It is perhaps also relevant to point out that one-dimensional conductors such as $Ir(CO)_3Cl_{1.1}$,[13] $K_{0.98}Ir(CO)_2Cl_{2.42}\cdot 0.2CH_3COCH_3$,[14] and $K_{0.60}Ir(CO)_2Cl_2\cdot 0.5H_2O$[14] also exhibit weak Curie-type temperature-dependent paramagnetism, giving rise to μ_{eff} values of 0.07–0.091, 0.05–0.28, and ~0.17 μ_B/(mole) iridium, respectively. The average value of 0.1 μ_B is again very close to our average μ_a value. Assuming an average μ_{eff} of 0.1 μ_B/per Ir and an average chain length of 25 Ir atoms/cluster, we obtain $\mu_{eff} \approx 25^{1/2} \times 0.1 = 0.5$ μ_B/cluster, roughly in the same size range and μ_{eff} range observed here.

It is also interesting to compare the observed μ_{eff} range of 0.35–0.55 μ_B/cluster reported here with the decrease in μ_{eff} per (mole) atom of silica-supported nickel particles reported by Carter and Sinfelt.[15] These authors found that as the particle size decreases from 2.6×10^4 (bulk) to 65 to 27 to 12 Å in diameter, the effective magnetic moment per nickel, obtained from the Curie–Weiss law fit to the temperature-dependent paramagnetism above the Curie temperature $\Theta(\chi = C_M/(T - \Theta))$, decreases from the bulk value 1.73 to 1.69 to 1.51 to 1.1 μ_B, respectively.

Theoretical Developments. It is clear that the explanation of the Curie-type temperature dependence of the observed paramagnetism must await further theoretical investigation. As cautioned by Johnson et al.,[2] the questions that need to be answered are, for example, whether the assumption of Boltzmann-type statistics, which is prevalent in magnetism, is indeed valid for a metal cluster reaching the quantum-size regime; or perhaps Fermi–Dirac statistics would be more appropriate? Furthermore, will the particulate metal theory[16] (which attempts to approach the problem from the bulk metal), or certain extensions of such, be able to account for the observed temperature-dependent paramagnetism of high-nuclearity metal clusters? Or perhaps should one approach the problem from small clusters via molecular orbital theory[17] or some variants of it? In the absence of a detailed theory, it is safe to say that as the cluster grows in size, the electronic levels change from discrete (as in small molecules) to quasi-continuous (as in high-nuclearity clusters) to band structure (as in bulk). The concomitant evolution of magnetic behavior changes from diamagnetism to Curie-type temperature-dependent paramagnetism to temperature-independent Pauli paramagnetism. Indeed, theoretical prediction[12,16] and experimental observation of enhanced low-temperature susceptibility have been made for particles of metals such as platinum.[11,18]

Summary. In summary, the high-nuclearity metal clusters exhibit diamagnetic behavior (χ_o in eq 2 is negative) at high temperatures since the diamagnetic contribution (χ_d) to the magnetic susceptibility outweighs the paramagnetic molecular susceptibility (χ_p in eq 2 is positive). The term χ_p increases as the cluster size increases, consistent with the decrease in energy gap between the frontier orbitals. As the cluster reaches a critical *size* and *shape* (viz., entering the so-called quantum-size regime), *intrinsic* temperature-dependent Curie-type paramagnetism at low temperatures ($\lesssim$70 K) is observed. We define the critical size and shape as the size and shape of the cluster at which the metal valence electrons (responsible for metallic bonding) are completely delocalized and can be considered collectively as a whole. The effective magnetic moment per (mole) cluster falls in the narrow range 0.35–0.67 μ_B for the size range of Pt_6–Pt_{38}. It is pointed out, for the first time, that the effective magnetic moment per (mole) atom, with the exception of Pt_6, falls within the narrow range of 0.1 ± 0.02 μ_B for Pt_9–$Pt_{\sim 400}$. The fact that these molecular platinum clusters have magnetic properties very similar to (indeed approaching) those of the small crystallites is a strong indication that these clusters begin to enter the quantum-size regime where the magnetic properties are distinctly different from that of the bulk as well as that of the molecules (viz., an anomaly). Magnetic properties of high-nuclearity metal cluster systems containing platinum as well as other metals will be subjects of future publications.

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Notes

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Novel Peroxo Complexes of Zirconium Containing Organic Ligands

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In recent years there has been considerable interest in the investigation of peroxo complexes of transition metals because of their interesting coordination chemistry as well as their role in synthetic organic chemistry.[1-11] The synthesis and properties of organo peroxo complexes of thorium(IV)[12] and titanium(IV)[13] have been reported. As zirconium is also a group 4B element, it was of interest to discover whether it would form analogous peroxo complexes that contain organic moieties. The present paper describes several novel organoperoxo complexes of Zr(IV) along with their properties with respect to oxygen transfer to various substrates.

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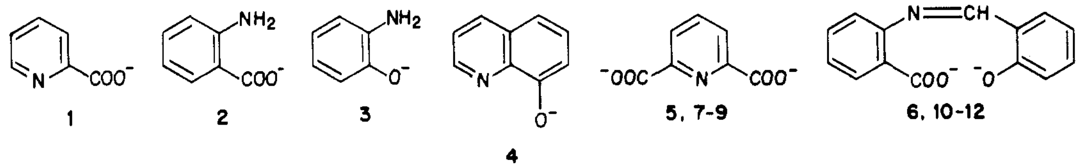
Table I. Analytical and Molar Conductance Data of the Zr(IV) Complexes[a]

no.	compd	% Zr		% C		% H		molar conductance, Ω^{-1} cm^2 mol^{-1} [b]
		calcd	found	calcd	found	calcd	found	
1	$[Zr(C_5H_4NCOO)_2(O_2)]$	24.84	25.00	39.21	39.12	2.72	2.72	0.1
2	$[Zr(C_6H_4NH_2COO)_2(O_2)]$	23.08	23.41	42.50	42.38	3.03	3.02	0
3	$[Zr(C_6H_4NH_2O)_2(O_2)]$	26.89	27.00	42.45	42.36	3.53	3.51	0
4	$[Zr(C_9H_6ON)_2(O_2)]$	22.18	22.32	52.52	52.50	2.91	2.90	0
5	$[Zr(C_5H_3N(COO)_2)(O_2)H_2O]$	29.78	30.15	27.43	27.20	1.63	1.63	3
6	$[Zr(C_{14}H_9NO_3)(O_2)H_2O]$	23.99	24.23	44.18	44.15	2.89	2.83	2.1
7	$[Zr(C_5H_3N(COO)_2)(O_2)\cdot OPPh_3]$	16.11	16.30	52.98	52.83	3.17	3.16	5.0
8	$[Zr(C_5H_3N(COO)_2)(O_2)\cdot OAsPh_3]$	14.94	15.02	49.16	49.03	2.94	2.94	0.2
9	$[Zr(C_5H_3N(COO)_2)(O_2)\cdot ONC_5H_5]$	23.80	23.94	37.57	37.52	2.08	2.06	0
10	$[Zr(C_{14}H_9NO_3)(O_2)\cdot OPPh_3]$	14.24	14.51	59.67	59.83	3.74	3.73	7.5
11	$[Zr(C_{14}H_9NO_3)(O_2)\cdot OAsPh_3]$	13.33	13.43	56.12	55.86	3.50	3.48	2.0
12	$[Zr(C_{14}H_9NO_3)(O_2)\cdot CNC_5H_5]$	19.95	19.97	49.86	49.38	3.06	3.05	1.5

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



1 **2** **3** **4** **5, 7-9** **6, 10-12**

[b] The values are for ca. 10^{-3} M solutions of the complexes in Me_2SO.

Experimental Section

Physical Measurements. Infrared spectra (as KBr pellets) were recorded with a Pye Unicam SP3-300 infrared spectrophotometer. ^{13}C NMR spectra of a few samples in Me_2SO-d_6 were obtained on an AM-250 spectrometer. Tetramethylsilane was employed as internal standard. Conductivities of solutions in Me_2SO were measured at 298 K with a conductivity bridge, Type M.C.3, from Electronic Switchgear Ltd. (London, England).

Reagents. Zirconium nitrate dihydrate, picolinic acid, anthranilic acid, 2-aminobenzoic acid, 8-hydroxyquinoline, pyridine-2,6-dicarboxylic acid, triphenylphosphine oxide, triphenylarsine oxide, pyridine oxide, triphenylphosphine, triphenylarsine, and salicylaldehyde were used as supplied by Merck.

Preparation of the Schiff Base. *N*-(2-Carboxyphenyl)salicylideneamine. It was prepared from anthranilic acid and salicylaldehyde by following the published procedure.[11]

Preparation of Complexes. Peroxobis(pyridine-2-carboxylato)zirconium(IV) (1). A solution of $Zr(NO_3)_4{\cdot}2H_2O$ (3.2 g, 0.0085 mol) in 30% H_2O_2 (30 mL) was added to a solution of pyridine-2-carboxylic acid (2.09 g, 0.0017 mol) in boiling acetone (50 mL). A white precipitate was separated, washed with water and finally with *n*-hexane, and dried in vacuo over P_2O_5; yield 2.8 g (89.7%). **1** is soluble in methanol and Me_2SO.

Peroxobis(aniline-2-carboxylato)zirconium(IV) (2). The same procedure applied to 3.75 g (0.01 mol) of $Zr(NO_3)_4{\cdot}2H_2O$ and 2.74 g (0.02 mol) of anthranilic acid yielded 2.9 g (73.3%) of the complex. **2** is soluble in methanol and Me_2SO.

Peroxobis(2-aminophenoxido)zirconium(IV) (3). The analogous complex **3**, prepared similarly from 3.75 g (0.01 mol) of $Zr(NO_3)_4{\cdot}2H_2O$ and 2.1 g (0.02 mol) of 2-aminophenol, gave 2.4 g (70.7%) of the complex. **3** is soluble in all polar solvents tried.

Peroxobis(8-hydroxyquinolinato)zirconium(IV) (4). The complex **4** was prepared similarly from 3.75 g (0.01 mol) of $Zr(NO_3)_4{\cdot}2H_2O$ and 2.9 g (0.02 mol) of 8-hydroxyquinoline, which afforded 3.18 g (77.3%) of the complex. **4** is soluble in methanol and Me_2SO.

Peroxo(pyridine-2,6-dicarboxylato)zirconium(IV) Hydrate (5). A solution of 3.75 g (0.01 mol) of $Zr(NO_3)_4{\cdot}2H_2O$ in 30% H_2O_2 (30 mL) was treated with a solution of pyridine-2,6-dicarboxylic acid (L′) (1.66 g, 0.01 mol) in boiling acetone (200 mL). A white precipitate formed. It was separated and washed successively with water and *n*-hexane. The product was dried in vacuo over P_2O_5; yield 1.8 g (58.7%). **5** is soluble in methanol, Me_2SO, and nitromethane.

Peroxo[*N*-(2-carboxyphenyl)salicylideneaminato]zirconium(IV) (6). The same procedure applied to 3.75 g (0.01 mol) of $Zr(NO_3)_4{\cdot}2H_2O$ and 2.39 g (0.01 mol) of *N*-(2-carboxyphenyl)salicylideneamine (L′) yielded 2.1 g (55.2%) of the complex. **6** is soluble in methanol, Me_2SO, and nitromethane.

General Method for the Preparation of Complexes $ZrL'(O_2)L''$ (7-12, L″ = $OPPh_3$, $OAsPh_3$, and ONC_5H_5). $ZrL'(O_2)H_2O$ complexes (0.005 mol) synthesized as above were dissolved in a 1:1 mixture of acetone and methanol (50-100 mL) and was mixed with a solution of L″ (0.005 mol) in acetone (15 mL). The resulting solution was refluxed for 12 h and slowly cooled, whereupon colorless crystals appeared. These were separated, washed with acetone and *n*-hexane, and dried. **7-12** are soluble in methanol, Me_2SO, and nitromethane.

Analyses. Zirconium was determined gravimetrically.[14] Methanolic solutions of the peroxo complexes were titrated with Ce(IV) to determine the number of active oxygen atoms present.[11,14] Carbon and hydrogen analyses were done by Mikroanalytisches Labor Pascher, Bonn-1, West Germany.

Attempted Reaction of 1 with Allyl Alcohol and Cyclohexanone (Reaction A). Typically 0.01 mol of **1** was suspended in tetrahydrofuran (THF, 25 mL) and a stoichiometric quantity of allyl alcohol or cyclohexanone was added to it. Refluxing the mixture for 48 h failed to produce any reaction. Attempts were also made to do the same reactions in Me_2SO but were unsuccessful. The peroxo complex was recovered unchanged after each reaction.

Attempted Reaction of 5 with Allyl Alcohol (Reaction B). Compound **5** (6.2 g, 0.02 mol) was suspended in 15 mL of THF, and a stoichiometric amount of allyl alcohol was added. The mixture was refluxed at 90 °C for 48 h, which failed to produce any reaction. The unreacted complex was recovered after the reaction.

Attempted Reaction of 6 and H_2O_2 with Allyl Alcohol (Reaction C). A 30-mL quantity of allyl alcohol (25.5 g, 0.440 mol) was dissolved in 30 mL of dioxane, and 1.3 g of **6** was added followed by 30 mL of 30% H_2O_2. Refluxing the mixture at 90 °C for 48 h failed to produce any reaction. The unaltered complex was recovered from the mixture.

Reaction of 1 with Triphenylphosphine (Reaction D). A solution of triphenylphosphine (1.5 g, 0.0057 mol) in THF (100 mL) was added to the suspension of complex **1** (2.1 g, 0.0057 mol) in the same solvent (45 mL). The mixture was refluxed for 60 h. TLC indicated that phosphine was converted entirely into phosphine oxide. The solution was filtered and the residue collected. Evaporation of the filtrate yielded the product, mp 155-157 °C (lit.[14] mp 152 °C).

Reaction of 1 with Triphenylarsine (Reaction E). A solution of triphenylarsine (1.3 g, 0.0042 mol) in THF (90 mL) was added to the suspension of complex **1** (1.56 g, 0.0042 mol) in the same solvent (60 mL). The mixture was refluxed for 72 h. TLC indicated that the reaction was complete. The solution was filtered and the residue collected. Evaporation of the filtrate produced triphenylarsine oxide, mp 188-189 °C (lit.[14] mp 188 °C).

The complexes **2-4** were also found to be effective stoichiometric reagents for the oxidation of PPh_3 and $AsPh_3$ to their oxides.

Results and Discussion

The analytical and molar conductance data for the complexes (Table I) are consistent with sixfold coordination of the zirconium atom. Titrations of methanolic solutions of the peroxo complexes

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Table II. Titration of Methanolic Solutions of the Perexo Complexes by Aqueous Acidified Standard Ceric Sulfate Solution

complex no.	equiv of ceric sulfate/mol of complex	complex no.	equiv of ceric sulfate/mol of complex
1	1.97	**7**	2.10
2	2.10	**8**	2.12
3	2.03	**9**	2.20
4	2.20	**10**	2.00
5	2.11	**11**	1.99
6	2.02	**12**	2.00

with Ce(IV) (Table II) indicated that the complexes **1**–**12** were monoperoxo complexes. The electrical conductivities of ca. 10^{-3} M solutions in Me$_2$SO revealed that all of the complexes were undissociated.

Complexes 1–6. Infrared spectral data are shown in Table III. Complex **1** shows a decrease in ν(C=O) by 90 cm^{-1} compared to the value for free picolinic acid (1725 cm^{-1}).[11] This suggests a strong carboxylato binding in **1**. Besides, the presence of the ν(C=N) vibration at 1600 cm^{-1} indicates that the picolinic anion is also bonded to the metal through the nitrogen of the ring.[7,13] The ^{13}C NMR spectrum (Table IV) of **1** in Me$_2$SO-d_6 afforded further evidence for coordination of the nitrogen. Upon coordination with zirconium, there are significant downfield shifts of all the carbon resonances except for the atoms in positions 3 and 5 of the picolinato ligand. The C-3 and C-5 resonances in **1** appeared upfield compared to the free-ligand values. Paramagnetic anisotropy attributable to the metal is a major influence in causing upfield shifting. The C-4 resonance in complex **1** displays a downfield shift of 5.4 ppm with respect to the free-ligand value. This obviously arises because the inductive effect originating at the nitrogen atom is strengthened upon coordination to the metal. Westland and Tarafder[12] pointed out that the C-4 resonance in the picolinato ligand and its complexes is the least influenced by magnetic anisotropy; instead it is believed to be determined by the inductive effect through the nitrogen heteroatom by its coordination to the metal. The C-4 resonance in the peroxo complex of Th(IV) containing a picolinato ligand displays a downfield shift of 0.8 ppm compared to the free-ligand value.[12] Again in complex **1**, the carboxylic carbon shows a downfield shift of 6.5 ppm relative to the free ligand. A smaller shift was reported for the thorium analogue.[12] It therefore follows that Zr(IV) is a significantly stronger acceptor than Th(IV). Lavalle et al.[15] have also reported larger chemical shifts for C-4 resonances in pyridine-containing complexes of smaller, highly charged metal ions. Complexes **2** and **3** show two medium-intensity bands (**2**, 3178 and 3095 cm^{-1}; **3**, 3302 and 3245 cm^{-1})—significantly lower than the values for 2-aminobenzoic acid and 2-aminophenol (3390, 3300 and 3414, 3342 cm^{-1},[11] which indicate coordination by nitrogen. Complex **2** shows a very strong carboxylato band at 1595 cm^{-1}. The ν(O—H) band observed at 3405 cm^{-1} for the free ligand (8-hydroxyquinoline) disappears upon coordination, which indicates deprotonation and coordination at the oxygen site. Further, in complex **4**, the ν(C=N) mode appears at 1585 cm^{-1}, indicating that the ring nitrogen is coordinated to the metal atom.[13] Complex **5** exhibits a strong carboxylato band at 1650 cm^{-1}. This is significantly shifted with respect to the uncoordinated pyridine-2,6-dicarboxylic acid (1710 cm^{-1}).[11] The ligand is potentially tridentate, the available coordination sites being the nitrogen atom and the two carboxylate groups. The ^{13}C NMR spectrum of **5** in Me$_2$SO-d_6 was obtained to gain information on whether the ring nitrogen is coordinated with the metal. The directions of changes of different carbon resonances were analogous to those observed in the peroxo complexes of thorium, molybdenum, and tungsten containing pyridinedicarboxylic acid.[7,12] The resonance of C-4 in complex **5** appears at 5.4 ppm downfield compared to the free-ligand value (Table IV), for example. The carboxylic carbon resonances are also shifted by 6.5 ppm from the free-ligand value. Smaller shifts were reported for different carbon resonances in the analogous peroxo complex of thorium. This again points out that Zr(IV) is a stronger acceptor than its heavier analogue. **5** is apparently hexacoordinate; the pyridinedicarboxylato ligand occupies three coordination positions, the remaining positions having been occupied by a peroxo and an aquo ligand. In complex **6**, the Schiff base behaves as a tridentate dinegative ligand, coordinating at the imine nitrogen and two oxygen atoms. The decrease of ν(C=N) and ν(C=O) by 55 and 75 cm^{-1}, respectively, relative to the frequencies of the free Schiff base, indicates that the imino nitrogen and carboxylato group are coordinated to the metal atom.[16-18] The ν(O—H) band observed in the free Schiff base (3120 cm^{-1})[12] disappears upon coordination, which indicates deprotonation and coordination at the oxygen site. Further evidence for the presence of Zr–O′ (O′ = oxygen in organic ligand) and Zr–N bonds in the complexes **1**–**6** comes from the appearance of ν(Zr—O′) and ν(Zr—N) modes at 400–410 and 375–395 cm^{-1}, respectively.[12,19-21] Complexes **5** and **6** show broad bands at 3400 cm^{-1}, arising from the coordinated water molecules.

The metal peroxo grouping (local C_{2v} symmetry) gives rise to three infrared- and Raman-active vibrational modes. These are predominantly O–O stretching (ν_1), symmetric M–O stretching (ν_2), and antisymmetric M–O stretching (ν_3). The characteristic stretching vibrations, ν_1(O—O), of the present peroxo complexes **1**–**6** appear at 825–870 cm^{-1}. The ν_3 and ν_2 modes appear at 645–690 and 500–600 cm^{-1}, respectively. The assignments shown in Table III are based on comparisons with other peroxozirconium(IV) complexes.[22-24] The ν_1(O—O) frequencies in our complexes are somewhat higher than those reported for organoperoxo complexes at Th[12] and considerably lower than the value ~900 cm^{-1}, reported for the complexes of Ti.[13,25-26]

Complexes 7–12. Treatment of complexes **5** and **6** with a stoichiometric amount of an ancillary ligand (OPPh$_3$, OAsPh$_3$, and ONC$_5$H$_5$) resulted in replacement of an aquo group from the coordination sphere, thereby forming adduct type peroxo complexes. These are the first reported examples of this kind. We failed to prepare such compounds from similar reactions using complexes **1**–**4**, which suggests that Zr(IV) prefers six-coordination. Complexes **7** and **10** show a decrease in ν(P—O) by 97 cm^{-1} each, compared to the free-ligand value.[27] This indicates coordination by the oxygen of OPPh$_3$. In complexes **8** and **11**, complexing causes a decrease in ν(As—O) by 30 and 25 cm^{-1}, respectively, from the free-ligand value.[28] In complexes **9** and **12**, ν(N—O) is decreased by 32 and 37 cm^{-1}, respectively, compared to the value for free pyridine oxide.[29] The present data suggest that the ancillary ligands are strongly coordinated with the metal.

It is noteworthy that ν_1(O—O) stretching frequencies are lower in the arsenic compounds, **8** and **11**, than in the phosphorus analogues, **7** and **10**. This is attributed to the greater polarity of OAsPh$_3$ relative to that of OPPh$_3$. Griffith has noted that when fluorine replaces a less electronegative element bonded to the central atom of a peroxo complex, the O–O stretching frequency is increased.[23] The derived charge separations in the E–O (E =

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Table III. Infrared Spectral Data for the Zirconium(IV) Perexo Complexes[a] (Band Maxima, cm^{-1})

compd no.	ν(O—H)	ν(N—H)	ν(C=O)	ν(C=N)	ν(E=O)	ν_1(O—O)	ν_3(Zr(O—O))[b]	ν_2(Zr(O—O))[b]	ν(Zr—O′)	ν(Zr—N)
1			1635 vs	1600 s		870 vs	675 s	590 s	400 br	380 w
2		3178 m 3095 m	1595 vs			825 vs	645 br	500 br	400 s	375 m
3		3302 m 3245 m				840 m	675 m	600 m	410 w	395 m
4				1585 s		830 m	690 m	600 w	400 m	380 m
5	3400 br		1650 s	1600 m		840 s	680 s	590 s	405 br	385 w
6	3402 br		1625 s	1570 s		850 s	685 m	582 w	405 w	385 sh
7			1655 s		1095 s	860 s	680 m	585 sh	400 br	380 br
8			1660 s		850 s	830 s	690 w	580 m	402 br	390 br
9			1650 s		1210 s	840 s	695 s	580 m	405 br	388 br
10			1630 s	1590 s	1095 s	865 s	670 s	590 m	400 br	390 s
11			1630 s	1585 m	855 s	835 s	685 s	580 m	400 br	380 w
12			1625 s	1580 m	1205 s	845 s	695 m	582 s	405 br	390 w

[a] Relative band intensities are denoted by vs, s, m, w, br, and sh, meaning very strong, strong, medium, weak, broad, and shoulder, respectively. E stands for P, As, and N. [b] Bands for the Zr(O—O) configuration

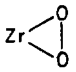
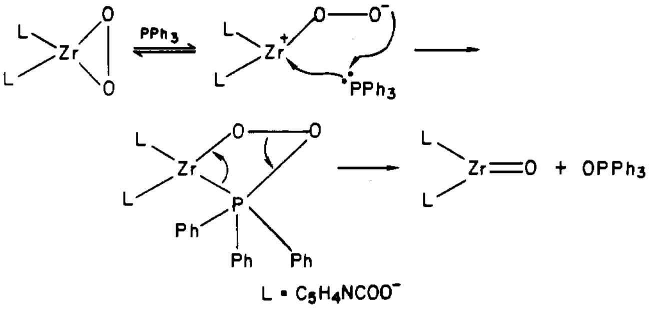


Table IV. Chemical Shift Relative to That of $(CH_3)_4Si$ in ^{13}C NMR of Zr(IV) Complexes[a]

	ring C					carboxylic C	
compd	C-2	C-3	C-4	C-5	C-6	C-7	C-8
pyridine-2-carboxylic acid[b]	148.3	124.8	137.8	127.2	149.4	166.3	
1	152.0	123.2	143.2	126.2	147.6	172.8	
pyridine-2,6-dicarboxylic acid[b]	148.0	127.7	139.4	127.7	148.0	165.5	165.5
5	152.6	124.3	144.8	124.3	152.6	172.0	172.0

[a] In ppm downfield relative to $(CH_3)_4Si$ as internal standard. [b] Chemical shifts for carbons of the free acids refer to the literature values.[12]

Scheme I



P, As) bonds show that the oxygen in the arsine oxide bears more negative charge, and hence $OAsPh_3$ is a stronger donor than $OPPh_3$.[9,11,30] This argument also seems to apply for the lower ν_1 values observed for **8** and **11** compared to **7** and **10**, respectively. The remaining features of the infrared spectra were similar to those obtained for complexes **1**–**6**.

The peroxo complexes of Zr(IV) were found to be very stable. Their reduction by iodide was slow and required 6–7 h elapsed time before any brown coloration appeared in the solution. To explore their reactivity toward olefins and other compounds, **1** was allowed to react with allyl alcohol and also with cyclohexanone (reaction A), separately, under anaerobic conditions. Refluxing for 48 h failed to produce a reaction. In contrast, six-coordinate peroxo complexes of thorium were reactive toward allyl alcohol and other substrates.[12] Peroxo complexes of zirconium are probably kinetically stable. The coordination of nucleophilic substrates to zirconium, forming seven-coordinate intermediates prior to oxygen transfer, is not favorable, whereas six-coordinate thorium can adopt an expanded coordination shell very readily. Complexes **5** and **6** also failed to oxidize allyl alcohol even when refluxing at 90 °C was continued for 48 h. This is presumably due to the enhanced stability of the peroxozirconium moiety, afforded by the tridentate ligands. Negative results were also found by Westland et al. for $ThC_5H_3N(COO)_2(O_2)\cdot H_2O$.[12] Complex **1** was, however, found to react with substrates that can directly insert into the metal–peroxide bond.[10,13,31] Reaction D, for example, produced triphenylphosphine oxide. The infrared spectrum of the product showed ν(P—O) at 1192 cm^{-1}.[27] The infrared spectrum of the metal residue left after oxidation showed disappearance of ν_1(O—O) band but exhibited a diagnostic band at 930 cm^{-1}, attributed to the ν(Zr=O) mode. A possible reaction path is shown in Scheme I. So that additional evidence that the peroxo oxygen is transferred to PPh_3 could be gained, a blank experiment was performed in the absence of the complex under identical conditions, which failed to give the product. This precludes autoxidation of PPh_3 under the experimental conditions used. Reaction E, with triphenylarsine, produced triphenylarsine oxide, as was evident from the infrared band at 880 cm^{-1} assigned to ν(As—O).[28] The infrared spectrum of the metal residue showed the presence of a Zr=O bond. The complexes **2**–**4** also oxidized phosphines and arsines. A 30% H_2O_2 solution itself oxidizes PPh_3 and $AsPh_3$ to their oxides, which therefore limits the scope of zirconium complexes to be used as catalysts along with H_2O_2 for the above oxidation.

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Registry No. **1**, 102149-86-0; **2**, 102149-87-1; **3**, 102149-88-2; **4**, 102149-89-3; **5**, 102149-90-6; **6**, 102149-91-7; **7**, 102149-92-8; **8**, 102149-93-9; **9**, 102210-46-8; **10**, 102149-94-0; **11**, 102149-95-1; **12**, 102210-47-9; allyl alcohol, 107-18-6; cyclohexanone, 108-94-1; triphenylphosphine, 603-35-0; triphenylarsine, 603-32-7.

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(31) Sheldon, R. A.; VanDoorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115.