m), 519 (m). ³¹P NMR (CDCl₃): δ 27.2. ¹H NMR (CDCl₃): δ 8.43 (d, $J_{\rm HH}$ = 4.0 Hz, py), 8.30 (d, ${}^{3}J_{\rm HP}$ = 11.5 Hz, 4 H), 8.05 (s, 2 H), 7.61 (t, ${}^{3}J_{HH} = 6.0$ Hz, 1 H), 7.32 (d, ${}^{3}J_{HH} =$ 7.7 Hz, 1 H), 7.10 (t, ${}^{3}J_{HH} = 4.5$ Hz, 1 H), 4.09 (d, ${}^{1}J_{HP} = 15.5$ Hz, 2 H). ¹³C NMR (CDCl₃): δ 150.6 (d, ² J_{CP} = 7.3 Hz, py), 149.6 (py), 137.1, 134.5 (d, ${}^{1}J_{CP} = 98.7$ Hz), 132.4 (dq, ${}^{2}J_{CF} = 34.2$ Hz, ${}^{3}J_{CP} =$ 12.0 Hz), 131.5 (m, py), 126.2 (d, $J_{CP} = 3.3$ Hz), 125.1 (d, $J_{CP} =$ 4.7 Hz), 124.0 (q, $J_{CF} = 272.9$ Hz, CF₃), 122.7 (d, $J_{CP} = 2.5$ Hz, py), 41.0 (d, ${}^{1}J_{CP} = 66.3$ Hz, CH₂).

Oxidative syntheses of 1c and 1d

Samples of **3c** and **3d** (1 equiv.) were dissolved in CH_2Cl_2 (10 mL) and combined with *m*-chloroperbenzoic acid (77%, 1.3 equiv). The resulting mixtures were stirred and refluxed (12 h) then quenched with saturated aqueous NaHCO₃ solution (30 mL). The phases were separated, the aqueous phase extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phases dried (Na₂SO₄).

Ic was isolated as a tan solid following purification by flash chromatography using gradient elution with MeOH in CH₂Cl₂ (1–10%) (0.34 g, 58%), mp 142–144 °C. X-Ray quality crystals were obtained by recrystallization from MeOH (Found: C, 53.60; H, 3.41; N, 3.09). C₂₀H₁₄NO₂F₆P requires C, 53.95; H, 3.17; N, 3.15. HRMS (ESI): m/z 446.0749 [M + H⁺], 468.0566 [M + Na⁺]: C₂₀H₁₅F₆NO₂P requires 446.0745. IR (KBr, cm⁻¹): 3106 (m),

3068 (s), 3025 (s), 2973 (m), 2924 (m), 2884 (s), 2792 (w), 2456 (w), 2094 (w), 1993 (m), 1951 (w), 1880 (m), 1812 (w), 1735 (m), 1692 (w), 1652 (w), 1585 (m), 1490 (s), 1438 (s), 1313 (vs), 1262 (vs), 1256 (vs), 1235 (vs), 1190 (vs), 1116 (vs), 1035 (s), 903 (w), 863 (m), 825 (m), 817 (m), 783 (s), 727 (m), 708 (m), 644 (m), 602 (m). ³¹P NMR (CDCl₃): δ 32.7. ¹H NMR (CDCl₃): δ 8.2 (m, 3 H), 7.85 (dd, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 2.5 Hz, ⁴J_{HH} = 2.5 Hz, 1 H), 7.80 (m, 2 H), 7.65 (m, 4 H), 7.2 (m, 2 H), 4.35 (d, J_{HP} = 14.3 Hz, 2 H). ¹³C NMR (CDCl₃): δ 143.1 (d, ⁴J_{CP} = 6.5 Hz), 139.1 (py), 133.7 (d, J_{CP} = 9.3 Hz), 132.2 (d, J_{CP} = 11.7 Hz), 131.1 (d, ¹J_{CP} = 95.3 Hz), 129.1 (d, J_{CP} = 3.8 Hz, py), 127.7 (m), 126.1 (q, ¹J_{CF} = 204 Hz), 31.9 (d, ¹J_{CP} = 72.5 Hz).

1d was isolated as a solid and purified by crystallization from EtOAc (0.24 g, 60%) mp 156–158 °C (Found: C, 45.14; H, 2.25; N, 2.42). C₂₂H₁₂NO₂F₁₂P requires C, 45.46; H, 2.08; N, 2.41. HRMS (ESI): m/z 582.0487 [M + H⁺], 604.0312 [M + Na⁺]: $C_{22}H_{13}NO_2F_{12}P$ requires 582.0492. IR (KBr, cm⁻¹): 3056 (m), 3030 (m), 2961 (m), 2922 (s), 2854 (m), 1938 (w), 1824 (w), 1737 (m), 1617 (s), 1493 (m), 1446 (s), 1366 (s), 1282 (vs), 1176 (vs), 1129 (vs), 950 (w), 908 (m), 885 (m), 836 (m), 770 (s), 683 (s), 612 (m), 583 (w), 571 (m), 527 (s). ³¹P NMR (CDCl₃): δ 28.7. ¹H NMR (CDCl₃): δ 8.47 (d, ${}^{3}J_{HP} = 11.7$ Hz, 4 H) 8.01 (d, ${}^{4}J_{HP} =$ 6.3 Hz, 1 H), 8.05 (s, 2 H), 7.60 (ddd, ${}^{3}J_{HH} = 7.8$ Hz, ${}^{4}J_{HH} = 2.3$ Hz, ${}^{4}J_{\rm HH} = 2.3$ Hz, 1 H), 7.20 (m, 2 H), 4.30 (d, $J_{\rm HP} = 15.3$ Hz, 2 H). ¹³C{¹H} NMR (CDCl₃): δ 142.5 (d, $J_{CP} = 9.0$ Hz), 139.90 (py), 134.2 (d, ${}^{1}J_{CP} = 100.4$ Hz), 132.4 (dq, ${}^{2}J_{CF} = 34.2$ Hz, ${}^{3}J_{CP} =$ 12.7 Hz), 131.1 (d, ${}^{2}J_{CP} = 8.0$ Hz), 127.6 (d, $J_{CP} = 4.9$ Hz, py), 126.3 (d, $J_{CP} = 3.1$ Hz), 125.8 (d, $J_{CP} = 2.6$ Hz, py), 125.1 (d, $J_{CP} =$ 2.9 Hz, py), 122.5 (q, ${}^{1}J_{CF} = 273.5$ Hz), 33.4 (d, ${}^{1}J_{CP} = 68.7$ Hz).

Synthesis of complex

A sample of **1c** (0.2 g, 0.4 mmol) in MeOH (5 mL) was combined with Yb(NO₃)₃·5H₂O (0.2 g, 0.4 mmol) in MeOH (5 mL) and the solution stirred (23 °C). During 15 min a precipitate formed and stirring was continued (12 h). The resulting white solid was recovered by filtration (0.3 g, 93% based upon Yb(**1c**)(NO₃)₃). Crystals were obtained by dissolution of the solid in hot DMF followed by slow evaporation. IR (KBr, cm⁻¹): 3099 (s), 3033 (s), 2941 (s), 2815 (w), 2598 (w), 2521 (m), 2458 (w), 2352 (w), 2314 (m), 2226 (w), 2166 (w), 2103 (w), 2060 (m), 2019 (m), 1984 (m), 1903 (w), 1865 (w), 1666 (vs), 1498 (vs), 1389 (vs), 1312 (vs), 1239 (vs), 1173 (s), 1123 (vs), 1032 (vs), 873 (s), 813 (s), 777 (s), 688 (s), 653 (m), 630 (m), 606 (m), 587 (m), 531 (s), 512 (s).

Single-crystal X-ray diffraction

Single-crystals of the ligands and complex were placed in glass capillaries and sealed. Crystal data were collected on a Bruker X8 Apex 2 CCD-based X-ray diffractometer outfitted with an Oxford Cryostream 700 low temperature attachment and a normal focus Mo X-ray tube ($\lambda = 0.71073$ Å) operated at 1.5 kW. The data frames were integrated with Bruker SAINT software and processed with SADABS. The structures were solved and refined with Bruker SHELXTL.¹⁸ Lattice and data collection parameters are presented in Table 3. Some specific comments on each structure determination follow.

Table 3	Crystallographic and	d X-ray data	collection	parameters
---------	----------------------	--------------	------------	------------

	3c	1c	3d	1d	[Yb(1c)(NO ₃) ₃ (DMF)]· DMF·0.5H ₂ O
Identification code	rpsl21	rpsl32	rpsl20a	rpsl22	rpec17
CCDC number	715684	715686	715683	715685	715682
Empirical formula	$C_{20}H_{14}NOF_6P$	$C_{20}H_{14}NO_2F_6P$	$C_{22}H_{12}NOF_{12}P$	$C_{22}H_{12}NO_2F_{12}P$	$C_{26}H_{29}N_6O_{13}5F_6PYb$
$M_{\rm r}$	429.29	445.29	565.30	581.30	959.56
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	C2/c	C2/c
a/Å	8.9554(4)	7.8219(6)	11.6362(12)	18.7789(6)	29.2303(17)
b/Å	9.6902(4)	8.8196(7)	19.362(3)	24.0769(8)	13.5964(8)
c/Å	11.0339(4)	14.4992(12)	10.6850(13)	11.4618(4)	21.6915(12)
$\alpha/^{\circ}$	88.599(2)	84.198(4)	90	90	90
$\beta/^{\circ}$	74.127(2)	81.657(4)	104.192(6)	117.727(2)	124.507(2)
$\gamma/^{\circ}$	88.578(2)	72.516(4)	90	90	90
$V/Å^3$	920.57(7)	942.18(13)	2333.9(5)	4587.2(3)	7104.0(7)
Ζ	2	2	4	8	8
$D_{c}/{\rm g}~{\rm cm}^{-3}$	1.549	1.570	1.609	1.683	1.794
μ/mm^{-1}	0.219	0.221	0.230	0.239	2.781
T/K	223	225	223	223	225
Reflections collected	19527	25744	32662	38656	100265
Reflections unique	6424	7013	6258	5720	13060
$R_{\rm int}$	0.0162	0.0237	0.0172	0.0219	0.0336
$R\widetilde{1}[I > 2\sigma(I)]$	0.0500	0.0426	0.0537	0.0473	0.0204
wR2 (all data)	0.1615	0.1254	0.2327	0.1354	0.0500

3c. Colorless prism $0.12 \times 0.28 \times 0.48$ mm. The structure solution and refinement were well behaved. All non-hydrogen atoms refined anisotropically and H-atoms were included and refined in ideal positions with fixed $U_{\rm iso} = 1.2U_{\rm eq}$ of C. There was no disorder present.

1c. Colorless prism $0.138 \times 0.276 \times 0.509$ mm. The structure solution and refinement were well behaved. All non-hydrogen atoms refined anisotropically and H-atoms were included and refined in ideal positions with fixed $U_{\rm iso} = 1.5U_{\rm eq}$ of CH₂ and $1.2U_{\rm iso}$ of CH. There was no disorder in the structure.

3d. Colorless prism $0.276 \times 0.440 \times 0.460$ Å. All non-hydrogen atoms were refined anisotropically and H-atoms were included and refined in ideal positions with fixed $U_{iso} = 1.2 U_{eq}$ of C. Three of the four CF₃ groups were rotationally disordered (F on C13, C14 and C21). The F atoms are mostly in two orientations slightly rotated from each other.

1d. Colorless prism $0.161 \times 0.230 \times 0.322$ mm. All nonhydrogen atoms were refined anisotropically and H-atoms were included and refined in ideal positions with fixed $U_{iso} = 1.2U_{eq}$ of C. Residual difference peaks were seen about all CF₃ groups and those about C21 and C22 were larger. These two CF₃ were refined in two positions with 51/49% occupancies.

Yb(1c)(NO₃)₃(DMF). Irregular shape $0.092 \times 0.12 \times 0.414$ mm. The asymmetric unit contains [Yb(1c)(NO₃)₃(DMF)] and one solvent DMF H-bonded to a partially occupied water molecule. All non-hydrogen atoms were refined anisotropically except on the water (O14/O15). All hydrogen atoms were included in ideal positions: terminal methyl hydrogens with $U_{iso} = 1.5U_{eq}$ of C and all other H-atoms on C with $U_{iso} = 1.2U_{eq}$. The partially occupied water (50% occupancy disordered over three positions) was refined isotropically. The F atoms on the C13 and C20 were disordered and treated with a two-position model with disorder

occupancies C13F1F2F3 (77%), C13F4F5F6 (23%); C20F7F8F9 (75%), C20F10F11F12 (25%).

Full descriptions of the disordered groups in 3d, 1d and the complex are presented in ESI. \dagger

Computational analyses

Geometry optimization of ground-state structures and corresponding vibrational frequencies were carried out with the Gaussian 03 suite of programs.¹⁹ Analytic calculations of the energy Hessian confirmed that minimum energy structures had no imaginary frequencies. Given that Pople type triple- ζ are adequate for phosphorus atoms,²⁰ all calculations were performed in the gas-phase with the B3YLP hybrid density functional²¹ and 6-311G(d,p) and 6-311++G(d,p) Pople basis sets. Based on evaluation of the resulting vibrational frequency values produced for both basis sets for 2a and several model compounds, i.e. pyridine N-oxide and triphenylphosphine oxide, the 6-311G(d,p)basis set offered the best balance between computational cost and frequency accuracy. The geometries and energies were not corrected for basis set superposition error (BSSE) since the larger basis sets combined with Density Functional Theory were expected to produce smaller errors.²² The harmonic frequency algorithm employed by Gaussian 03 generates a set of atom motions for each frequency. The visualizer option in GaussView 3.0²³ was employed to identify the frequency values corresponding to v_{PO} and $v_{\rm NO}$. The geometry optimized coordinates and frequencies for the compounds of interest in this paper can be found in the supplemental information.

Acknowledgements

Financial support for this study at UNM was provided by the U.S. Department of Energy (DOE), Chemical Sciences, Geosciences and Biosciences Office, Office of Basic Energy Sciences (Grant DE-FG02–03ER15419).

References

- 1 B. M. Rapko, E. N. Duesler, P. H. Smith and R. R. Ryan, *Inorg. Chem.*, 1993, **32**, 2164.
- 2 K. L. Nash, C. Madic, and J. N. Mathur, Actinide Separation Science in The Chemistry of the Actinide and Transactinide Elements, ed. L. R. Morss, N. M. Edelstein and J. Fuger, Springer, Dordrecht, 2006, ch 24, p. 2622.
- 3 X. Gan, E. N. Duesler and R. T. Paine, Inorg. Chem., 2001, 40, 4420.
- 4 K. L. Nash, C. Lavalette, M. Borkowski, R. T. Paine and X. Gan, *Inorg. Chem.*, 2002, **41**, 5849.
- 5 V. N. Romanovskiy, I. V. Smirnov, V. A. Babain, T. A. Todd, R. S. Herbst, J. D. Law and K. N. Brewer, *Solv. Extr. Ion Exch.*, 2001, **19**, 1.
- 6 J. D. Law, R. S. Herbst, T. A. Todd, V. N. Romanovskiy, V. A. Babain, V. M. Esimantovskiy, I. V. Smirnov and B. N. Zaitsev, *Solv. Extr. Ion Exch.*, 2001, **19**, 23.
- 7 R. S. Herbst, J. D. Law, T. A. Todd, V. N. Romanovskiy, V. A. Babain, V. M. Esimantovskiy, I. V. Smirnov and B. N. Zaitsev, *Solv. Extr. Ion Exch.*, 2002, **20**, 429.
- 8 V. N. Romanovskiy, V. A. Babain, M. Yu. Alyapyshev, I. V. Smirnov, R. S. Herbst, J. D. Law and T. A. Todd, *Sep. Sci. Technol.*, 2006, 41, 2111.
- 9 J. M. Casper and E. E. Remsen, Spectrochim Acta, Part A, 1978, 34, 1.
- 10 V. K. Manchanda and M. S. Subramanian, Aust. J. Chem., 1974, 27, 1573.
- 11 R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectroscopic Identification of Organic Compounds, J. Wiley, New York, 5th edn, 1991, p 130.
- 12 J. R. Klaehn, D. R. Peterman, M. K. Harrup, R. D. Tillotson, T. A. Luther, J. D. Law and L. M. Daniels, *Inorg. Chim. Acta*, 2008, 41, 2522.
- 13 C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sorvestavi, S. Shen, R. Varsolona, X. Wei and C. H. Senanayoke, *Org. Lett.*, 2005, 7, 4277.
- 14 These angles are between the planes C6NC1C2C3C4C5 and C6PO or C6P101 or C6P02 or C6P102.

- 15 E. Szbyk, Z. Y. Zhang, G. J. Palenik, R. C. Palenik and S. O. Colgate, Acta Crystallogr., Sect. C, 1989, 45, 1234.
- 16 J. Boudi, Phys. Chem., 1964, 68, 441.
- 17 Disorder occupancies are: C13F1F2F3 (77%), C13F4F5F6 (23%); C20F7F8F9 (75%), C20F10F11F12 (25%).
- 18 The crystallographic software used in these structure determinations include: G. M. Sheldrick, SHELXTL, v. 6.14, Bruker Analytical X-ray Madison, WI, 2001; G. M. Sheldrick, SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 2003; SAINTPlus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.
- 19 Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. KIene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- 20 A. D. McLean and G. S. Chandler, J. Chem. Phys., 1980, 72, 5639.
- 21 S. P. Sousa, S. A. Fernandes and M. J. Ramos, J. Phys. Chem. A, 2007, 111, 10439.
- 22 Y. Zhano and D. G. Truhlar, J. Chem. Theory Comput., 2005, 1, 415.
- 23 Gauss View, Version 3.09, R. Dennington II, K. Roy, M. Todd, E. John, H. Ken, W. Lee and R. Gilliland, Semichem, Inc., Shawnee Mission, KS, 2003.