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Oxy and Thio Phosphorus Acid Derivatives of Tin. 9. Di- and Triorganotin(IV) Diphenyl Phosphate Esters[1]

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Six triorgano- and five diorganotin(IV) diphenyl phosphates, $R_3SnO_2P(OC_6H_5)_2$, where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5, and n-C_8H_{17}, are synthesized by five routes: elimination of water by condensation of diphenylphosphoric acid with triorganotin(IV) hydroxides (R = CH_3, C_6H_5, and c-C_6H_{11}), bis[triorganotin(IV)] oxide (R = n-C_3H_7, n-C_4H_9), or diorganotin(IV) oxides (R = CH_3, n-C_4H_9, n-C_8H_{17}, C_6H_5) where the released water is removed azeotropically to drive the reactions forward or precipitation of sodium chloride from the reaction of sodium diphenyl phosphate with tri- (R = C_6H_5) or diorganotin(IV) (R = C_2H_5) chlorides. The products are crystalline solids, soluble in polar and nonpolar solvents, except for the triorganotin(IV) derivatives below R = CH_3 which are oils. An NMR $|^2J(^{119}Sn-C-^1H)|$ coupling constant of 73.0 Hz is consistent with a five-coordinated structure for the trimethyltin(IV) derivative in solution. In none of the mass spectra are there parent molecular ions, ions of mass higher than the parent, or any di- or polytin-bearing species, thus ruling out association in the gas phase. The highest mass fragments derive from the loss of one organic group from tin from the triorganotin and from the loss of one ligand moiety from the diorganotin derivatives. Successive loss of phenyl groups can be seen in the phenyltin spectra. The tin-119m Mössbauer isomer shift (IS) values (1.26–1.74 mm s^{-1}), ρ [ratio of quadrupole splitting (QS) to IS] (2.60–3.54), and QS values (3.54–4.91 mm s^{-1}) specify higher coordination for the triorganotin(IV) complexes and six-coordinated, *trans*-diorganotin(IV) octahedral geometries with nearly linear C–Sn–C moieties for the diorganotin(IV) complexes.

In the early 1960's Kubo synthesized triphenyltin(IV) diphenyl phosphate and demonstrated its fungi-, insect-, and phytotoxicity.[3] The importance of organotins in biology and the environment is now well-known,[4–6] and in previous portions of this series of papers we have reported on the synthesis of organotin(IV) derivatives of the phosphorus acids.[7,8] We now report the preparation by several different methods and spectroscopic properties of a series of di- and triorganotin(IV) derivatives of diphenyl phosphate and draw conclusions concerning the structures of these species.

Experimental Section

Organotin starting materials and diphenyl phosphate were of commercial grade and were used without further purification. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on CsI plates. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectrometer at an exciting voltage of 70 eV. Tin-119m Mössbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with an NaI scintillation counter and using $Ca^{119m}SnO_3$ as standard reference material for zero velocity. Velocity calibration was based upon β-tin and natural iron. Standard, nonlinear, least-squares techniques were used to fit the data to Lorentzian curves. Raman data were recorded on a Spex Ramalog 5 laser Raman spectrometer. NMR spectra were recorded on a Varian T-60 spectrometer using deuteriochloroform as solvent.

Five different methods of preparing the organotin derivatives of diphenyl phosphate were used. Details of a typical example of each method are given below. All compounds studied are listed with the preparatory method used and their yields, melting points, and microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table II.

(Diphenyl phosphato)triphenyltin(IV), $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$.[3] To a toluene solution (150 mL) of triphenyltin(IV) hydroxide (3.67 g, 0.01 mol) was added diphenyl phosphate (2.50 g, 0.01 mol) and the mixture refluxed. The water formed in the reaction was removed azeotropically with toluene and the mixture filtered. The filtrate, after cooling overnight, gave the product as colorless crystals (3.02 g, 50.1%), mp 178–180 °C (lit. 170 °C[3]).

(Diphenyl phosphato)tri-*n*-propyltin(IV), $(n$-$C_3H_7)_3SnOP(O)(OC_6H_5)_2$. To a benzene (a suspected carcinogen) solution (150 mL) of bis[tri-*n*-propyltin(IV)] oxide (2.56 g, 0.005 mol) was added diphenyl phosphate (2.50 g, 0.5 mol) and the mixture refluxed. The water formed in the reaction was removed azeotropically. Excess solvent was removed under reduced pressure yielding a pale, oily product (4.25 g, 85.5%).

Bis(diphenyl phosphato)dimethyltin(IV), $(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$. To a toluene solution (150 mL) of dimethyltin(IV) oxide (0.998 g, 0.006 mol) was added diphenyl phosphate (3.00 g, 0.006 mol) and the mixture refluxed. The water formed in the reaction was removed azeotropically. The insoluble product was isolated by filtration and dried in vacuo (3.70 g, 95.3%), mp >250 °C.

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Table I. Physical Data for the Organotin(IV) Diphenyl Phosphates, $R_nSn[OP(O)(OC_6H_5)_2]_{4-n}$ (n = 2, 3)

compd	prep	mp, °C	% C found[a]	% H found[a]	yield, %
$(CH_3)_3SnOP(O)(OC_6H_5)_2$	1	79–80	43.86 (43.62)	4.76 (4.63)	24.2
$(C_2H_5)_3SnOP(O)(OC_6H_5)_2$	4		46.15 (47.50)	5.46 (5.55)	92.4
$(n\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$	2		50.95 (50.73)	6.36 (6.28)	85.5
$(n\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$	2		53.76 (53.40)	6.90 (6.91)	39.1
$(C_6H_5)_3SnOP(O)(OC_6H_5)_2$	1	178–180[b]	60.85 (60.13)	4.39 (4.21)	50.1
$(c\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$	1	>250	58.77 (58.37)	7.31 (7.01)	80.2
$(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$	3	>250	48.05 (48.25)	4.02 (4.04)	95.3
$(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	5	>250	49.90 (49.84)	4.81 (4.47)	77.9
$(n\text{-}C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$	3	>250	52.77 (52.55)	5.36 (5.23)	98.6
$(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	3	>250	52.89 (56.05)	3.81 (3.91)	84.3
$(n\text{-}C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$	3	>250	56.92 (56.95)	6.55 (6.45)	80.8

[a] Calculated values in parentheses. [b] Reported as 170 °C in ref 3.

Table II. Tin-119m Mössbauer Data for the Organotin(IV) Diphenyl Phosphates, $R_nSn[OP(O)(OC_6H_5)_2]_{4-n}$ (n = 2, 3) at 77 K

compd	IS (±0.03)	QS (±0.06)	Γ (±0.03)[a]	ρ = QS/IS
$(CH_3)_3SnOP(O)(OC_6H_5)_2$	1.36	4.10	1.65	3.01
$(n\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$	1.50	4.12	1.06	2.75
$(n\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$	1.49	4.09	0.97	2.74
$(C_6H_5)_3SnOP(O)(OC_6H_5)_2$	1.26	3.54	1.93	2.81
$(c\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$	1.60	4.15	1.63	2.59
$(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.38 1.15[b]	4.91 4.93[b]	1.73 1.14[b]	3.56 4.29[b]
$(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.50	4.86	2.82	3.24
$(n\text{-}C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.54	4.58	2.56	2.97
$(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$	1.46	3.84	1.44	2.63
$(n\text{-}C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$	1.74	4.78	0.98	2.75

[a] The fitting program constrained both wings of the doublet to equal line widths. [b] Data recorded at ambient temperatures.

(Diphenyl phosphato)triethyltin(IV), $(C_2H_5)_3SnOP(O)(OC_6H_5)_2$. To a solution of freshly prepared sodium ethoxide (0.01 mol) in dry ethanol (100 mL) was added diphenyl phosphate (2.5 g, 0.01 mol) and the mixture stirred at room temperature for 10 min. Triethyltin(IV) chloride (1.68 mL, 0.01 mol) was then added, and a white precipitate formed immediately. After 1 h of refluxing, the mixture was allowed to cool, the precipitate separated by filtration, and the filtrate concentrated under reduced pressure to give the product as an oil (3.75 g, 92.4%).

Bis(diphenyl phosphato)diethyltin(IV), $(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$. To a solution of freshly prepared sodium ethoxide (0.01 mol) in dry ethanol (150 mL) was added diphenyl phosphate (5.00 g, 0.01 mol) and the mixture stirred at room temperature for 30 min. Diethyltin(IV) dichloride (2.47 g, 0.01 mol) was then added, and a white precipitate formed immediately. After 1 h of refluxing, the mixture was allowed to cool, the precipitate separated by filtration, and the filtrate concentrated under pressure to give the product as a white solid (5.26 g, 77.9%), mp >250 °C.

Results and Discussion

The di- and triorganotin(IV) derivatives of diphenyl phosphate were synthesized by five routes: elimination of water by condensation of diphenylphosphoric acid with triorganotin(IV) hydroxides

$$R_3SnOH + HOP(O)(OC_6H_5)_2 \xrightarrow{C_6H_6\text{ or }C_6H_5CH_3} R_3SnOP(O)(OC_6H_5)_2 + H_2O \quad (1)$$

$$R = CH_3,\ c\text{-}C_6H_{11},\ C_6H_5$$

with bis[triorganotin(IV)] oxides

$$(R_3Sn)_2O + 2HOP(O)(OC_6H_5)_2 \xrightarrow{C_6H_6\text{ or }C_6H_5CH_3} 2R_3SnOP(O)(OC_6H_5)_2 + H_2O \quad (2)$$

$$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9$$

or with diorganotin(IV) oxides

$$R_2SnO + 2HOP(O)(OC_6H_5)_2 \xrightarrow{C_6H_6\text{ or }C_6H_5CH_3} R_2Sn[OP(O)(OC_6H_5)_2]_2 + H_2O \quad (3)$$

$$R = CH_3,\ n\text{-}C_4H_9,\ n\text{-}C_8H_{17},\ C_6H_5$$

where the released water is distilled azeotropically to drive the reactions forward, or precipitation of sodium chloride from an ethanol solution of sodium diphenyl phosphate with a triorganotin(IV) chloride

$$R_3SnCl + NaOP(O)(OC_6H_5)_2 \xrightarrow{C_2H_5OH} R_3SnOP(O)(OC_6H_5)_2 + NaCl \quad (4)$$

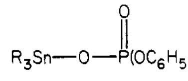
$$R = C_2H_5$$

or with a diorganotin(IV) chloride

$$R_2SnCl_2 + 2NaOP(O)(OC_6H_5)_2 \xrightarrow{C_2H_5OH} R_2Sn[OP(O)(OC_6H_5)_2]_2 + 2NaCl \quad (5)$$

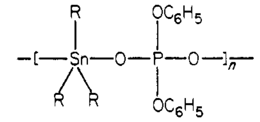
$$R = C_2H_5$$

The organotin diphenyl phosphates listed in Table I are colorless, crystalline solids, which are soluble in polar and nonpolar solvents, except for the trialkyltin(IV) derivatives which are oils. The compounds do not yield conducting solutions in either acetonitrile or nitrobenzene. Limited solubility precluded molecular weight determination and the recording of NMR data for the diorganotin compounds.



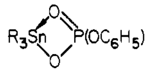
$$R_3Sn{-}O{-}\overset{\overset{\displaystyle O}{\|}}{P}(OC_6H_5)_2$$

A

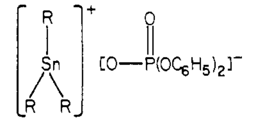


$$-[-\underset{R\ \ R}{\overset{R}{Sn}}-O-\underset{OC_6H_5}{\overset{OC_6H_5}{P}}-O-]_n-$$

B



C



$$\left[R_3Sn\right]^+ [O-\overset{\overset{\displaystyle O}{\|}}{P}(OC_6H_5)_2]^-$$

D

For the triorganotin(IV) derivatives three covalent structures are in principle possible. The monodentate form (A) is extremely unlikely for the diphenyl phosphate ligand, although we have recently reported an analogous sulfur-containing example in (*O,O'*-diethyl dithiophosphato)triphenyltin(IV).[9] Oxygenated derivatives have a greater propensity for employing the bidentate phosphorus ligand fully, and moreover, in the bridging form (B) rather than in the chelated form (C) which are favored by their sulfur analogues. For each of the latter two, the question of whether the connections in the oxygen–tin–oxygen systems are equivalent or skewed (anisobidentate) is relevant, but spectroscopic evidence alone will not be able to decide, and X-ray diffraction data will be the final arbiter. Purely ionic forms (D) are also possible but

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Table VII. Selected Assignments in the Infrared Spectra of $R_nSn[OP(O)(OC_6H_5)_2]_{4-n}$ (n = 2, 3) (cm^{-1})

n = 3						n = 2					
R = CH_3	R = C_2H_5	R = n-C_3H_7	R = n-C_4H_9	R = c-C_6H_{11}	R = C_6H_5	R = CH_3	R = C_2H_5	R = n-C_4H_9	R = n-C_8H_{17}	R = C_6H_5	
1093 vs	1102 vs	1102 vs	1103 vs	1108 s	1110 vs	1152 sh	1120 s	1115 vs	1105 s	1112 vs	$\nu_{asym}(PO_4)$
1024 w	1004 vs	1006 w	1009 w	995 w		1008 vw	968 vw		1008 w	1008 vw	$\nu_{sym}(PO_4)$

unlikely given the good solubility in nonpolar organic solvents. On the other hand, in the related (α-phenyl phosphonato)trimethyltin(IV) we have discovered a unique, more complex ionic formulation, $\{[(CH_3)_3Sn]^+[C_6H_5P(O)(OH)OSn(CH_3)_3OP(O)(OH)C_6H_5]^-\}_n$.[11]

For the diorganotin(IV) derivatives both a four-coordinated, $R_2Sn[OP(O)(OC_6H_5)_2]_2$ configuration containing monodentate diphenyl phosphate groups and an ionic, $[R_2Sn]^{2+}[O_2P(OC_6H_5)_2]^{2-}$ form are unlikely, given the availability of the ubiquitous trans-diorgano, octahedral geometry with bidentate diphenyl phosphate groups.[12] However, the propensity for bridging rather than chelation cannot be ignored in these oxygen derivatives, and a structure consisting of sheetlike polymers has been proposed for the simplest analogues, the hypophosphites, $R_2Sn(O_2PH_2)_2$.[13]

Infrared Spectra. The tin–carbon frequencies in the two methyltin derivatives can yield important information bearing upon the structures of our compounds, and a guide to the positions of the absorptions can be found in work on the analogous di- and trimethyltin(IV) hypophosphites[13] and diorgano phosphinates.[14] However, bands in the parent diphenyl phosphate are found at 560, 524, and 508 cm^{-1} and at 538, 514, and 500 cm^{-1} in the Raman, obscuring the region of interest, and ruling out the use of evidence from the ν(SnC) modes to draw conclusions concerning the planarity of the SnC_3 or the linearity of the SnC_2 groupings.

In addition, $\nu_{asym}(PO_4)$ and $\nu_{sym}(PO_4)$ modes appear as strong absorptions at 1016 and 971 cm^{-1} in the infrared spectrum of tin(II) orthophosphate,[15] $SnHPO_4$, and in the 1150–950-cm^{-1} region in dimethyltin(IV) orthophosphate,[13] $[(CH_3)_2Sn]_3PO_4$, and we have scanned the infrared spectra of our derivatives for features separated by ca. 100 cm^{-1} in these regions. A consistent set is found listed in Table VII for the ν_{asym} and $\nu_{sym}(PO_4)$ modes. We judge the strong absorption at 950–925 cm^{-1} in each spectrum to be too low in energy to arise from the $\nu_{sym}(PO_4)$ mode.

NMR Spectra. The spectra exhibit the expected resonances arising from the organotin and phenyl group moieties; for example, in trimethyltin(IV) diphenyl phosphate the ten phenyl protons fall in the range 6.8–7.7 ppm with the nine methyltin protons at 0.33 ppm. The methyltin coupling constants can yield important structural information, and the magnitude of $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ = 73.0 Hz is consistent with a five-coordinated tin atom[16] in the dilute $CDCl_3$ solution in which the spectrum was recorded.

Mass Spectra. In none of the spectra are there detectable parent molecular ions, fragments of mass higher than the parent or any di- or polytin-bearing species, thus ruling out any gas-phase association of the compounds in the spectrometer. As we have seen before in studying the di-[8] and triorganotin(IV)[7] dithiophosphate esters, the highest mass fragments derive from the loss of one organic group from tin in the tri- and from the loss of one phosphorus ligand moiety in the diorganotin derivatives. In the triorganotin series the former is frequently the most abundant peak in the spectrum, with $[SnO_2P(OC_6H_5)_2]^+$ (m/e 369), $[SnO_2POC_6H_5 - H]^+$ (275), and $[SnO_2P]^+$ (183) fragments prevalent. Tin ions are found in each spectrum at m/e 120. Successive loss of phenyl groups can be seen in the phenyltin spectra. The spectrum of the diphenyltin derivative exhibits an abundant $(C_6H_5)_3Sn^+$ fragment, presumably arising frm a gas-phase rearrangement of phenyl groups. In the syntheses of the related (*O,O'*-diisopropyl dithiophosphate)triphenyltin(IV), we also observed phenyl group rearrangements.[7] The fragments at m/e 213 in the tri- and diorganotin derivatives could in each case be assigned as $C_6H_5SnO^+$, also formed through a phenyl group rearrangement from the ligand. Most of the high abundance ions are even-electron species.

Mössbauer Spectra. The tin-119m Mössbauer data listed in Table II are consistent with organotin(IV) species in a higher than four-coordination geometry. The magnitudes of the isomer shift (IS) values (1.26–1.74 mm s^{-1}) confirm a tin(IV) oxidation state,[17] the magnitudes of the ρ values, the ratio of the quadrupole splitting (QS) to the IS values (2.60–3.54), reflect a higher coordination at tin, while the extremely high QS values in the diorganotin series specify a *trans*-diorganotin configuration in an octahedral geometry for those systems.

We have previously used a treatment based upon a point-charge model[18] to link the magnitude of the QS values with the C–Sn–C angle in six-coordinated diorganotin(IV) compounds.[8,19] This treatment assumes that the partial QS values for the ligands will be small compared to those for the R groups and that the magnitude of the QS will reach ca. 4.0 mm s^{-1} when the R_2Sn system becomes linear in a trans-octahedral geometry. We have lately, however, examined several series of diorganotin(IV) derivatives which exhibit QS values much above 4.0 mm s^{-1}, including the $R_2Sn[OP(O)(C_6H_5)OH]_2$[20] and $R_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$[21] systems analogous to the compounds reported here. In these cases the partial QS values for the ligands obviously cannot be ignored, and the model breaks down. We surmise that in these examples the *trans*-diorganotin(IV) octahedra contain nearly linear R_2Sn systems.

Our diphenyltin(IV) derivative, on the other hand exhibits a QS value of only 3.84 mm s^{-1}. Although the structural data for these phenyl systems are much more sparse than for the dimethyl analogues,[12] a correlation between doublet splitting and bond angle can be drawn[8] and used to calculate a phenyl–tin–phenyl angle of 175.2° for our compound. This must represent a maximum value owing to the contribution to the QS by the ligands (see above).

The dimethyltin(IV) derivative exhibits quite a strong Mössbauer spectrum at room temperature. While spectra can be recorded at these temperatures for several monomeric molecular solids of known structure,[22] we interpret this ob-

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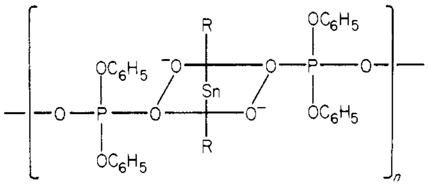
servation in terms of a lattice consisting of intermolecularly associated units propagating in at least one dimension.[17]

The trimethyl- and triphenyltin(IV) derivatives, on the other hand, fail to yield resolvable spectra at ambient temperatures, even after long counting times. We interpret this negative evidence as ruling out an intermolecularly associated polymeric lattice.

Structural Conclusions. While the vibrational spectra for the dimethyltin(IV) derivative fail to provide evidence which can be used to decide the question of the linearity of the carbon-tin-carbon skeleton, the magnitude of the Mössbauer QS and ρ values specify a *trans*-diorganotin, octahedral geometry. The question of bridging vs. chelation is decided, at least tentatively, by the ambient temperature spectrum, and we depict the polymer in the all trans-configuration in structure E. A similar, sheetlike polymeric structure has been proposed for the hypophosphite analogues, $R_2Sn(O_2PH_2)_2$.[13]



E

Again, for the triorganotin(IV) derivatives, the $\nu(SnC_3)$ region is obscured but the magnitudes of the Mössbauer QS and ρ values specify a higher than four-coordinated situation at tin, although the absence of resolvable ambient temperature spectra suggest that the value of n in structure B is finite. We have recently solved the structure of (diphenyl phosphato)triphenyltin(IV), which forms a solid composed of cyclic hexamers,[23] $[(C_6H_5)_3SnO_2P(OC_6H_5)_2]_6$. The related compound, (α-phenyl phosphonato)trimethyltin(IV), which is capable of hydrogen bonding, forms a helical polymer in the solid.[11] Model studies show that the smallest cyclic oligomer capable of incorporating linear O-Sn-O units is the pentamer ($n = 5$ in structure B) whose O-P-O angles would average 108°. In our cyclic triphenyltin(IV) solid, one phenyl group on each tin atom is thrust into the center of the oligomeric ring, which must expand to the hexamer in order to accommodate them.

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Registry No. $(CH_3)_3SnOP(O)(OC_6H_5)_2$, 80632-30-0; $(C_2H_5)_3SnOP(O)(OC_6H_5)_2$, 80632-32-2; $(n\text{-}C_3H_7)_3SnOP(O)(OC_6H_5)_2$, 80632-34-4; $(n\text{-}C_4H_9)_3SnOP(O)(OC_6H_5)_2$, 80632-36-6; $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$, 80632-37-7; $(c\text{-}C_6H_{11})_3SnOP(O)(OC_6H_5)_2$, 80632-39-9; $(CH_3)_2Sn[OP(O)(OC_6H_5)_2]_2$, 80632-41-3; $(C_2H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$, 80632-43-5; $(n\text{-}C_4H_9)_2Sn[OP(O)(OC_6H_5)_2]_2$, 80632-45-7; $(C_6H_5)_2Sn[OP(O)(OC_6H_5)_2]_2$, 80632-47-9; $(n\text{-}C_8H_{17})_2Sn[OP(O)(OC_6H_5)_2]_2$, 80632-49-1; $(C_6H_5)_3SnOH$, 76-87-9; $((n\text{-}C_3H_7)_3Sn)_2O$, 1067-29-4; $(CH_3)_2SnO$, 2273-45-2; $(C_2H_5)_3SnCl$, 994-31-0; $(C_2H_5)_2SnCl_2$, 866-55-7; $(CH_3)_3SnOH$, 56-24-6; $(c\text{-}C_6C_{11})_3SnOH$, 13121-70-5; $((n\text{-}C_4H_9)_3Sn)_2O$, 56-35-9; $(n\text{-}C_4H_9)_2SnO$, 818-08-6; $(n\text{-}C_8H_{17})_2SnO$, 870-08-6; $(C_6H_5)_2SnO$, 2273-51-0; $HOP(O)(OC_6H_5)_2$, 838-85-7.

Supplementary Material Available: Tables of mass spectral data (Tables III and IV) and infrared spectral frequencies (Tables V and VI) (6 pages). Ordering information is given on any current masthead page.

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Chemistry of Bipyridyl-like Ligands. 2. Mixed Complexes of Ruthenium(II) with 2-(Phenylazo)pyridine: A New π-Bonding Probe[1]

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A series of complexes of ruthenium(II) with the strong π-acceptor ligand 2-(phenylazo)pyridine (Azpy), $[Ru(Azpy)_2(AB)]^{n+}$, have been prepared. The coligands (AB) include Azpy, 2,2'-bipyridyl, 4,4'-bithiazole, 1,2-diaminoethane, 2,4-pentanedione anion, and X_2 ($X = NO_2^-, CN^-, Br^-, N_3^-$, and thiourea). Infrared spectra show the Azpy azo stretching mode to be diagnostic of the coligand (AB) π-accepting behavior, with strongly π-accepting coligands giving the highest Azpy $\nu(N{=}N)$. Visible spectra of the complexes consist of intense charge-transfer bands; the first CT band is not found to be a valid criterion for Ru-ligand π bonding. It is proposed that both σ and π effects are important, causing the observed nonlinear behavior. Emission spectra could be obtained for three of the compounds, one compound appearing to give multiple emissions. Cyclic voltammetry data support the strong π stabilization. Oxidation to Ru(III) could be observed in only a few complexes. However, all reduce at relatively high potentials, with $RuAzpy_3^{2+}$ reducing near 0 V (vs.SCE). A new thin-layer chromatography technique for cationic ruthenium complexes has been developed.

Introduction

In the first paper of this series,[2] we characterized three isomeric complexes of ruthenium(II) and 2-(phenylazo)pyridine (Azpy)[3] of the formula $[Ru(Azpy)_2Cl_2]$. In these complexes the ligand azo stretching mode was observed to be considerably shifted (ca. 100 cm^{-1}) below the free ligand value; this observation was interpreted as an indication of substantial ruthenium-Azpy π back-bonding. Since the question of the importance of ruthenium-ligand multiple bonding on complex

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(3) Other ligand abbreviations used in this paper: bpy, 2,2'-bipyridyl; Btz, 4,4'-bithiazole; en, 1,2-diaminoethane, tu, thiourea; acac, 2,4-pentanedionate anion, phen, 1,10-phenanthroline.

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