were dissolved in a 2:1 ethanol–benzene mixture dried over magnesium ethoxide. The product, mp 122°, had an infrared absorption spectrum identical with that reported by McGrady and Tobias.[1] *Anal.* Calcd for $C_{22}H_{24}O_4Sn$: C, 56.08; H, 5.14; Sn, 25.20. Found: C, 56.23; H, 5.60; Sn, 26.9.

The solvent was AR grade benzene purified by partial freezing; the remelted solid was stored over sodium.

Procedures described elsewhere[10-13] were used in making the measurements summarized in Tables I and II. Concentrations are shown as weight fractions w_2. Incremental quantities, indicated by the prefix Δ, are the differences between properties measured for solutions and solvent. Suffixes 1 and 2 refer, respectively, to solvent and solute. For benzene at 25°, and $w_2 = 0$, the dielectric constant, density, and refractive index (Na light) are,[10] in order, ϵ_1 2.2725, d_1 0.87378, and n_1 1.4973.

TABLE I

INCREMENTAL DIELECTRIC CONSTANTS, DENSITIES, AND REFRACTIVE INDICES FOR SOLUTIONS OF $(C_6H_5)_2Sn(acac)_2$ IN BENZENE AT 25°

10^5w_2	676	880	931	935	1206	2095
$10^4\Delta\epsilon$	221	277	299	...	380	557
$10^5\Delta d$	233	...	...	321	414	688
$10^4\Delta(n^2)$	15	18	...	...	21	42

TABLE II

INCREMENTAL LOSS TANGENTS FOR SOLUTIONS OF $(C_6H_5)_2Sn(acac)_2$ IN BENZENE AT 25°

(a) 3109 MHz

10^5w_2	880	1206	2095
$10^3\ \Delta\tan\delta$	2.589	4.363	6.713

(b) 9400 MHz

10^5w_2	676	931	935	1206	1587	2095
$10^3\ \Delta\tan\delta$	0.864	1.437	1.471	2.565	2.929	3.928

Results and Discussion

Mean values (± standard variations) of quotients drawn from Table I are $\Delta\epsilon/w_2 = 3.09 \pm 0.24$, $\Delta d/w_2 = 0.3399 \pm 0.0024$, and $\Delta n^2/w_2 = 0.200 \pm 0.019$, so that at infinite dilution the total polarization and molecular refraction of the solute follow[10-12] as 372 ± 22 cm^3 and 114 ± 2 cm^{-3}, respectively. Its apparent dipole moment falls in 0.1 D steps from 3.6 to 3.1 D (±0.2 D) as the distortion polarization is increased 1.0, 1.1, . . . , 1.5 times the molecular refraction. However, from ref 14 and 15 it seems that only about 14 cm^3 of atomic polarization should be attributed to each 2,4-pentanedionato chelate group; when this is the case μ emerges as 3.35 ± 0.2 D.

Table II reports dielectric loss measurements which give mean values of $(\Delta \tan \delta)/w_2$ of 0.325 at 3109 MHz and 0.17 (±0.03 standard variation) at 9400 MHz. Such results strongly suggest that $(C_6H_5)_2Sn(acac)_2$ in benzene solution exhibits an orientation polarization which is large and "real." The two values just quoted for $(\Delta \tan \delta)/w_2$ are found—by accepting the Debye model for a solute behaving as a rigid dipole in a low viscosity, nonpolar solvent[16] and by using the equations given by Le Fèvre and Sullivan[12]—to be consistent with a relaxation time τ of 61×10^{-12} sec and a dipole moment of 2.5 D. A τ of this order is reasonable for a solute molecule of the size of $(C_6H_5)_2Sn(acac)_2$—compare 62×10^{-12} sec for $(C_6H_5)_3CCl$ and 51×10^{-12} sec for $C_8H_8Rh(acac)$.[17]

The dipole moment deduced from the dielectric loss measurements is lower than others suggested above by the refractivity method; however the correct allowance to make for atomic polarization is unknown. Only if this allowance is slightly larger than the molecular refraction can the same moment be deduced from the data of Tables I and II. No precedent exists to justify making such a suggestion.

Accordingly we conclude that bis(2,4-pentanedionato)diphenyltin(IV) dissolved in benzene is, in fact, polar with a dipole moment lying between 2.5 and 3.6 D. It follows that in solution the complex cannot exist as the (nonpolar) *trans* form alone but must prefer the *cis* configuration although the existence of a mixture of *cis* and *trans* forms (with the former predominant) cannot be precluded. Further studies of this nature on other organometallic complexes are in progress.

Acknowledgment.—The authors wish to thank Drs. M. J. Aroney and J. D. Saxby for several helpful discussions.

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Identification of the "Lead(II) Hydroxide" of Robin and Theólier

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The uncertain status of the existence of lead(II) hydroxide, $Pb(OH)_2$, has been pointed out by Robin and Theólier,[1] who claimed to have made it by the thermal decomposition, at 280–300°, of a basic salt precipitated by ammonium hydroxide from a solution of lead(II) nitrate. The thermogravimetric curve of the basic salt resembled that given by Duval[2] and showed two stages of weight loss, the second corresponding exactly to that expected for the dehydration of $Pb(OH)_2$. In earlier studies of basic lead(II) nitrates precipitated by sodium hydroxide Nicol[3] obtained a

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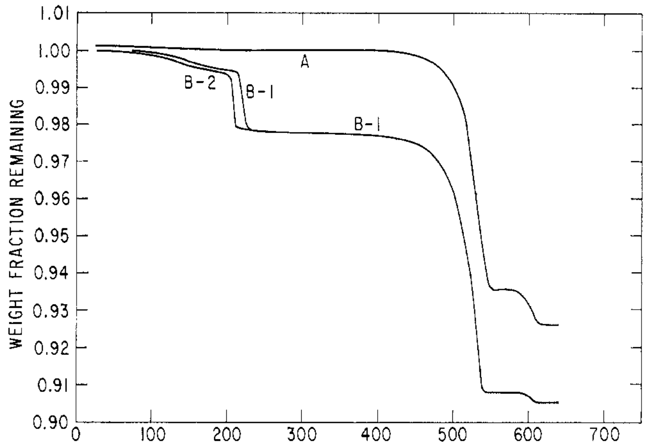

Figure 1.—Thermograms in air: (A) $Pb(NO_3)_2 \cdot 5PbO$, 0.5012 g at 150°/hr; (B-1) $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$, 0.3686 g at 150°/hr; (B-2) $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$, 0.4008 g at 25°/hr (all in Coors No. 4/O porcelain crucibles).

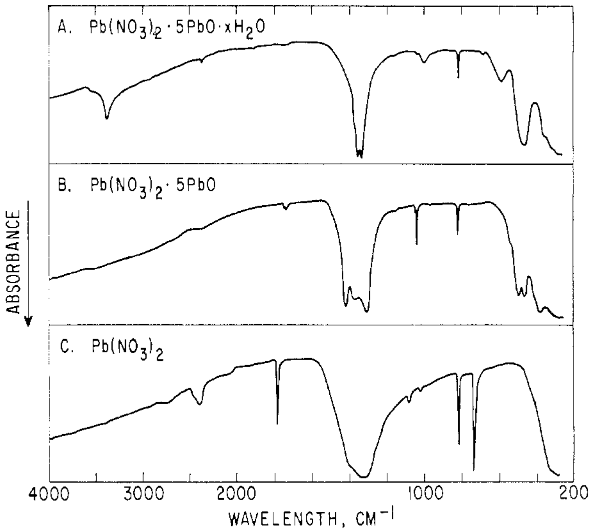

Figure 2.—Infrared spectra from mulls in Nujol and in hexachlorobutadiene.

similar thermogravimetric curve which he attributed to $Pb(NO_3)_2 \cdot 5PbO \cdot 2H_2O$ decomposing first to $Pb(NO_3)_2 \cdot 5PbO$ and then transitorily to Pb_3O_4 and finally PbO.

Recently, Kwestroo, Langereis, and van Hal[4] reported that $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, when heated at 300° for 3 hr gave a solid containing 8.0% NO_3 whose X-ray diagram was identical with that given by Robin and Theólier for $Pb(OH)_2$. Also, Brusset, Martin, and Peltier[5] have reported that $Pb(NO_3)_2 \cdot 5PbO \cdot 2H_2O$, when heated in air at 150°/hr to 330°, held 1 hr, and quenched, formed a creamy yellow powder, $Pb(NO_3)_2 \cdot nPbO$ (n = 4.96–5.17), with an X-ray diffraction pattern the same as that given by Robin and Theólier for $Pb(OH)_2$. On further heating it formed PbO directly without the intermediate stage of Pb_3O_4 reported by Nicol. The present work was undertaken to repeat directly the work of Robin and Theólier and to determine whether $Pb(OH)_2$ could be made by their method.

Experimental Section

Preparation of the Basic Salt $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$.—Several samples of the basic salt were made by the method of Robin and Theólier and with variations with the additional precaution of nitrogen blanketing to exclude atmospheric carbon dioxide. The yield was about 40% when the reaction was carried out in an open beaker and better than 97% when the reaction was carried out in a flask fitted with a reflux condenser. The products were dried over Drierite in air or under vacuum until they reached constant weight.

Anal. Calcd for $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$: Pb, 83.82 for $x = 2$; 84.85 for $x = 1$. Found for five different preparations: Pb air-dried, 84.10, 83.98; Pb vacuum dried, 84.55, 84.44, 84.54. Samples fired in air to 550° produced brown fumes in the range 450–500°. The X-ray diffraction pattern was in substantial agreement with those published.[4,5]

Preparation of the "Hydroxide."—A 12.002-g portion of the basic salt was heated 23 hr at 280° in a stream of clean dry air to form 11.742 g of the tan "hydroxide."

Anal. Calcd for $Pb(OH)_2$: Pb, 85.90; weight loss, 7.47. Calcd for $Pb(NO_3)_2 \cdot 5PbO$: Pb, 85.90; NO_3, 8.57; weight loss, 7.46. Found: Pb, 85.90, NO_3, 8.28; weight loss, 7.40. The X-ray diffraction pattern was in good agreement with that published by Brusset, *et al.*, for $Pb(NO_3)_2 \cdot 5PbO$.

Analyses and Instrumental Methods.—Lead content of the samples was determined by air-firing 1 g at 550° for 1 hr, cooling, then reducing the lead oxide thus obtained in flowing hydrogen for 1 hr at 500° and 1 hr at 600°, cooling, and weighing the lead.

Dynamic thermograms were obtained with a Chevenard Model TH59 II C thermobalance. Reported weight changes have been corrected appropriately for apparent weight gain.

Infrared spectra were obtained in the 200–4000-cm^{-1} region with a Perkin-Elmer 521 spectrophotometer.

Powder X-ray diffraction patterns were obtained photographically in a 5-cm diameter camera using Ni-filtered Cu Kα radiation.

Results and Discussion

The Basic Salt.—Five preparations were examined thermogravimetrically. The results are represented by one example, Figure 1, curve B-1. A slower heating rate had the usual effect,[6] curve B-2. In some preparations the plateau centered at approximately 300° was preceded by a short sloping section from about 210 to 250°, and in others the entire plateau was horizontal. One preparation made in an open beaker showed only a sloping plateau in this region. The appearance of brown fumes is related to the rapid decomposition above 450°. The short plateau from 540 to 590° was present on all but one thermogram. The plateau centered at 300° may be assigned the composition $Pb(NO_3)_2 \cdot 5PbO$, the plateau centered at 565°, the composition Pb_3O_4–PbO, and the final plateau, the composition PbO. The weight loss from room temperature to 300° is 2.25% (calcd for dihydrate, 2.43%).

There appears to be general agreement in the literature that lead nitrate solution when treated with a base forms a salt of the composition $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$, but there is no agreement on the value of "x" or on the nature of the water present; some authors prefer to express the formula in terms of the ratio of $Pb(NO_3)_2$ to $Pb(OH)_2$. Most work has been done by conductometric, thermometric, or calorimetric methods, but in

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TABLE I

ANALYSES FOR $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$

	Pb	NO_3	OH	Sum	Wt loss to PbO
$Pb(NO_3)_2 \cdot 5PbO \cdot 5H_2O$	80.87	8.07	11.06	100.00	12.89
Pauley and Testerman[7]	80.2	7.8	11.9	99.9	...
Kwestroo, *et al.*[4]	83.7	8.3	11.6[a]	103.6	...
Brusset, *et al.*[5]	...[b]	...	...	...	10.0
$Pb(NO_3)_2 \cdot 5PbO \cdot 2H_2O$	83.83	8.36	11.46[a]	103.64	9.71
This work (B-1)	84.07	...	...	...	9.57

[a] By dissolution in standard nitric acid and back-titrating. [b] Ratio $Pb(NO_3)_2:PbO = 4.96–5.17$.

three papers analyses are given for the solid phase. Pauley and Testerman[7] added 1.0 *N* NaOH to 0.1 *N* $Pb(NO_3)_2$ at 25° to a potentiometric equivalence point, filtered the resulting precipitate, dried it at 110°, and analyzed for Pb, NO_3, and OH. Kwestroo, *et al.*,[4] added 10 *N* NaOH to 1 *N* $Pb(NO_3)_2$ in the calculated ratio, stirred for 2 hr, filtered, washed with water and acetone, dried at 40°, and analyzed for Pb, NO_3, and OH. Brusset, *et al.*,[5] added 0.4 *N* NaOH to 1 *N* $Pb(NO_3)_2$ at 20°, stirred 10 min, washed by decantation, centrifuged, dried in air or over $CaCl_2$, and analyzed for total lead and lead as PbO or $Pb(OH)_2$. Table I shows their results, calculated compositions, and one analysis from the present work. Although Kwestroo, *et al.*, identified their compound as $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, their results are more closely represented by $Pb(NO_3)_2 \cdot 5PbO \cdot 2H_2O$. Titration for OH cannot distinguish between the two formulas, and emphasis, therefore, must be placed on their results for Pb and NO_3. Also, their X-ray diffraction pattern agreed with that of Brusset, *et al.*, for the lower hydrate. Thus, except for the work of Pauley and Testerman, prior work, including that of Nicol, indicates that the composition of the basic nitrate is best represented by $Pb(NO_3)_2 \cdot 5PbO \cdot 2H_2O$.

The "Hydroxide."—Thermogravimetric analysis, Figure 1, curve A, showed a 0.16% weight loss up to 170° which was assumed to be adsorbed water, and the overall weight loss was corrected to a dry basis by this amount. A second run was halted at 550°, held for 70 min, and quenched in air to room temperature. The temperature, 550°, was selected as being below that at which Pb_3O_4 decomposes, 570°, but above that at which PbO oxidizes, 450°, according to Otto.[8] The residue was identified by X-ray diffraction as primarily a mixture of PbO and Pb_3O_4. The weight losses from 170 to 550° were 6.48 and 6.38%, respectively, in the two runs (theory: Pb_3O_4, 5.25%; PbO, 7.46%).

It seems clear from these studies that Robin and Theólier's compound was probably the basic salt $Pb(NO_3)_2 \cdot 5PbO$, which may also be formulated $Pb_6O_5(NO_3)_2$, hexalead pentoxide dinitrate. Additional evidence was obtained from infrared spectra.

Infrared Spectra.—The spectrum of Mallinckrodt AR $Pb(NO_3)_2$ is shown in Figure 2C. In agreement with Miller and Wilkins[9] and Addison and Gatehouse,[10] samples mulled in air reacted with the window material to produce spectral bands due to potassium nitrate. However, it was found unnecessary to protect the windows if the samples were mulled, mounted, and examined in an atmosphere of dry nitrogen. The spectrum is similar to those previously reported for mulls for the low-frequency region except that absorption at 831–836 cm^{-1} was not found. This has been reported as stronger[9,10] and weaker[11] than the absorption at 807 cm^{-1} but may have been due to contamination from alkali nitrate. Many more absorption frequencies have been reported by Gross and Shultin[12] and by Schroeder, *et al.*,[13] who measured single crystals at low temperatures. Except for the splitting of the forbidden transition ν_1, 1010 and 1070 cm^{-1}, the spectrum is essentially that due to the internal vibrations of the nitrate ion. The splitting of ν_1 was attributed by Gross and Shultin to the interaction of molecular and lattice vibrations and by Schroeder, *et al.*, to sum and difference tones of the libration and the symmetric stretch.

A wet precipitate of $Pb(NO_3)_2 \cdot 5PbO \cdot xH_2O$ mounted between Irtran plates gave an initial spectrum containing broad bands due to liquid water at 3370 and 1630 cm^{-1} and a broad absorption with peaks at 1353 and 1333 cm^{-1} probably due to nitrate ion. As the sample dried, the bands due to liquid water decreased in intensity, the bands attributed to nitrate increased in intensity, and new absorption peaks appeared at 2350, 1748, 1733, 1037, 1000, and 811 cm^{-1}. A vacuum dried sample gave the mull spectrum shown in Figure 2A. The strong band at 3380 cm^{-1} and the absence of a band near 1630 cm^{-1} indicates that OH^- is present, not H_2O. The bands below 700 cm^{-1} are probably due to Pb–O vibrations[14] but not to $Pb_4(OH)_4^{4+}$ or $Pb_6(OH)_8^{4+}$.[15]

The "hydroxide" spectrum 2B resembles 2A but lacks OH^- absorption at 3380 cm^{-1} and contains, as does spectrum 2A, strong bands in the 1300–1400 cm^{-1} region which may be attributed to nitrate. The absence of strong bands at 1530–1480 and 1290–1250 cm^{-1} indicates that the nitrate is not coordinated to the central atom.[16,17]

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Metal-Phosphorus Stretching Frequencies of Some Tetrakis(bicyclic phosphite) Complexes of Nickel(0), Palladium(0), Platinum(0), Copper(I), and Silver(I)

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A recently reported far-infrared investigation of tetrakis(triethyl phosphite)metal complexes wherein M = Ni, Pd, and Pt[1] prompts us to describe the results we have obtained with the bicyclic phosphite species $(CH_3C(CH_2O)_3P)_4M$ and $((CH_2)_3(CHO)_3P)_4M$ in which M = Ni, Pd, Pt, Cu^+, and Ag^+. Three bands were assigned by Myers, Basolo, and Nakamoto to M–P stretching modes for each of the triethyl phosphite complexes. The two bands in the 340–290-cm^{-1} region were assigned to the M–P stretching frequency of the split F_2 species and one band at 220–190 cm^{-1} was ascribed to the A_1 mode. The splitting of the F_2 species and the appearance of the unallowed A_1 were attributed to deviation of the complexes from T_d symmetry. Inasmuch as the bicyclic phosphites $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ are constrained and therefore highly symmetrical, spectra of these complexes are expected to be somewhat simpler and thus more amenable to interpretation. Recently we assigned the M–P stretching frequency in $(CH_3C(CH_2O)_3P)_4Ni$ at 157 cm^{-1},[2] and since this value is significantly lower than those reported by Myers, *et al.*, for the triethyl phosphite analog,[1] a broader far-infrared study is presented here.

Experimental Section

Reagents.—The ligands $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ have been described previously.[3] Triethyl phosphite was purchased from J. T. Baker Chemical Co. and used without further purification. The copper(I) and silver(I) bicyclic phosphite complexes were prepared following the method reported earlier.[4] Although we previously reported a preparation of the tetrakis(bicyclic phosphite)nickel(0) complexes involving the displacement of CO from $Ni(CO)_4$ by the appropriate bicyclic phosphite,[5,6] it was found more convenient to synthesize them in the manner described by Vinal and Reynolds.[7] The yields with both bicyclic phosphites were nearly quantitative.

Anal. Calcd for $C_{20}H_{36}O_{12}P_4Ni$: C, 36.87; H, 5.57; P, 19.02. Found: C, 37.15; H, 5.60; P, 18.91. Calcd for $C_{24}H_{36}O_{12}P_4Ni$: C, 41.23; H, 5.19; P, 17.72. Found: C, 40.91; H, 5.38; P, 17.51.

$(CH_3C(CH_2O)_3P)_4M$ and $((CH_2)_3(CHO)_3P)_4M$ (M = Pd or Pt).—The starting materials for these complexes were $((C_6H_5)_3P)_4Pd$ and its platinum analog which were prepared by the method reported by Malatesta and Cariello.[8] The colorless bicyclic phosphite complexes were precipitated in nearly quantitative yields by dissolving 40 mmol of the appropriate phosphite in 75 ml of ethanol in which was suspended 8 mmol of the appropriate starting complex. Completion of the heterogeneous reaction was signaled by conversion of the yellow starting complex to the colorless product after stirring for several hours at room temperature. Filtration and washing of the products with ethanol yielded complexes of sufficient purity for this study. The near-infrared spectra were found to be devoid of phenyl proton vibrations which suggested that complete substitution of the triphenylphosphine ligands had taken place. The palladium complex of $CH_3C(CH_2O)_3P$ was also prepared following the method which Vinal and Reynolds[7] described for $((C_2H_5O)_3P)_4Ni$ to provide additional assurance that none of the assigned bands in the far-infrared region could be associated with undisplaced triphenylphosphine. The platinum and nickel complexes appear to be quite stable in air while the palladium compounds show evidence of air oxidation within several hours.

Anal. Calcd for $C_{20}H_{36}O_{12}P_4Pd$: C, 34.37; H, 5.19; P, 17.72. Found: C, 34.15; H, 5.10; P, 17.50. Calcd for $C_{20}H_{36}O_{12}P_4Pt$: C, 30.50; H, 4.60; P, 15.73. Found: C, 30.29; H, 4.71; P, 15.49. Calcd for $C_{24}H_{36}O_{12}P_4Pd$: C, 38.74; H, 4.85; P, 16.58. Found: C, 36.68; H, 4.90; P, 16.35. Calcd for $C_{24}H_{36}O_{12}P_4Pt$: C, 34.50; H, 4.34; P, 14.82. Found: C, 34.43; H, 4.26; P, 14.60.

Spectra.—Proton nmr spectra were obtained on a Varian A-60 spectrometer on saturated benzene solutions in which the complexes were slightly soluble. Tetramethylsilane was used as an internal standard. Integration of all three spectra gave the expected 2:1 ratio for the CH_2 to CH_3 proton absorptions which appeared, respectively, at 4.00 and 0.45 ppm in the nickel, 3.82 and 0.27 ppm in the palladium, and 4.02 and 0.40 ppm in the platinum complex. The CH_3 proton peak was sharp while the CH_2 band was broader with several unresolved shoulders. The proton spectrum of $((CH_2)_3(CHO)_3P)_4Ni$ showed broad doublets for H_{ax} (1.74 ppm), H_{eq} (2.84 ppm), with $^2J_{HH}$ = 12.9 Hz, and a broad single resonance for H_{CH} (4.37 ppm). A similar spectrum was exhibited by the platinum analog wherein these parameters were 1.75 ppm, 2.70 ppm, 12.2 Hz, and 4.70 ppm, respectively, while the palladium compound decomposed in benzene solution.

Far-infrared spectra were obtained with a Beckman Model 11 grating spectrometer. The $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ complexes were too insoluble for recording spectra in solution and so Nujol mulls were placed between two polyethylene plates each 1 mm in thickness which were sparated from one another by a gasket constructed from a third plate of equal thickness. All palladium complexes were mulled in a nitrogen-filled glove bag. Twenty per cent benzene solutions of $(C_2H_5O)_3P$ were measured in 1-mm polyethylene cells while spectra of $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ were recorded in fused polyethylene. The spectra in the region studied are shown in Figures 1–3.

Results and Discussion

The ligand $CH_3C(CH_2O)_3P$ gives rise to a reasonably

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