NMR spectra of Co(dmho)$_3$ and H[Ru(dmho)$_3$] suggest fluxional cyclohexane rings for these complexes. Indeed, with a rigid structure, the two methylene protons H(4) or H(6) are not magnetically equivalent; nevertheless, each methylene group displays one single ^{1}H NMR signal, in good accordance with fluxional cyclohexane rings. The stereochemistry of the compounds in solution is better clarified with ^{13}C NMR spectroscopy. The proton-decoupled natural-abundance ^{13}C NMR spectra of Co(dmho)$_3$ (Figure 2a) and H[Ru(dmho)$_3$] contain eight distinct signals. The intensities of the signals corresponding to the quaternary carbons are optimized by selected experimental conditions (see Experimental Section). The fact that the ^{13}C NMR spectra display only eight signals suggests, as for the ^{1}H NMR data, three equivalent coordinated ligands in solution.

The proton-coupled spectra obtained by the gated-decoupling technique give the unequivocal assignment of the ^{13}C resonances (Figure 2b). Generally the magnitude of ^{13}C–^{1}H one-bond coupling constants ^{1}J is found to be around 125 Hz for sp$_3$-hybridized carbon.[32] One-bond coupling of C(7) to three H(7) atoms and C(8) to three H(8) atoms yields quadruplets centered at 28.08 and 28.38 ppm with relative intensities 1:3:3:1. Each component of the quadruplet ^{13}C–^{1}H exists with smaller coupling constant values $^{3}J(^{13}\mathrm{C}-^{1}\mathrm{H}) < 12$ Hz.[33] Consequently the two expected quadruplets for C(7) and C(8) resonances appear as a single quadruplet because of the width of each component. Only an evaluation of the bond coupling constant values is extracted: ^{1}J(C(7)–H(7)) $\approx$ ^{1}J(C(8)–H(8)) $\approx$ 130 Hz. An accidental coincidence is observed between one component of the quadruplet and the broad single peak centered at 31.96 ppm, and this latter peak is assigned to the C(5) resonance. Large one-bond ^{13}C–^{1}H couplings are also detected for the C(4) and C(6) resonances. They yield two separated triplets (Figure 2b), which are centered respectively at 49.65 and 51.49 ppm with relative intensities of 1:2:1 (^{1}J(C(4)–H(4)) $\approx$ ^{1}J(C(6)–H(6)) $\approx$ 130 Hz).[33]

Previous assignments of the ^{13}C resonances of the carbon atoms of the chelating ketoximato function are based on spectral comparison of the ketoximato complexes and several (ketonato)cobalt(III) complexes.[34,35] The present assignment is based on ^{3}J(C(2)–H(4)), ^{3}J(C(2)–H(6)) and ^{2}J(C(3)–H(4)), ^{2}J(C(1)–H(6)) couplings. It has been shown earlier that the magnitude of the vicinal $^{3}J(^{13}\mathrm{C}-^{1}\mathrm{H})$ coupling constant depends on the Karplus dihedral angle Φ[36] (^{3}J is very small for $\Phi \approx 90°$). The proton-coupled ^{13}C spectrum of Co(dmho)$_3$ (Figure 2b) exhibits one singlet at 151.85 ppm and two triplets centered at 183.23 and 210.94 ppm, respectively.

The triplets are analogous and nearly symmetrical. The ^{13}C spectrum appears sufficiently first order to permit the extraction of the coupling constants. The two triplets are assigned to the C(3) and C(1) atoms linked to the carbonyl functions (^{2}J(C(1)–H(6)) = ^{2}J(C(3)–H(4)) = 6.2 Hz). The singlet at 151.85 ppm is assigned to the C(2) linked to the oxime function. With a rigid structure of the puckered cyclohexane rings, it is not possible to give a first interpretation of the proton-coupled ^{13}C spectrum. However, fast inversion of the ring is consistent both with the apparent equivalence of the two H(4) and the two H(6) protons given by the ^{1}H NMR spectrum and with the nearly first order appearance of the proton-coupled ^{13}C NMR spectrum. ^{13}C–^{15}N couplings[37] indicate that coordination occurs via N(2) and O(1) atoms in solution, the C(1) signal being more deshielded than the C(3) signal. The ^{13}C NMR spectrum of H[Ru(dmho)$_3$] is very analogous to that of Co(dmho)$_3$ with eight resonances observed in (CD$_3$)$_2$SO: 27.10 (C(7) or C(8)), 28.95 (C(7) or C(8)), 31.89 (C(5)), 48.45 (C(4)), 52.86 (C(6)), 155.27 (C(2)), 185.56 (C(3)), 204.46 ppm (C(1)). Attempts to examine the conformational preference of the cyclohexane rings in solution by NMR spectroscopy are difficult because of the weak solubility of Co(dmho)$_3$ and H[Ru(dmho)$_3$] at low temperature in solvents such as CDCl$_3$ or CD$_2$Cl$_2$. On the basis of the results obtained, it is reasonable to conclude that inversion between conformers is rapid within the time scale of NMR and that there is no conformational preference. Even on fast inversion of the cyclohexane ring the methyl groups C(7) and C(8) cannot be equivalent and the nonequivalence is not conformational in origin.[38]

Registry No. Co(dmho)$_3$, 81987-95-3; H[Ru(dmho)$_3$], 81987-96-4; Na$_3$[Co(NO$_2$)$_6$], 13600-98-1; Na$_2$[Ru(NO)(NO$_2$)$_4$OH], 13859-66-0.

Supplementary Material Available: Listings of anisotropic thermal parameters of the non-hydrogen atoms, least-squares planes and atomic deviations, bond lengths and angles in the ligands, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(32) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

(33) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: New York, 1975; p 48.

(34) Epps, L. A.; Wiener, K.; Stewart, R. C.; Marzilli, L. G. *Inorg. Chem.* **1977**, *16*, 2663.

(35) Gurrieri, S.; Siracusa, G. *Inorg. Chim. Acta* **1971**, *5*, 650.

(36) Ewing, D. F. *Annu. Rep. NMR Spectrosc.* **1975**, *6A*, 389.

(37) Bremard, C.; Mouchel, B.; Sueur, S. *J. Chem. Soc., Chem. Commun.* **1982**, 300.

(38) Beattie, J. K. *Acc. Chem. Res.* **1971**, *4*, 253.

Notes

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Novel Peroxo Complexes of Thorium Containing Organic Ligands

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There is considerable interest in peroxo complexes of transition metals as such compounds serve as reagents and catalysts in organic synthesis.[1-5] We have been interested in extending our studies to the actinide elements uranium[6] and thorium. Thorium is of interest as an analogue of titanium. The propoxide of the latter element is an especially useful catalyst in epoxidation reactions with *tert*-butyl hydroperoxide.[7]

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(1) Westland, A. D.; Haque, F.; Bouchard, J. M. *Inorg. Chem.* **1980**, *19*, 225.

(2) Muccigrosso, D. A.; Jacobson, S. E.; Apgar, P. A.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 7063.

(3) Mimoun, H.; de Roch, I. S.; Sajus, L. *Tetrahedron* **1970**, *26*, 37.

(4) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1.

(5) Olah, G. A.; Welch, J. *J. Org. Chem.* **1978**, *43*, 2830.

(6) Westland, A. D.; Tarafder, M. T. H. *Inorg. Chem.* **1981**, *20*, 3992.

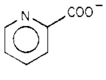
(7) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

0020-1669/82/1321-3228$01.25/0

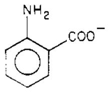
Table I. Analytical Data and Other Physical Properties of the Th(IV) Complexes[a]

no.	compd	% Th calcd	% Th found	% C calcd	% C found	% H calcd	% H found	molar conductance, Ω^{-1} cm^2 mol^{-1} [b]
1	$[Th(C_5H_4NCOO)_2Cl_2]$	42.49	42.61	26.37	26.42	1.46	1.45	43.05
2	$[Th(C_6H_4NH_2COO)_2Cl_2]$	40.41	39.96	29.26	29.22	2.09	2.11	48.0
3	$[Th(C_6H_4NH_2O)_2Cl_2]$	44.78	44.83	27.79	27.74	2.31	2.33	45.5
4	$[Th(C_5H_3N(COO)_2)_2]$	41.28	41.35	29.89	29.78	1.06	1.06	7.8
5	$[Th(C_{14}H_9NO_3)_2]$	32.67	32.71	47.32	47.53	2.53	2.55	3.5
6	$[Th(C_5H_4NCOO)_2(O_2)]$	45.66	45.79	28.34	28.52	1.57	1.59	0.60
7	$[Th(C_6H_4NH_2COO)_2(O_2)]$	43.28	43.36	31.34	31.45	2.23	2.23	4.40
8	$[Th(C_6H_4NH_2O)_2(O)_2]$	48.33	48.35	30.00	30.18	2.50	2.52	3.04
9	$[Th(C_5H_3N(COO)_2)(O_2)H_2O]$	51.90	51.98	18.79	18.87	1.11	1.21	0.22
10	$[Th(C_{14}H_9NO_3)(O_2)H_2O]$	44.52	44.81	32.24	32.35	2.11	2.16	1.5

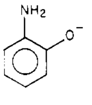
[a] The organic moieties are for the compounds indicated:



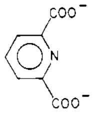
1 and **6**



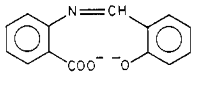
2 and **7**



3 and **8**



4 and **9**



5 and **10**

[b] The values are for 5×10^{-4} M solutions of the complexes in Me_2SO.

The present work reports some peroxo complexes of thorium along with a description of their precursors.

Experimental Section

Purification of Solvents. Spectrograde acetone was purified as described previously.[6] Spectrograde acetonitrile was refluxed over P_2O_5 and distilled. Other solvents were simply distilled. All solvents were stored in contact with molecular sieves. Other organic reagents (Eastman) were used as supplied. The Schiff base *N*-(2-carboxyphenyl)salicylideneamine, $C_{14}H_{11}NO_3$, was prepared as described previously.[6]

Preparation of $ThCl_4$. The compound formed when CCl_4 vapor entrained in a stream of dry N_2 was passed over ThO_2 at 600 °C for 3 h.[8]

Preparation of Complexes. The complexes and their elemental analyses are listed in Table I. Complexes **1–5** were prepared by adding a stoichiometric quantity of the ligand in acetonitrile to $ThCl_4$ suspended in the same solvent. Recrystallization from hot acetone was induced by partial evaporation and addition of ether while cooling. Complexes **6–10** were prepared from the appropriate precursor, i.e., one of the complexes **1–5**, by dissolving in 150 mL of 1:1 acetone and methanol containing 0.5 mL of pyridine. The resulting solution was boiled for 5 min and cooled. A precipitate was separated, washed with acetone, and dried in vacuo.

Reaction of 6 with *trans*-Stilbene (Reaction A). *trans*-Stilbene (1.5 g, 0.0086 mol) was added to a suspension of **6** (4.37 g, 0.0086 mol) in CH_2Cl_2 (30 mL). The mixture was stirred under reflux for 24 h after which the solution was filtered and the solvent evaporated. The residue was extracted with ether, and the extract was placed on a 25-g column of alumina (Shawinigan Chemicals, pH of slurry 9.0) and eluted first with 250 mL of petroleum ether and then with 250 mL of benzene. A 1.1-g quantity of unreacted *trans*-stilbene was recovered from the petroleum ether fraction. Evaporation of the benzene solution yielded 0.49 g (90% yield based on conversion) of *trans*-stilbene oxide, mp 59–61 °C (lit. mp 65–67 °C). Anal. Calcd for $C_{14}H_{12}O$: C, 85.71; H, 6.12; O, 8.16. Found: C, 85.57; H, 6.06; O, 8.13.

Catalytic Reaction of 6 and H_2O_2 with *trans*-Stilbene (Reaction B). A 0.96-g quantity (0.0053 mol) of *trans*-stilbene was added to 0.048 g of **6** suspended in 20 mL of dioxane and 20 mL of 30% H_2O_2. The mixture was heated under reflux at 90 °C for 24 h. It was cooled and filtered, and the filtrate was evaporated to dryness. The residue was extracted with ether, and the extract was dried with Na_2SO_4 and evaporated to dryness. A yellow solid (0.93 g, 82.7% yield) was identified as benzoin by IR, NMR, and mass spectrometry as well as by elemental analysis; mp 137–138 °C (lit. mp 134–136 °C). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66; O, 15.09. Found: C, 79.38; H, 5.79; O, 15.23. No starting material was detected.

Reaction of 7 with Allyl Alcohol (Reaction C). Compound **7** (2.5 g, 0.0047 mol) was dissolved in 8 mL of tetrahydrofuran, and the stoichiometric amount of allyl alcohol was added. The mixture was stirred under reflux at 60 °C for 36 h. Microdistillation under ca. 20 mmHg pressure yielded the epoxide (glycidol) as a high-boiling fraction (149–153 °C) (0.12 g, ca. 70% yield as about one-third of the starting material was unreacted). The glycidol was identified from its boiling point and its ^1H NMR spectrum.

Catalytic Reaction of 7 and H_2O_2 with Allyl Alcohol (Reaction D). A 20-mL quantity of allyl alcohol (17.04 g, 0.294 mol) was dissolved in 20 mL of dioxane, and 0.91 g of **7** was added followed by 20 mL of 30% H_2O_2. The mixture was kept under reflux at 90 °C for 20 h. The reaction mixture was filtered and the filtrate distilled at 20 mmHg pressure until the oil-bath temperature reached 210 °C. Continued distillation at 0.002 mmHg pressure yielded a product at 130–135 °C that was identified as glycerol (12.0 g, 44.3% yield). In a second attempt, a yield of 49.3% was obtained.

Analyses and Spectra. Thorium was determined as the oxide produced by direct ignition. Infrared spectra (Nujol mulls) were recorded with a Pye Unicam SP 1100 or a Beckman IR-20 spectrometer. Spectra between 800 and 200 cm^{-1} were obtained with a Perkin-Elmer 283 spectrometer. Raman spectra of the solids were obtained as described previously.[6] Proton and ^{13}C NMR spectra were obtained with Varian T-60 and FT-80 instruments. Tetramethylsilane was employed as an internal standard.

Conductivities of solutions in dimethyl sulfoxide were measured at 25 °C with an Industrial Instruments Model RC16B2 conductivity bridge and a cell of the Washburn type with platinized electrodes.

Results and Discussion

Complexes 1–5. These served as precursors of the peroxo complexes. The analytical and other data for these are consistent with sixfold coordination of the thorium atom. Some of the uranium analogues are six-coordinate while others are seven-coordinate with a water molecule in the coordination sphere.[6] The conductivity data in Table I for solutions of compounds in Me_2SO indicate that compounds **4** and **5** are nonelectrolytes, but **1–3** exhibited conductance values intermediate between those typical of 1:1 and 2:1 electrolytes. By comparison, the 2:1 electrolytes $UO_2(NO_3)_2{\cdot}6H_2O$ and $MgCl_2{\cdot}6H_2O$ gave values of 60.0 and 60.6 Ω^{-1} cm^2 mol^{-1}, respectively, at a concentration of 5×10^{-4} mol L^{-1} and potassium iodide at the same concentration exhibited a value of 29.7 Ω^{-1} cm^2 mol^{-1}. Literature values[9,10] for 1:1 and 2:1

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(8) The product so obtained is not entirely pure. A pure product was obtained by vacuum sublimation in a platinum tube. This was found to be unnecessary for the present work.

(9) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 113.

(10) Kundu, P. C.; Roy, P. S.; Banerjee, R. K. *J. Inorg. Nucl. Chem.* **1980**, *42*, 851.

Table II. Infrared and Raman Spectral Data for the Th(IV) Complexes[a]

	band maxima, cm^{-1}							
compd no.	ν(O–H)	ν(N–H)	ν(C=O)	ν(C=N)	ν_1(O–O)	ν(Th–O)	ν(Th–N)	ν(Th–Cl)
1			1655 vs			395 sh	350 s	225 vs
2		3170 ms 3100 m	1615 s			388 vs	335 ms	250 sh
3		3230 m 3150 m				390 vs	325 s	220 vs
4			1660 s			400 s	325 ms	
5			1650 br	1600 ms		392 s	330 s	
6			1650 vs		822 br			
7		3125 ms 3090 m	1590 br		820 s			
8		3200 w 3110 ms			825 ms			
9	3400 br		1650 s		840 ms			
10	3405 br		1645 s	1600 m	825 br			

[a] Relative band intensities are denoted by vs, ms, s, m, w, br, and sh, meaning very strong, medium strong, strong, medium, weak, broad, and shoulder, respectively.

Table III. Chemical Shift[a] Relative to That of Me_4Si in ^{13}C NMR of Some Th(IV) Complexes

	ring carbons					carboxylic carbons	
compd	C2	C3	C4	C5	C6	C7	C8
pyridine-2-carboxylic acid	148.3	124.8	137.8	127.2	149.4	166.3	
1	151.0	124.3	139.0	126.8	148.3	169.2	
6	150.8	124.4	138.6	126.7	147.8	169.3	
pyridine-2,6-dicarboxylic acid	148.0	127.7	139.4	127.7	148.0	165.5	165.5
4	150.5[b]	125.8	142.0	125.8	149.9[b]	170.4[b]	170.0
9	150.2[b]	125.6	141.7	125.6	149.6[b]	170.1[b]	169.8

[a] Ppm downfield relative to Me_4Si as internal standard. [b] The assignment of these narrow doublets to C2 and C6 or to C7 and C8, respectively, is arbitrary. A reversed assignment is equally likely.

electrolytes are comparable to ours. It is suggested that the conductivity of solutions of **1**–**3** arises by displacement of chloride ion from the coordination sphere as shown:

$$[ThL_2Cl_2] + Me_2SO = [ThL_2Cl(Me_2SO)]^+ + Cl^-$$

$$[ThL_2Cl(Me_2SO)]^+ + Me_2SO = [ThL_2(Me_2SO)_2]^{2+} + Cl^-$$

where L refers to the bidentate, uninegative ligands. Figure 1 shows that the molar conductivities decrease with increasing concentration and approach values typical of 1:1 electrolytes at the upper end of the concentration range. The ^{13}C NMR spectrum of **1** indicated that the picolinato ligand is not displaced in Me_2SO solution; therefore the conductivity arises from ionization of chloride rather than the organic group.

The IR spectra of the chloro complexes (Table II) display strong bands at 220–250 cm^{-1}, which we assign to the Th–Cl stretching.[11-13] The Th–O and Th–N bonds in complexes **1**–**5** give rise to bands at 388–400 (Th–O) and 325–350 cm^{-1} (Th–N).[14-16] The organic ligands reveal characteristic frequencies that confirm their expected bi- and tridentate character. Thus, ν(N—H) bands at 3100–3230 cm^{-1} in compounds **2** and **3** are significantly lower in frequency than the corresponding bands of the free ligands.[6] Similarly, ν(C=O) bands in **1**, **2**, **4**, and **5** have frequencies 50–70 cm^{-1} lower than the free-ligand values. This shows that amino and carboxylato groups are coordinated to the metal atom in each case.

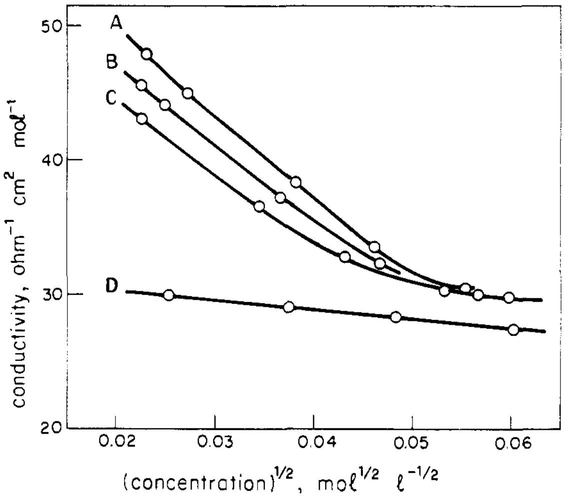

Figure 1. Plot of molar conductivities vs. $(\text{concentration})^{1/2}$ in Me_2SO solutions: (A) $[Th(C_6H_4NH_2COO)_2Cl_2]$; (B) $[Th(C_6H_4NH_2O)_2Cl_2]$; (C) $[Th(C_5H_4NCOO)_2Cl_2]$; (D) KI.

Further, in compound **5**, the decrease in ν(C=N) by 25 cm^{-1} relative to the frequency for the free Schiff base indicates that imino nitrogen is coordinated to the metal atom.[17-19] The ν(O—H) band at 3120 cm^{-1}, observed in the Schiff base, disappears upon coordination, which indicates that there is deprotonation and coordination at the oxygen site.

In order to obtain additional information on the mode of coordination of the substituted pyridines, we obtained ^{13}C NMR spectra with solutions of **1**, **4**, **6**, and **9** in Me_2SO-d_6 (Table III). These afforded comparisons with an analogous uranium compound[6] and several pyridine complexes.[20] As-

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(11) Faraglia, H.; Zarli, B.; Sindellari, L.; Dall'olio, G. *Inorg. Chim. Acta* **1976**, *19*, 39.
(12) Bagnall, K. W.; du Preez, J. G. H.; Bajorek, J.; Bonner, L.; Cooper, H.; Segal, G. *J. Chem. Soc., Dalton Trans.* **1973**, *23*, 2682.
(13) Brown, D. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *7*, 87.
(14) Karayannis, N. M.; Mikulski, C. M.; Stroko, M. J.; Pytlewski, L. L.; Labes, M. M. *Inorg. Chim. Acta* **1970**, *4*, 455.
(15) Agarwal, R. K.; Srivastava, M.; Srivastava, A. K. *J. Inorg. Nucl. Chem.* **1981**, *43*, 204.
(16) Agarwal, R. K.; Srivastava, A. K.; Srivastava, M.; Bhakru, N.; Srivastava, T. N. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1778.
(17) Burns, G. R. *Inorg. Chem.* **1968**, *7*, 277.
(18) Ali, M. A. *Can. J. Chem.* **1980**, *58*, 727.
(19) Kovacic, J. E. *Spectrochim. Acta, Part A* **1967**, *A23*, 183.

signments were based in part upon the proton couplings in off-resonance spectra and in part upon a consideration of nuclear Overhauser enhancement. Signals of the substituted ring carbon in position 2 of picolinic acid are less intense than for position 6, where the substituent is hydrogen. We are led to conclude that the assignment of the spectrum by Jacobson et al.[21] is incorrect, the bands for carbons in positions 2 and 6 having been reversed. We agree with the assignments reported by Moore et al.[22]

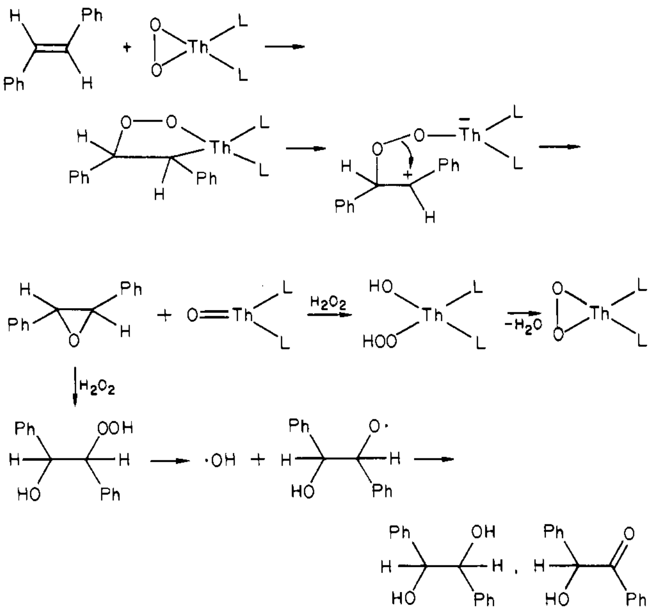
Upon coordination with thorium, there are significant shifts of all of the carbon resonances other than those for the atoms in positions 3 and 5. Lavallee et al.[20] pointed out that the shifts of the α-carbons in coordinated pyridines are governed by factors that are poorly understood. Paramagnetic anisotropy attributable to the metal atom is a major influence in causing upfield shifting. It can be seen from Table III that the resonances for the α-carbons in the complexes are only slightly downfield from the values for the free ligands. On the other hand, the carboxylic carbon resonances are shifted considerably further downfield. There is evidently a small difference between the 2- and 6-carbons and also in the 7- and 8-carbons in the complexes containing pyridinedicarboxylic acid. This could arise if the complex lacks a plane of symmetry. This would be the case if the nitrogen atoms of the two ligands were in a mutually cis arrangement. Alternatively there may be coordination by a solvent molecule in two different orientations. The proton spectra failed to reveal splitting, but the hydrogen atoms are rather remote from the first coordination sphere and are presumably not much influenced by the point symmetry at the thorium atom.

The γ-position is the least influenced by magnetic anisotropy; therefore changes in the chemical shifts of the γ-carbon are believed to be largely determined by the inductive effect of the solvent interaction in the case of the free ligand and the coordinating metal atom in the case of the complex. The downfield shift of the γ-carbon in complexes **1** and **4** shown in Table III is much smaller than the corresponding shift reported by Lavallee et al. for pyridine complexes of Co(III) and Rh(III).[20] Our data refer to solutions in Me_2SO while Lavallee et al. employed D_2O as solvent, and although there is a solvent effect, particularly with the free ligands, that effect is small compared to that of complexing. It may be concluded that Th(IV) is a significantly weaker acceptor than the smaller trivalent ions. The γ-carbon resonance appeared at 139.0 ppm in $[U(C_5H_4NCOO)_2Cl_2]\cdot C_5H_4NCOOH$ dissolved in Me_2SO-d_6, i.e. at virtually the same field as that with the thorium compound. Larger shifts were reported for Mo(VI) and W(VI) complexes of picolinic acid.[2]

Peroxo Compounds. Treatment of compounds **1–5** with a solution of H_2O_2 resulted in partial replacement of ligands. With complexes **1–3** two chloro groups were replaced by a peroxo group while one of the organic ligands in **4** and **5** was replaced by a peroxo group and an aquo group. The resulting complexes are apparently hexacoordinate. Pyridine was used to scavenge hydrogen ion that was generated in the course of the synthesis reactions. In the absence of pyridine, only ThO_2 was recovered from the reaction mixtures. Attempts to prepare organo–peroxo complexes from $ThCl_4\cdot 2L$ (L = $OPPh_3$, $OAsPh_3$) were unsuccessful.

The infrared spectra were unsatisfactory in the low-energy region so that Th–O and Th–N assignments were not attempted. The ν(O–O) stretch is IR inactive, as is the case with peroxo complexes of uranium,[6] but in the Raman spectrum it appears at 820–840 cm^{-1}. By contrast, the ν(O–O) mode is IR active in complexes of light transition elements and it occurs with higher frequencies. It is to be presumed that, in the actinide complexes, the peroxo group has more nearly the character of the O_2^{2-} ion. In particular, the ν(O–O) frequency in our complexes is somewhat lower than those reported for some peroxofluoro complexes of Zr[23] and considerably lower than the value, ~900 cm^{-1}, reported for complexes of Ti.[24,25] The two ν(Th–O) modes associated with the $Th(O_2)$ grouping could not be located with certainty.

Scheme I



$L = C_5H_4NCOO^-$

The remaining features of the IR spectra were similar to those obtained for complexes **1–5** with the exception of broad bands at ~3400 cm^{-1} in complexes **9** and **10**, which arise from coordinated water molecules.

Reactions with Olefinic Compounds. Titanium isopropoxide has been used with *tert*-butyl hydroperoxide to convert allylic alcohols to epoxides.[7] As thorium is also quadrivalent, we have examined the behavior of a peroxo–thorium complex toward allyl alcohol. In addition, we have investigated a similar reaction with *trans*-stilbene. The various conditions are described in the Experimental Section.

Reaction A produced *trans*-stilbene oxide as indicated by a medium-strong IR band at 1060 cm^{-1} assigned to the C–O–C stretching mode and the ^{1}H NMR spectrum, which showed a methine absorption at 3.8 ppm as required for *trans*-stilbene oxide. Further, the mass spectrum of the product gave a molecular ion peak at *m/e* 196. Only 27% of the starting material underwent conversion to products, but the yield (90%) based on the percent conversion was high. Apparently, the thorium complex did not survive the long refluxing period.

In reaction B, **6** was used to catalyze the oxidation of *trans*-stilbene by H_2O_2 to produce a high yield of product that, however, in this case was benzoin. The IR spectrum of the product (Nujol mull) displayed ν(C=O) at 1685 (s) cm^{-1} and ν(O–H) at 3380 (s) cm^{-1}. The ^{1}H NMR spectrum showed methine absorption at 6.0 ppm. The mass spectrum showed a molecular ion peak at *m/e* 212 as well as further diagnostic peaks. A possible reaction path is shown in Scheme I.

The various steps are analogous to mechanistic processes suggested by Mimoun et al.,[3] Olah et al.,[5] and Dzhemilev et

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[20] Lavallee, D. K.; Banghman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718.

[21] Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3061.

[22] Moore, G. G. I.; Kirk, A. R. *J. Heterocycl. Chem.* **1979**, *16*, 789.

[23] Jere, G. V.; Santhamma, M. T. *Inorg. Chim. Acta* **1977**, *24*, 57.

[24] Wendling, E. *Bull. Soc. Chim. Fr.* **1967**, *16*.

[25] Guilard, R.; Fontesse, M.; Fournari, P.; Lecompte, C.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1976**, 161.

al.[26] Support for the mechanism was provided by the fact that, in addition to benzoin, we were able to isolate the diol 1,2-dihydroxy-1,2-diphenylethane, $C_{14}H_{14}O_2$ (15% yield), mp 146–148 °C (lit. mp 149–150 °C), from the reaction of *trans*-stilbene oxide with H_2O_2 in dioxane. The IR spectrum of the diol indicates ν(O—H) at 3300 cm^{-1} and the absence of ν(C=O). The ^1H NMR spectrum shows methine absorption at 6.0 ppm. Opening of the epoxide ring has been shown to occur readily in the presence of excess oxidant[26,28] with the subsequent formation of diol and α-hydroxy ketone. In the presence of catalyst, diols may be oxidized further to α-hydroxy ketones.[26]

An alternative mechanism for the formation of the epoxide is suggested by the work of Chong and Sharpless.[27] Those authors concluded that the epoxy oxygen is derived from the peroxy oxygen which is proximal to the metal atom in the transition state, at least in reactions employing alkyl hydroperoxide. With H_2O_2, we are not able to distinguish between the two possibilities.

The epoxide glycidol was obtained by oxidation of allyl alcohol (reaction C). This was evident from the ^1H NMR spectrum, which showed three multiplets centered at 2.7, 3.2, and 3.7 ppm. With H_2O_2 and only a catalytic amount of thorium complex (reaction D), the product isolated was glycerol. Its ^1H NMR spectrum showed methylene and methine absorptions at 3.61 and 5.15 ppm, respectively, as required by glycerol. The mass spectrum was identical with that of an authentic sample.

Katsuki and Sharpless[7] comment on the low yields of epoxide whenever the product is water soluble. Possibly the hydrolysis involved in the above mechanism is more facile when the epoxide is soluble.

Compounds **9** and **10** failed to oxidize the organic substrates even when refluxing at 120 °C was continued for 24 h. This is presumably due to the enhanced stability afforded by the tridentate ligands.

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Registry No. **1**, 81802-63-3; **2**, 81802-64-4; **3**, 81802-65-5; **4**, 69480-50-8; **5**, 81802-66-6; **6**, 81802-67-7; **7**, 81802-68-8; **8**, 81802-69-9; **9**, 81802-70-2; **10**, 81802-62-2; $ThCl_4$, 10026-08-1; *trans*-stilbene, 103-30-0; allyl alcohol, 107-18-6.

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[26] Dzhemilev, U. M.; Yur'ev, V. P.; Tolstikov, G. A.; Gersharov, F. B.; Rafikov, S. R. *Dokl. Chem.* (*Engl. Transl.*) **1971**, *196*, 79. See also: Sheldon, R. A. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 370.

[27] Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.

[28] Barusch, M. R.; Payne, J. Q. *J. Am. Chem. Soc.* **1953**, *75*, 1987.

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Hydrido(triphenylsilyl)tetracarbonyliron Derivatives with Phosphine Ligands

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$[Fe(CO)_4(H)SiPh_3]$ complexes are intermediates in the hydrosilylation reaction of alkenes, catalyzed photochemically by iron pentacarbonyl.[1] Their formation is not sufficient to account for the catalytic action, since they do not give hydrosilylation of alkenes in the absence of light.[1]

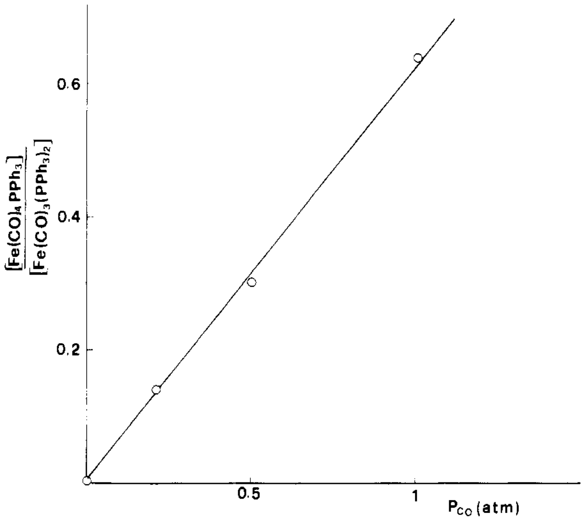

Figure 1. $[Fe(CO)_4PPh_3]/[Fe(CO)_3(PPh_3)_2]$ vs. P_{CO} plot for the reaction between $[Fe(CO)_4(H)SiPh_3]$ and PPh_3 at 25 °C in toluene ($[PPh_3] = 5 \times 10^{-2}$ M], $[Fe(CO)_4(H)SiPh_3] = 6 \times 10^{-3}$ M). The concentration ratio was obtained by measuring the absorbance ratio of the CO stretching bands of the mono- and disubstituted complexes.[3]

So that information about the nature of these catalytic intermediates could be obtained, a study of the thermal reactivity of $[Fe(CO)_4(H)SiPh_3]$ with various nucleophiles was started.

Information about the reaction between $[Fe(CO)_4(H)SiPh_3]$ and PPh_3 is given in the literature:[2] a reductive elimination of $HSiPh_3$ along with the formation of $[Fe(CO)_4]$ and subsequently the reaction with PPh_3 producing $[Fe(CO)_4PPh_3]$ was proposed. This mechanism is questionable, because if the intermediate $[Fe(CO)_4]$ is formed, the reaction with PPh_3 should give a mixture of $[Fe(CO)_4PPh_3]$ and $[Fe(CO)_3(PPh_3)_2]$.[3] Therefore the formation of $[Fe(CO)_4PPh_3]$ suggests a reaction mechanism that follows a different way.

In this work the results of a study of the reactivity of $[Fe(CO)_4(H)SiPh_3]$ and phosphine ligands of different basicities are given.

Experimental Section

$[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$ (L = $SbPh_3$, PPh_3, $AsPh_3$) were prepared with the standard methods described in the literature.[3]

$[Fe(CO)_4(H)SiPh_3]$ was prepared and purified as described by Graham.[2] Because of the extreme reactivity of $[Fe(CO)_4(H)SiPh_3]$ with oxygen, the solvents used were deaerated with nitrogen purified by bubbling in Fieser solutions and appropriately dried. All the IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer; NMR spectra were obtained with a JEOL CHL60 spectrometer, with Me_4Si as reference.

$[Fe(CO)_3(H)(SiPh_3)PPh_3]$ (I). The reaction was carried out at −18 °C in ethyl ether dried with $LiAlH_4$, with $[Fe(CO)_4HSiPh_3)$ and PPh_3 mixed in the molar ratio 1/2. Two CO stretching bands at 2060 and 2000 cm^{-1} were immediately observed, which were attributed to the complex I. At the same time the formation of small quantities of $[Fe(CO)_3(PPh_3)_2]$ was observed. It was not possible to separate these two complexes by fractional crystallization because the complex I reacted quickly, forming $[Fe(CO)_3(PPh_3)_2]$. Therefore only a spectroscopic characterization of the solid obtained after evaporation of the solvent was possible. This reaction occurred in the same way when other solvents (benzene, toluene, etc.) were used. When the reaction was carried out under a controlled CO atmosphere (P_{CO} = 0–1 atm), the formation of a mixture of $[Fe(CO)_4PPh_3]$ and $[Fe(CO)_3(PPh_3)_2]$ was observed. The plot of the $[Fe(CO)_4PPh_3]/[Fe-$

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[1] Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

[2] Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

[3] Cardaci, G.; Narciso, V. *J. Chem. Soc., Dalton Trans.* **1972**, 2289. Cardaci, G. *Int. J. Chem. Kinet.* **1973**, *5*, 805. Cardaci, G. *Inorg. Chem.* **1974**, *13*, 368, 2974.

0020-1669/82/1321-3232$01.25/0