(ii) As far as CO_2 electroreduction is concerned, $Ni_2(\mathbf{2})^{4+}$ shows no particular properties as compared to $Ni(\mathbf{1})^{2+}$. In particular, it does not lead to coupling reactions.

(iii) On the other hand, the electroreduction of water is markedly more efficiently catalyzed by the dinuclear complex than by $Ni(\mathbf{1})^{2+}$. The involvement of dihydride intermediates of the type Ni(H)-Ni(H) might account for this result.

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Registry No. $Ni(\mathbf{1})^{2+}$, 46365-93-9; $Ni_2(\mathbf{2})^{4+}$, 102649-30-9; DMF, 68-12-2; CO_2, 124-38-9; H_2O, 7732-18-5; H_2, 1333-74-0; CO, 630-08-0; $HCOO^-$, 71-47-6; Hg, 7439-97-6; C, 7440-44-0.

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Utility of Cyclodichlorophosphazene as a NaC_5H_5 Scavenging Reagent: Synthesis of an Organoyttrium Hydroxide Complex and the X-ray Crystal Structure of the Layered Compound $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$

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$(C_5H_5)_3Y(THF)$ reacts with NaOH in THF to form NaC_5H_5 and $(C_5H_5)_2Y(OH)(THF)$. Treatment of the mixture of solids from this reaction with an 80%:20% mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$ in toluene allows the separation of the hydroxide complex by filtration. $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$, formed by partial hydrolysis of a $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)/C_6H_5C{\equiv}CC_6H_5$ mixture, crystallizes from a 1:2 mixture of THF/hexane in the presence of $C_6H_5C{\equiv}CC_6H_5$ in space group $P2_1/c$ with unit cell dimensions $a = 9.346$ (7) Å, $b = 21.284$ (8) Å, $c = 8.262$ (5) Å, $\beta = 112.50$ (3)°, and $Z = 2$ for $D_{calcd} = 1.43$ g cm^{-3}. Least-squares refinement on the basis of 513 observed reflections converged to a final $R = 0.068$. The molecular structure consists of two $(C_5H_5)_2Y$ units bridged by OH groups with Y-O distances of 2.33 (2) and 2.36 (2) Å. The $C_6H_5C{\equiv}CC_6H_5$ molecules occupy alternate layers between layers of the hydroxide molecules. The layers are oriented such that the hydroxide ligands are oriented toward the $C{\equiv}C$ bonds of the diphenylethyne molecules.

Introduction

Hydrolysis is a common mode of decomposition for the organometallic complexes of yttrium and the f elements, and hydroxide complexes are usually assumed to be the products.[2-4] Despite the apparent prevalence of hydroxide complexes in these reactions and the presumed existence of intermediates containing both organometallic ligands and hydroxide ligands, no structural evidence has previously been presented on organometallic hydroxide yttrium or f element species.[5] We recently were able to isolate crystals of an organometallic yttrium hydroxide complex cocrystallized with $C_6H_5C{\equiv}CC_6H_5$, and we report here on the resulting layered structure. In addition, we describe a novel synthesis of $(C_5H_5)_2Y(OH)(THF)$ using a reagent that may have utility in other reactions which form NaC_5H_5 as a byproduct.

Experimental Section

All of the complexes described below are air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted by using Schlenk, vacuum-line, and glovebox (Vacuum/Atmospheres HE-43 Dri Lab) techniques.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were obtained on a Bruker 250-MHz spectrometer. Chemical shifts were assigned relative to C_4D_7HO, 1.79 ppm, for spectra in THF-d_8. Complexometric metal analyses were obtained as previously described.[7]

Materials. Hexane was washed with sulfuric acid, dried over $MgSO_4$, and distilled from sodium benzophenone ketyl solubilized with tetraglyme. Toluene and THF were distilled from sodium benzophenone ketyl. THF-d_8 and benzene-d_6 were vacuum transferred from sodium benzophenone ketyl. NaOH was ground to a fine powder and heated to 120 °C under vacuum. Technical grade $(NPCl_2)_x$ (80% $x = 3$ and 20% $x = 4$; Aldrich) was degassed before use. $(C_5H_5)_3Y(THF)$[8] and $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$[9] were prepared according to the literature.

$(C_5H_5)_2Y(OH)(THF)$. NaOH (9 mg, 0.22 mmol) was suspended in 45 mL of THF containing $(C_5H_5)_3Y(THF)$ (80 mg, 0.22 mmol). The reaction was stirred for 2 days and filtered through a fine frit. The solvent was removed from the filtrate by rotary evaporation, giving a mixture of $(C_5H_5)_2Y(OH)(THF)$ and NaC_5H_5 as a pink powder (50 mg). A solution of $(NPCl_2)_x$ (152 mg, 0.44 mmol) in 25 mL of toluene was added to the pink powder, and the mixture was stirred overnight. The suspension was filtered to give $(C_5H_5)_2Y(OH)(THF)$ (45 mg, 66%), which was pure by ^1H NMR spectroscopy. Anal. Calcd for $YC_{14}H_{19}O_2$: Y, 28.85. Found: Y, 28.0. ^1H NMR (THF-d_8): δ 6.07 (s, C_5H_5). IR (KBr) 3540 m, 3060 s, 2960 s, 2920 m, 2900 m, 1700 m, 1620 m, 1580 m, 1560 m, 1520 m, 1500 m, 1360 w, 1100 s, 1080 s, 1060 s, 1050 s, 770 s cm^{-1}.

$(C_5H_5)_2Y(OH)(THF)$ can be desolvated by heating it to 110 °C overnight under vacuum (10^{-5} Torr). Anal. Calcd for $YC_{10}H_{11}O$: Y, 37.66. Found: Y, 38.7. Only decomposition was observed in attempts to sublime this material at temperatures as high as 300 °C. The desolvate is not soluble in toluene. Addition of THF regenerates $(C_5H_5)_2Y(OH)(THF)$.

$(C_5H_5)_2Y(OH)(THF)$ was also synthesized from $(C_5H_5)_3Y(THF)$ (228 mg, 0.64 mmol) and H_2O (11.5 mL, 0.64 mol). The degassed water in 10 mL of THF was added over 45 min to 40 mL of a solution of $(C_5H_5)_3Y(THF)$ cooled to −78 °C. The reaction was allowed to slowly warm to room temperature. Solvent was removed by rotary evaporation, and the remaining white solid was washed several times with toluene. The ^1H NMR spectrum of this product showed it to be a mixture of $(C_5H_5)_2Y(OH)(THF)$ (60% yield) and another THF-soluble product with a C_5H_5 resonance at δ 5.83. Since separation of these two species was not readily accomplished, the synthesis given above is preferable.

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(1) (a) University of California, Irvine. (b) University of Alabama.
(2) Evans, W. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds., Wiley: New York, 1982, Chapter 12.
(3) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474-493.
(4) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds., Pergamon: 1982; Chapter 21.
(5) Very few references to discrete organometallic f element hydroxide complexes are in the literature. $(C_5H_5)_3UOH$ has been mentioned in a review article.[6]
(6) Kanellakopulos, B. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D. Eds., D. Reidel: Dordrecht, Holland, 1978; pp 1-37.
(7) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115-4119.
(8) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42-44.
(9) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008-2014.

0020-1669/88/1327-1990$01.50/0

Table I. Crystal Data for $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$

compd	$Y_2O_2C_{20}H_{22}C_{14}H_{10}$
mol wt	650.48
space group	$P2_1/c$
cell constants	
a, Å	9.346 (7)
b, Å	21.284 (8)
c, Å	8.262 (5)
β, deg	112.50 (3)
cell vol, Å	1518
molecules/unit cell	2
ρ(calcd), g cm^{-3}	1.43
temp, °C	23 ± 1
μ(calcd), cm^{-1}	38.72
radiation	Mo Kα; λ = 0.7169 Å
max cryst dimens, mm	0.08 × 0.25 × 0.40
scan width, deg	0.8 + 0.2 tan θ
std reflcns	200; 0.40; 0.02
decay of stds	<1%
no. of reflcns measd	1480
2θ range, deg	2–40
octants collcd	$\pm h,k,l$
no. of obsd reflcns	513 ($>3\sigma$)
no. of params varied	87
GOF	1.8
R	0.068
R_w	0.073

X-ray Crystallography of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$. X-ray-quality crystals were obtained from a toluene solution of $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$[9] and $C_6H_5C{\equiv}CC_6H_5$ that had been partially hydrolyzed. A single crystal measuring 0.08 × 0.25 × 0.40 mm was sealed under nitrogen in a thin-walled glass capillary. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[10] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[11]

Calculations were carried out with the SHELX system of computer programs.[12] Neutral-atom scattering factors for Y, O, and C were taken from Cromer and Waber,[13] and the scattering for yttrium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[14] Scattering factors for H were obtained from ref 15.

The position of the yttrium atom was revealed by the inspection of a Patterson map. Two subsequent difference Fourier maps phased on the metal atom revealed the positions of the other non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.095$. After an empirical absorption correction was applied, the Y and O atoms were refined with anisotropic thermal parameters to produce a refinement with $R = 0.082$. Hydrogen atoms were placed at calculated positions and allowed to ride on the appropriate carbon atoms with fixed thermal parameters. Due to the paucity of data, a result of poor crystal quality, carbon atoms were refined with isotropic thermal parameters. Refinement converged at final values of $R = 0.068$ and $R_w = 0.073$. The final difference Fourier showed no feature greater than 1.0 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

Results and Discussion

Table II. Final Fractional Coordinates for $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$

atom	*x*	*y*	*z*
Y	0.0393 (4)	0.0792 (1)	0.4537 (4)
O	0.135 (2)	0.004 (1)	0.674 (5)
C(1)	0.272 (4)	0.044 (1)	0.351 (4)
C(2)	0.150 (4)	0.042 (2)	0.206 (5)
C(3)	0.091 (4)	0.104 (1)	0.160 (4)
C(4)	0.189 (3)	0.142 (1)	0.290 (4)
C(5)	0.311 (4)	0.106 (1)	0.434 (4)
C(6)	−0.206 (4)	0.131 (1)	0.499 (4)
C(7)	−0.176 (4)	0.168 (2)	0.397 (5)
C(8)	−0.032 (3)	0.194 (1)	0.498 (4)
C(9)	0.028 (4)	0.169 (1)	0.681 (5)
C(10)	−0.092 (4)	0.128 (1)	0.656 (4)
C(11)	0.512 (4)	0.027 (1)	−0.002 (5)
C(12)	0.508 (4)	0.090 (2)	−0.041 (4)
C(13)	0.435 (4)	0.133 (1)	0.030 (5)
C(14)	0.436 (4)	0.197 (1)	0.006 (4)
C(15)	0.535 (4)	0.224 (1)	−0.071 (4)
C(16)	0.624 (4)	0.180 (1)	−0.127 (4)
C(17)	0.615 (4)	0.119 (2)	−0.101 (4)

Synthesis. The initial synthesis of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$ was accomplished by the partial hydrolysis of a toluene solution of a $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)/C_6H_5C{\equiv}CC_6H_5$ reaction mixture. Single crystals of this product were isolated from solution and had the structure described below.

Subsequent attempts to obtain $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$ by simple hydrolysis of $(C_5H_5)_2YZ$ complexes ($Z = C_5H_5$,[8] CH_3,[16] H[9]) gave mixtures of products.[17] $(C_5H_5)_2Y(OH)(THF)$ (see below) was a component of these mixtures but was not readily obtainable in pure form. An alternative synthesis of bis(cyclopentadienyl)yttrium hydroxide was to displace $C_5H_5^-$ from $(C_5H_5)_3Y(THF)$ with OH^- (eq 1). This reaction has precedence in the in situ synthesis

$$(C_5H_5)_3Y(THF) + NaOH \rightarrow (C_5H_5)_2Y(OH)(THF) + NaC_5H_5 \quad (1)$$

of selected bis(cyclopentadienyl) complexes by reaction of tris(cyclopentadienyl)lanthanide and -yttrium complexes with alkyl[18] or alkoxide[19] anions (eq 2). When the relative solubilities of

$$(C_5H_5)_3Ln(THF) + MZ \rightarrow (C_5H_5)_2LnZ(THF) + MC_5H_5 \quad (2)$$

$$Ln = Nd, Lu;\ Z = t\text{-}C_4H_9,\ sec\text{-}C_4H_9$$

$$Ln = Pr;\ Z = n\text{-}C_4H_9$$

$$Ln = Y;\ Z = OCH_3$$

$$M = \text{alkali metal}$$

$(C_5H_5)_2LnZ$ and MC_5H_5 are such that separation can be achieved by a simple extraction or filtration, eq 2 provides a route to pure $(C_5H_5)_2LnZ$ complexes.[19] For Z = OH, separation is not easily achieved by extraction, filtration, or sublimation, and an alternative method was needed.

We have found that commercially available hexachlorocyclotriphosphazene, $(NPCl_2)_x$ (80% $x = 3$ and 20% $x = 4$), efficiently scavenges NaC_5H_5 from the reaction mixture formed in eq 1 to make a toluene-soluble product that is easily separated from the less soluble $(C_5H_5)_2Y(OH)(THF)$. Pure $(NPCl_2)_3$ does not work as well as the $(NPCl_2)_x$ mixture. $(NPCl_2)_x$ also reacts with cyclopentadienyl yttrium complexes, but since it reacts with NaC_5H_5 faster, it can be used as an efficient scavenging reagent in this system. $(NPCl_2)_3$ is well-known to react with alkyllithium and alkylmagnesium reagents and often gives complex products.[20–24] The toluene-soluble phosphorus-containing product

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(10) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53.

(11) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962.

(12) Sheldrick, G. M. "SHELX", A System of Computer Programs for X-ray Structure Determination", 1976.

(13) Cromer, D. T.; Waber, J. T. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1965**, *A18*, 104–109.

(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 72.

(16) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291–1300.

(17) Cf.: Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472–5478.

(18) Schumann, H.; Jeske, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 225–226.

(19) Sollberger, M. S.; Evans, W. J., unpublished results.

(20) Allcock, H. R.; Desorcie, J. L.; Harris, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 2814–2819 and references therein.

(21) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11–16.

(22) Harris, P. J.; Fadeley, C. L. *Inorg. Chem.* **1983**, *22*, 561–564.

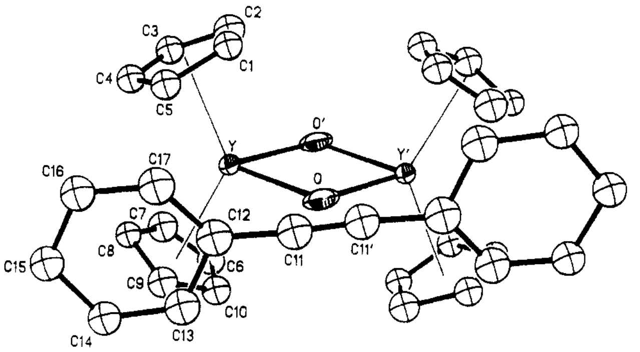

Figure 1. ORTEP diagram of the molecular structure of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$.

Table III. Bond Lengths (Å) for $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$

Y-Y	3.595 (6)	Y-O	2.33 (2)
Y-O′	2.36 (2)	Y-C(1)	2.72 (4)
Y-C(2)	2.74 (4)	Y-C(3)	2.70 (4)
Y-C(4)	2.65 (4)	Y-C(5)	2.66 (4)
Y-C(6)	2.70 (4)	Y-C(7)	2.67 (4)
Y-C(8)	2.60 (3)	Y-C(9)	2.71 (4)
Y-C(10)	2.64 (4)	C(1)-C(2)	1.30 (4)
C(1)-C(5)	1.47 (4)	C(2)-C(3)	1.42 (4)
C(3)-C(4)	1.37 (4)	C(4)-C(5)	1.50 (4)
C(6)-C(7)	1.26 (6)	C(6)-C(10)	1.33 (4)
C(7)-C(8)	1.40 (4)	C(8)-C(9)	1.50 (4)
C(9)-C(10)	1.37 (5)	C(11)-C(11)′	1.17 (6)
C(11)-C(12)	1.37 (4)	C(12)-C(13)	1.41 (5)
C(12)-C(17)	1.42 (6)	C(13)-C(14)	1.37 (4)
C(14)-C(15)	1.43 (6)	C(15)-C(16)	1.43 (5)
C(16)-C(17)	1.34 (5)		

obtained from the above $(NPCl_2)_x/NaC_5H_5/(C_5H_5)_2Y(OH)(THF)$ reaction system was also a mixture and was not investigated further.

If $(NPCl_2)_x$ is used as a NaC_5H_5 scavenger, $(C_5H_5)_2Y(OH)(THF)$ can be isolated as a pure material. IR and NMR spectroscopic data are typical for $(C_5H_5)_2YZ(THF)$ species. The THF of solvation can be removed by heating under vacuum, but the resulting unsolvated material is not soluble in hydrocarbon solvents less polar than THF.

Structure. The molecular structure of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$ (**1**) is shown in Figure 1. The $(C_5H_5)_2Y(OH)$ part of this molecule crystallizes as a dimer such that each yttrium atom is coordinated in a roughly tetrahedral geometry by two cyclopentadienyl rings and two bridging hydroxide ligands. This geometry is typical of bent metallocene molecules with two additional ligands[25] and is similar to that observed in other dimeric bis(cyclopentadienyl)yttrium complexes such as $[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ (**2**),[26] $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$ (**3**),[27] $[(C_5H_5)_2Y(\mu,\eta^2\text{-}HC{=}NCMe_3)]_2$ (**4**),[28] and $[(C_5H_5)_2Y(\mu\text{-}N{=}CHCMe_3)]_2$ (**5**).[16]

Examination of the bond distances and angles in the $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$ part of **1**, given in Tables III and IV, reveals similarities to the parameters of complexes **2**–**5**. The 2.68 (3) Å Y–C(ring) average, the 130° (ring centroid)–Y–(ring centroid) angle and the 3.595 (6) Å Y···Y nonbonded distance are all in the range of values observed for **2**–**5**. The Y–O distances of 2.33 (2) and 2.36 (2) Å can be compared to the values of 2.275 (3) and 2.290 (3) Å found in **2**. The O–Y–O′ angle of 80.3 (9)° is in the range observed for **3**–**5** and is larger than the 73.1 (1)° angle found in **2**. These comparisons show no particularly unusual features about OH as a ligand for complexes of this type.

Table IV. Selected Bond Angles (deg) for $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$[a]

O-Y-O′	80.3 (9)	C(11)-C(12)-C(13)	121 (4)
Cn(1)-Y-Cn(2)	130 (1)	C(11)-C(12)-C(17)	123 (4)
Cn(1)-Y-O	111 (1)	C(12)-C(13)-C(14)	124 (4)
Cn(1)-Y-O′	106 (1)	C(12)-C(17)-C(16)	125 (4)
Cn(2)-Y-O	109 (1)	C(13)-C(12)-C(17)	112 (3)
Cn(2)-Y-O′	108 (1)	C(13)-C(14)-C(15)	121 (3)
Y-O-Y′	100.4 (7)	C(14)-C(15)-C(16)	116 (3)
C(11)′-C(11)-C(12)	166 (4)	C(15)-C(16)-C(17)	120 (4)

[a] Cn(1) is the centroid of the cyclopentadienyl ring containing carbon atoms 1–5. Cn(2) corresponds to carbon atoms 6–10.

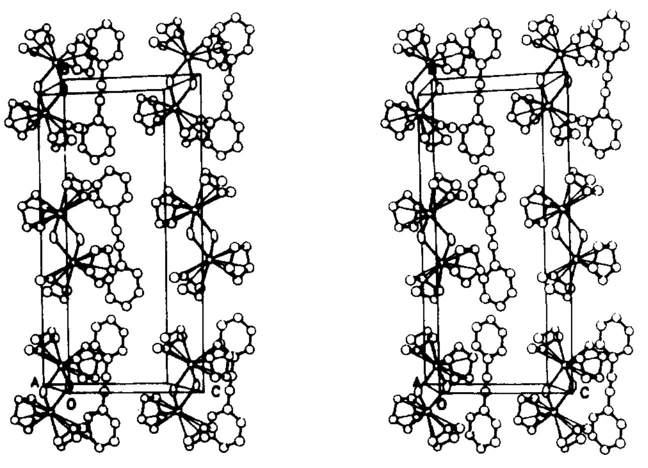

Figure 2. Unit cell of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$ showing the layered structure.

The most remarkable feature of the structure of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$ is the relative arrangement of the yttrium dimers vis-à-vis the diphenylethyne molecules. As shown in Figure 2, the yttrium dimers and the alkyne are arranged in layers with one layer of alkyne molecules per layer of hydroxide dimers. The layers are oriented such that each hydroxide oxygen atom is directed toward a C≡C bond of an alkyne. One such pair of molecules is shown in Figure 1. The $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$ unit is oriented such that the Y_2O_2 plane makes a 92.4° angle with the plane of the phenyl rings of $C_6H_5C{\equiv}CC_6H_5$. This means that some π-electron density of the C≡C bond is directed right toward the hydroxide ligand. It is probably no coincidence that the shortest distances between the $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$ and the $C_6H_5C{\equiv}CC_6H_5$ molecule are the distances between the oxygen atom of the hydroxide ligand and the carbon atoms of the C≡C triple bond. These distances range from 3.44–3.55 Å. For comparison, the shortest $C(C_5H_5)$–$C(C_5H_5)$ contact between dimers is 3.88 Å and the shortest C(alkyne)–C(alkyne) contact is 3.67 Å. Intermolecular $C(C_5H_5)$–$C(C_6H_5)$ contacts range from 3.63 to 3.98 Å.

The Y–O–(C≡C midpoint) and Y′–O–(C≡C midpoint) angles of 127 and 130°, respectively, are similar. Since the sum of these angles plus the Y′–O–Y angle of 100.4 (7)° is close to 360°, the two yttrium atoms, the oxygen atom, and the C≡C midpoint are nearly coplanar. The molecular arrangement in **1** allows the oxygen atom of the hydroxide ligand to approach within 3.45 Å of the midpoint of the C≡C triple bond. This distance and the resulting position of the hydrogen atom of the hydroxide group with respect to the electron density of the alkyne bond are within the range of distances observed in hydrogen-bonded systems.[29] Hydrogen bonding of hydroxyl protons to internal alkynes has been observed before by using phenol as the hydroxide source,[30,31]

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(23) Winter, H.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1986**, 1269–1275 and references therein.

(24) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119–157.

(25) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(26) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291–1296.

(27) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61.

(28) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1252–1254.

(29) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968; p 16.

(30) West, R.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1961**, *83*, 765–768.

Inorg. Chem. **1988**, *27*, 1993–1999

but we are unaware of previous X-ray studies that show this interaction.

Conclusion

Cyclodichlorophosphazene has been shown to be a viable reagent for scavenging NaC_5H_5 from mixtures containing organoyttrium complexes. The utility of this reagent depends on (1) the relative reaction rates for the cyclopentadienyl species to be removed versus the cyclopentadienyl complex to be isolated and (2) the relative solubility of the reaction products. The crystal structure of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$ shows that the hydroxide ligand can exhibit normal bonding parameters in an organoyttrium complex and that unusual layered structures may be possible with hydroxide-containing organometallic compounds via hydrogen bonding.

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Registry No. 1, 114199-08-5; $(C_5H_5)_2Y(OH)(THF)$, 114199-06-3; $(C_5H_5)_3Y(THF)$, 79533-63-4; $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$, 80642-66-6; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; $(NPCl_2)_x$, 26085-02-9.

Supplementary Material Available: An alternative view of **1** plus tables of complete bond angles, thermal parameters, intermolecular contact distances, and hydrogen atom positions (5 pages); a table of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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(31) Yoshida, Z.; Ishibe, N.; Ozoe, H. *J. Am. Chem. Soc.* **1972**, *94*, 4948–4952.

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Multinuclear Magnetic Resonance Studies of the Reactions of Bidentate Ligands with $Pt(S_2P\{OEt\}_2)_2$. Crystal and Molecular Structure of $(apeS)Pt(S_2P\{OEt\}_2)_2$ (ApeS = $Ph_2AsCH_2CH_2P(S)Ph_2$)

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The interactions in dichloromethane solution of $Pt(S_2P\{OEt\}_2)_2$ with a number of potentially bidentate ligands have been studied by multinuclear (^{31}P, ^{77}Se, ^{195}Pt) magnetic resonance techniques. The ligands used (L-L′) were $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2P(E)Ph_2$ (E = S, Se to give dpmS, dpmSe), and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe). All the ligands except apeS and apeSe react with $Pt(S_2P\{OEt\}_2)_2$ in 1:1 proportions to give initially $[(L\text{-}L')Pt(S_2P\{OEt\}_2)]^+$ and free $[S_2P(OEt)_2]^-$, but a slower reaction gives $(L\text{-}L')Pt(S_2P\{O\}OEt)$ and $EtS_2P(OEt)_2$ by attack of the free anion on the coordinated dithiophosphate ligand. In 1:2 proportions these ligands give $[Pt(L\text{-}L')_2]^{2+}$ and free $[S_2P(OEt)_2]^-$, except for dpm which gives $[(\eta^1\text{-dpm})(\eta^2\text{-dpm})Pt(\eta^1\text{-}S_2P\{OEt\}_2)]^+$. The same products are obtained by reacting 1 mol of L-L′ with 1 mol of $[(L\text{-}L')Pt(S_2P\{OEt\}_2)]^+$, but the $(L\text{-}L')Pt(S_2P\{O\}OEt)$ compounds do not react with further L-L′ ligand. The ligands apeE react with $Pt(S_2P\{OEt\}_2)_2$ to give only $(\eta^1\text{-apeE})Pt(\eta^1\text{-}S_2P\{OEt\}_2)(\eta^2\text{-}S_2P\{OEt\}_2)$. The structures of all the complexes in solution were determined by multinuclear magnetic resonance studies and that of $(\eta^1\text{-apeS})Pt(\eta^1\text{-}S_2P\{OEt\}_2)(\eta^2\text{-}S_2P\{OEt\}_2)$ in the solid state was confirmed by a single-crystal X-ray diffraction study. Crystal data for $(apeS)Pt(S_2P\{OEt\}_2)_2$: $M_r = 1039.98$, monoclinic space group $P2_1$, $a = 10.107$ (1) Å, $b = 20.002$ (2) Å, $c = 11.278$ (2) Å, $\beta = 114.23$ (2)°, $Z = 2$, $\rho_{measd} = 1.65$ (1) g cm^{-3}, Mo Kα radiation, $R = 0.030$, $R_w = 0.034$ for 7695 independent reflections. The structure contains discrete molecules with the square-planar stereochemistry about platinum being defined by three sulfur atoms from one bidentate and one monodentate $[S_2P(OEt)_2]^-$ ligand and an arsenic atom from the monodentate apeS ligand.

Introduction

There have been extensive studies by Stephenson[1-5] and Fackler[6,7] and their co-workers on the interactions of monodentate group 15 ligands with platinum(II) bis(dithiolate) compounds $Pt(S\text{-}S)_2$ (S-S = $[S_2CNR_2]^-$, $[S_2COR]^-$, $[S_2P(OR)_2]^-$, $[S_2PR_2]^-$). In general, 1 mol of tertiary phosphine or phosphite reacts to generate the species $(PR_3)Pt(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S)$, which often, at room temperature, display exchange on the NMR time scale between the monodentate and bidentate dithiolate ligands. Reaction of a second mole of phosphine or phosphite causes displacement of the η^1-dithiolate ligand to give $[(PR_3)_2Pt(\eta^2\text{-}S\text{-}S)]^+$. In the *O*,*O′*-dialkyl dithiophosphate (and xanthate) systems these products must be isolated quickly; otherwise, interaction between the free dithiolate anion and the remaining coordinated dithiolate occurs to give $RS_2P(OR)_2$ and coordinated $[S_2P(O)OR]^{2-}$. These reactions have been studied in solution by using proton, phosphorus-31, and platinum-195 NMR spectroscopies,[1-7] and X-ray crystallographic studies on some of the isolated products have confirmed the stereochemistries of several of these compounds.[1,6,7]

In this paper the results of reactions between $Pt(S_2P\{OEt\}_2)_2$ and several potentially bidentate ligands L-L′ are described where L-L′ = $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2P(E)Ph_2$ (E = S, Se to give dpmS, dpmSe), and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe). The products of the reactions have been characterized by NMR (^{31}P, ^{77}Se, ^{195}Pt) spectroscopic studies and a crystal structure determination on $(apeS)Pt(S_2P\{OEt\}_2)_2$.

Experimental Section

Materials. $Pt(S_2P\{OEt\}_2)_2$ was prepared by the interaction of aqueous solutions of $K_2[PtCl_4]$ and $K[S_2P(OEt)_2]$.[8] The precipitate was filtered

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(1) Alison, J. M. C.; Stephenson, T. A.; Gould, R. O. *J. Chem. Soc. A* **1971**, 3690.

(2) Alison, J. M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 254.

(3) Steele, D. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2124.

(4) Cornock, M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 501.

(5) Colton, R.; Stephenson, T. A. *Polyhedron* **1984**, *3*, 231.

(6) Lin, I. J. B.; Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394.

(7) Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stephenson, T. A.; Gould, R. O.; Alison, J. M. C.; Fraser, A. J. F. *Inorg. Chem.* **1982**, *21*, 2397.

(8) Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1571.

0020-1669/88/1327-1993$01.50/0