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Complexes of Organometallic Compounds. XLVI. Synthesis of Adducts Formed by Organotin(IV) Trichlorides with 1,2-bis(Diphenylphosphino)ethane, and Their Characterization by Mössbauer and Infrared Spectroscopy

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Adducts between $RSnCl_3$ ($R = Me, Bu^n, Oct^n, Ph$) and 1,2-bis(diphenylphosphino)ethane, DPE, have 1:1 composition. In Mössbauer spectroscopic experiences at variable absorber temperature the area under the resonant peaks, A, has been measured for $RSnCl_3 \cdot DPE$, $R = Me, Ph$; slopes of plots of ln A vs. *T suggest strong coupling between Mössbauer atoms, which has been interpreted in terms of solid state polymeric structures, due to DPE acting as a bridging bis-monodentate ligand. Infrared data indicate the covalency of Sn–Cl bonds.*

Three possible structural isomers of octahedral type are then proposed, one having trans-P_2 *and two* cis-P_2 *atoms. A choice between these structures has been attempted by point-charge model calculations of partial quadrupole splittings, from ΔE of the already known $SnCl_4 \cdot (AlkPh_2P)_2$ as well as of $RSnCl_3 \cdot DPE$ estimator compounds.*

Introduction

Previous studies from our laboratory on the coordination chemistry of monoorganotin(IV) moieties concerned the synthesis and configurational spectroscopic investigations of adducts and complexes where O, N and S atoms were donating charge to tin(IV) [1–5]. As a continuation of this research project, we have carried out the present study on the interaction between $RSnCl_3$ compounds (R = Me, Bu^n, Oct^n, Ph) and the ligand 1,2-bis(diphenylphosphino)ethane (DPE), having P donor atoms. Adducts with 1:1 stoichiometry have been synthesized, which have been subsequently studied in the solid state by IR and Mössbauer spectroscopy in order to get information on the coordinating behaviour of the ligand and the nature of the ideal polyhedron centered at Sn^{IV}.

Experimental

Pure reagents and solvents (C. Erba, Milano) have been used which, whenever necessary, have been purified and/or dried according to standard procedures. The ligand 1,2-bis(diphenylphosphino)ethane was from Alfa Inorganics; the organotins were gifts by dr. E. O. Wirth, Deutsche Advance Produktion G.M.B.H., Marienberg (BRD). Fluka and Alfa Inorganics products have been also used.

The synthesis of adducts $RSnCl_3 \cdot DPE$ has been carried out by mixing hot n-hexane solutions of DPE (1 mmol in about 100 ml) and equimolar $RSnCl_3$. The white crystalline precipitates, immediately formed, were filtered off, washed with solvent and dried under vacuum. The related analytical data are in Table I. It must be noticed that attempts of preparing 1:2 $RSnCl_3$–DPE adducts failed, since 1:1 compounds have been always recovered irrespective of the molar ratio of reagents used in the synthetic procedure.

The infrared spectra were measured on mulls in Nujol between CsI disks, using a Perkin–Elmer Mod. 457 spectrometer (calibrated with a polystyrene film), in the wavenumber region 4000–250 cm^{-1}. Some interesting bands in the far IR are reported in Table I. The expected ligand bands [6], as well as bands associated to RSn^{IV} [1, 2] (whenever not obscured by ligand vibrations), have been satisfactorily identified in the spectra of the adducts. No bands attributable to Sn–P modes were detected. It has been reported [7] that such modes would originate (in bis-phosphine adducts of $Snhal_4$) bands too weak to be assigned.

The Mössbauer spectra at liquid N_2 temperature have been measured as usual, employing the apparatus and procedures described earlier [2] (Elscint–Laben spectrometer, equipped with a Na(Tl)I detector DM 1-2 from Nuclear Enterprises, Edinburgh; AERE cryostat; $Ba^{119m}SnO_3$ source from R. C., Amersham, 10 mCi, constantly accelerated at RT, by a full sawtooth waveform; data reduction by a suitable computer program; *etc.*). The spectra of the Me and Ph derivatives (taken as representative terms) have been measured at various temperatures by a Ricor cryostat MC-3A (Ein Harod, Israel); the thickness of samples was about 0.5 mg

TABLE I. Experimental of 1:1 Adducts $RSnCl_3$·DPE[a].

Compound[a]	M.p. (°C)	Elemental Analysis Found (Calcd.) %					Infrared Bands[b]		
		C	H	P	Cl	Sn	$\nu(SnC)$[c]	$\nu(SnCl_3)$	Others
$MeSnCl_3$·DPE	136–137	50.63	4.50	9.50	16.71	18.77	525mw	285sh	555w
		(50.79)	(4.26)	(9.70)	(16.66)	(18.59)		275s	515s
Bu^nSnCl_3·DPE	75–76	52.72	5.00	9.12	15.48	17.54	525m, bd	285sh	550m
		(52.94)	(4.89)	(9.10)	(15.63)	(17.44)		275s	
								255sh	
Oct^nSnCl_3·DPE	126–128	55.18	5.80	8.44	14.67	15.99	520s	285sh	555mw
		(55.43)	(5.61)	(8.41)	(14.44)	(16.11)		275sh	
								255sh	
$PhSnCl_3$·DPE	185–187	54.74	4.21	8.70	15.15	17.04		285s	
		(54.86)	(4.17)	(8.84)	(15.18)	(16.94)		275s	
								255sh	

[a] DPE is 1,2-bis(diphenylphosphino)ethane. [b] Relevant absorptions in the 560–250 cm^{-1} region. Ligand bands [6] are omitted. Assignments are tentative. s = strong; m = medium; w = weak; bd = broad; sh = shoulder. [c] With possible contributions from ligand bands [6] (532 cm^{-1}, w; 503 cm^{-1} s).

TABLE II. Mössbauer Parameters for $RSnCl_3$·DPE.

Experimental Data					Calculations of p.q.s.'s:	
Temp.[a] (°K)	δ[b]	ΔE[c]	A[d]	Γ_{av}[e]	Structure[f] and	([P] – [X])[g]
$MeSnCl_3$·DPE						
79	1.18	2.10	19.32	0.92	I	+0.02
84	1.18	2.12	17.04		II	+0.02
104	1.17	2.11	13.29		III	–0.04
126.5	1.17	2.10	9.75			
137.5	1.17	2.09	8.46			
148.5	1.17	2.10	7.19			
Bu^nSnCl_3·DPE						
77	1.18	1.95		0.98	I	–0.06
					II	–0.05
					III	+0.11
Oct^nSnCl_3·DPE						
77	1.20	1.85		0.92	I	–0.13
					II	–0.10
					III	+0.27
$PhSnCl_3$·DPE						
78	1.06	1.80	26.31	0.90	I	–0.05
85.5	1.06	1.82	23.53		II	–0.05
125.5	1.06	1.83	13.38		III	+0.11
149.5	1.05	1.83	9.57			
$SnCl_4 \cdot (AlkPh_2P)_2$[h]						
		(+) 0.54[i]			[j]	–0.13

[a] Within about 0.5°. [b] Isomer shift, mm s^{-1}, with respect to RT $BaSnO_3$. [c] Nuclear quadrupole splitting, mm s^{-1}. [d] Total area under the resonant peaks, arbitrary units (see text. [e] Full width at half height of the peaks, average. [f] See Fig. 3. [g] ½e | Q | units, mm s^{-1}; P = $-CH_2-P(Ph)_2$; calculated by point-charge ΔE equations reported in ref. 2. [h] Alk = Me, Et. [i] Average value; sign is given according to literature reports; see text. [j] Axial P_2, equatorial Cl_4 (see text).

cm^{-2} of ^{119}Sn, the area of the Cu sample holder being 2.0 cm^2; the latter was in thermal contact with a coiled pipe through which liquid N_2 from a pressurized Dewar was flowing under controlled conditions; thermal shielding was fulfilled by evacuation of the cryostat at about 1μ, and by reflecting gold-plated copper covers; an heating element at the holder, operated by a MTC-3 temperature controller (Elscint, Haifa), ensured the constancy of the predetermined temperature within about 0.5° (nominal stability ~0.1°/day); actual temperatures were also checked on the Cu–constantan thermocouple operating the MTC-3 controller. In these conditions, about 5 × 10^5 counts per channel were scaled for each spectrum at the various temperatures: output data were fitted by simple Lorentzian lineshapes [2], and the area under the resonant peaks was subsequently calculated as the sum of areas of individual peaks of the doublet, A = 1.5708 y_m $\Delta H_{1/2}$ [8] (where y_m corresponds to the computed effect magnitude, ϵ, and $\Delta H_{1/2}$ to Γ, *i.e.*, the full width at half height of the fitting lineshapes). Gravimetric integration [9] gave essentially coincident results. The quality of the spectra is shown in Fig. 1, while Table II reports the determined parameters.

Discussion

From the analytical data of Table I it appears clearly that compounds $RSnCl_3$·DPE have a 1:1 stoichiometry. The infrared spectra (Table I; see also under Experimental) are fully consistent with adduct formation. The occurrence of ν(Sn–Cl) vibrational

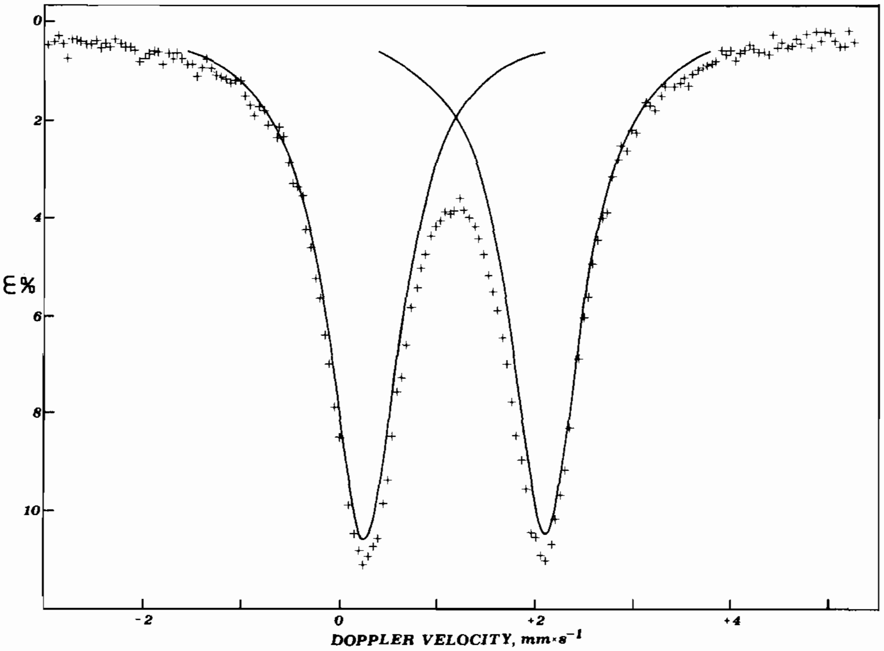

Figure 1. Mössbauer spectrum of $Oct^nSnCl_3 \cdot DPE$ at liquid N_2 temperature. Solid lines are computed Lorentzians.

modes indicates that Sn–Cl bonds are covalent; besides, the energy of these modes in $RSnCl_3 \cdot DPE$ essentially corresponds to that observed for adducts of $RSnCl_3$ with terminal Sn–Cl bonds [1, 2], so that the latter bonding situation may be reasonably assumed also for $RSnCl_3 \cdot DPE$.

The possible ways in which $Ph_2P(CH_2)_2PPh_2$ may link Sn are: i) as chelating bidentate ligand, in consonance with its behaviour towards many metal ions; ii) as monodentate; iii) as bridging bis-monodentate, by virtue of its flexibility due to free rotation along the C–C bond. The following general ideal configuration of solid $RSnCl_3 \cdot DPE$, including possible structural isomers, could then be advanced: i) octahedral, monomeric; ii) monomolecular structure with five-coordinated Sn^{IV}; iii) octahedral, polymeric. Before speculating on these hypotheses, it seems fit to discuss the temperature dependent Mössbauer data for $RSnCl_3 \cdot DPE$, reported in Table II, which may considerably help in limiting the bonding possibilities.

It is known that, on application of the Debye model for solids, the recoil-free fraction, F_a, of γ-rays emitted and absorbed by a Mössbauer atom is given by [10, 11]:

$$F_a = \exp\left\{-\frac{3}{2}\frac{E_R}{K\theta}\left[1+4\left(\frac{T}{\theta}\right)^2 \int_0^{\theta/T}\frac{x}{e^x-1}dx\right]\right\} \tag{1}$$

where $E_R = E_\gamma^2/2M_{eff}c^2$ is the recoil energy of the nucleus, θ is the Debye (or Mössbauer) temperature, and $x = h\omega/2\pi KT$. In the high-temperature limit ($T \geqslant \theta/2$) Eq. (1) takes the form [10, 11]:

$$F_a = \exp -\left\{\frac{3}{2}\frac{E_R}{K\theta}+\frac{6E_R}{K\theta^2}T\right\} \tag{2}$$

from which [11]:

$$d(\ln F_a)/dT = -6E_R/K\theta^2 \tag{3}$$

In the thin absorber approximation, the recoil free fraction is proportional to the total area, A, under the resonance curve; then, in cases of linear experimental plots of ln A *vs.* T, it follows that: i) the high-temperature limit assumption is valid; ii) the slope is described by Eq. (3), and depends on θ and M_{eff} (the effective mass related to the vibrational modes of the absorber atom). At comparable M_{eff} values, increasing θ (and decreasing slope d(ln A)/dT) means increase of the maximum vibrational frequency in the Debye model, which is interpreted in terms of progressive increase of intermolecular interactions [12–15]. In other words, low values of d(ln A)/dT are associated to solid state polymers (in the sense of large intermolecular forces acting between the environment of the Mössbauer atom), while larger slopes would indicate essentially monomolecular solids [12–14, 16]. A number of cases have been discussed on these grounds, mainly by Herber and his coworkers [1, 13–20].

As far as $RSnCl_3 \cdot DPE$ (R = Me, Ph) are concerned, the following is deduced from temperature dependent measurements: i) the invariance, with respect to temperature, of isomer shifts, δ [10], and nuclear quadrupole splittings, ΔE [10] (Table II), indicates that no phase transitions nor structural changes take place in the T range explored [13, 15]; ii) plots of log

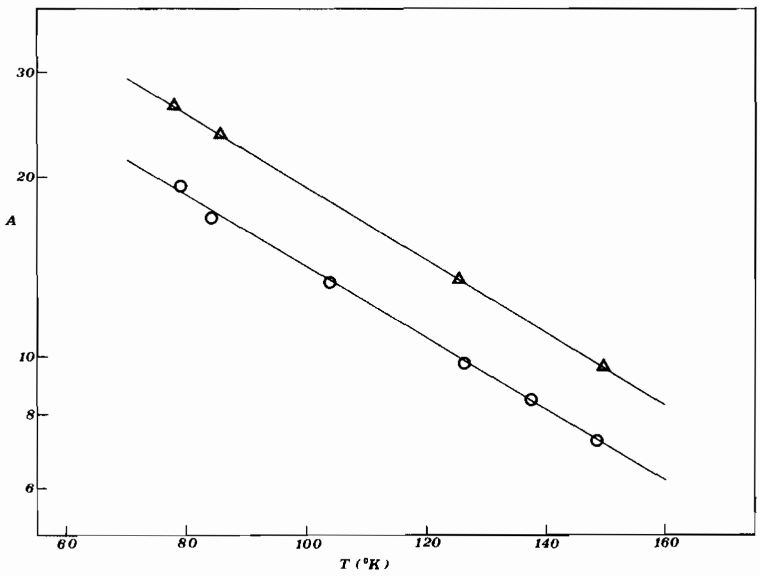

Figure 2. Temperature dependence of the total area A under the resonant peaks, arbitrary units, for: ○, $MeSnCl_3 \cdot DPE$; △, PhSn-$Cl_3 \cdot DPE$ (areas at 120 °K extrapolated for normalization purposes: Me, 10.75; Ph, 14.50).

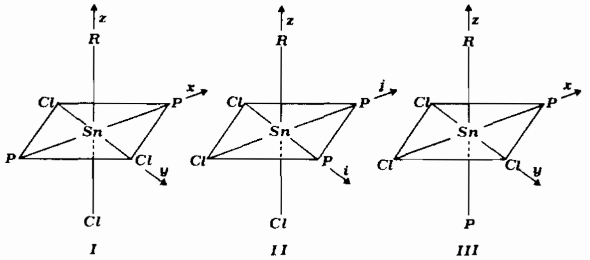

Figure 3. Possible idealized structural isomers for Sn^{IV} environments in $RSnCl_3 \cdot DPE$. The two P atoms in an individual structure belong to two different molecules of bridging $Ph_2P(CH_2)_2PPh_2$. Axes correspond to components of the electric field gradient tensor [25], and have been assigned by: 1) suitable $V_{\alpha\alpha}$ equations [2, 25]; ii) p.q.s. ([Alk] – [X]) = –1.03 [25], ([Ph] – [X]) = –0.95 [25], ([P] – [X]) = –0.13 mm s^{-1} (see Table II and text). For structure II, $V_{ii} = V_{jj}$, η [10, 25] = 0; for I and III, x and y may interchange as functions of actual p.q.s.'s (Table II).

A *vs.* T are linear (Fig. 2), so that the high temperature limit approximation is obeyed in these cases and slopes d(lnA)/dT may be described by Eq. (3); iii) the slope is practically coincident for both compounds (R = Me, slope = 1.379×10^{-2}; R = Ph, 1.413×10^{-2}; correlation coefficients are 0.999 and 1.000, respectively), lying between values pertaining to solids generally characterized by intermolecular forces (see data reported in Ref. 13; besides 6.13×10^{-3} for Me_3SnN_3 [17], polymeric in the Debye sense; 4.47×10^{-2} Me_3SnNCO [18], "polymeric"; 1.35×10^{-2} for the known solid state polymer $Me_2SnCl_2 \cdot H_2Salen$ [21, 22]); iv) the normalized straight lines ln (A/A_{120}) *vs.* T for $RSnCl_3 \cdot DPE$ insert between lines 4 and 5 of Fig. 3, Ref. (1), pertaining to "polymers" $Me_3SnCl \cdot H_2Acen$ and Me_3SnF; v) no consistent effect on d(lnA)dT due to increased M. W. is observed from Me to Ph derivative in $RSnCl_3 \cdot DPE$. These circumstances strongly suggest the occurrence of large intermolecular forces acting between RSn^{IV} moieties in $RSnCl_3 \cdot DPE$ (including Bu^n and Oct^n derivatives, which may be reasonably assumed to behave as the other two), *i.e.*, a strong coupling between Sn^{IV} atoms, which implies that DPE acts as bridging bis-monodentate ligand. It is concluded that $RSnCl_3 \cdot DPE$ are very probably solid state polymers, where the environment of Sn^{IV} is of octahedral type, corresponding to the possible structural isomers I, II and III, Fig. 3.

The ν(SnCl) vibrational bands of Table I cannot help in selecting the actual configuration; in fact, assuming that there are really three experimental bands attributable to ν(SnCl) modes, these would be predicted by group theory for both *mer*-and *fac*-Cl_3 [2]. Information on the probable coordination polyhedron around Sn is extracted from the rationalization of Mössbauer parameters, essentially ΔE, discussed in the following.

Isomer shifts, δ [10], of $RSnCl_3 \cdot DPE$ (Table II) are consistent with six-coordination of Sn^{IV}; in fact, these data insert quite well in the systematic shown in Fig. 1 of Ref. (23), where the approximate dependence of δ from the average electronegativity of atoms bound to Sn is reported for a large number of RSn^{IV} derivatives, as function also of the Sn coordination number.

In order to rationalize nuclear quadrupole splittings, ΔE [10], we employ here the point-charge model and the concept of additivity of partial electric field gradients (e.f.g.) [24, 25]. It has been observed that Sn 5s electronic charge is involved in all bonds formed by Sn in RSn^{IV} compounds which, in this respect, renders the latter in some way analogous to Sn^{IV} derivatives [23]. We have then calculated the relative partial quadrupole splitting [24, 25] (p.q.s.), due to P atoms, from ΔE of adducts $SnCl_4 \cdot (AlkPh_2P)_2$, whose structure is known with reasonable certainty, and discuss in the following the obtained p.q.s. ([P] − [X]) (where X stands for hal [24]), in conjunction with values extracted from ΔE of $RSnCl_3 \cdot DPE$ in the possible configurations I–III (see Table II). In fact, internally consistent p.q.s. values would be expected for Sn^{IV} and RSn^{IV} compounds, since charge would be donated in both cases by P atoms to Sn hybrid orbitals having comparable s,p (and d) characters.

Compounds $SnCl_4 \cdot (AlkPh_2P)_2$ exhibit $\Delta E = 0.58$; 0.57 (Alk = Me) and 0.46 (Alk = Et) mm s^{-1} [26, 27]. From vibrational spectroscopy it has been determined that bis-monodentate phosphine–$Snhal_4$ adducts are octahedral type species with (generally) *trans*-P_2 atoms, and this is the case for compounds mentioned above [7, 26–28]. Besides, it has been determined that the sign of the quadrupole coupling constant e^2qQ (and hence of ΔE) is positive for $SnCl_4 \cdot (Et_3P)_2$, which is consistent with a (distorted) octahedral geometry around Sn with *trans*-P_2 atoms, the latter being larger σ-donors than Cl [29]; this may be reasonably extended to other *trans*-P_2 species.

On these grounds the p.q.s. ([P] − [X]) = −0.13 mm s^{-1} (Table II) has been determined by the appropriate point-charge equation for ΔE [2, 25]. This value is consistent with tabulations of p.q.s.'s relative to octahedral structures [25], in the sense that it implies a σ-donor power towards Sn larger than that of, say, F, Cl, Br and, in general, N and O atoms [25], in consonance with electronegativity series (it must be recalled that, strictly speaking, such comparisons of p.q.s.'s would be valid only in cases of comparable s-character of acceptor Sn orbitals, being p.q.s. $\propto -\sigma(1 - s)$ [30]). The suitability of this p.q.s. is also demonstrated by the point-charge interpretation of the experimentally determined $\Delta E = 0$ for the *cis*-P_2 octahedral derivatives $SnCl_4 \cdot DPE$ ($\Gamma = 0.83$) [26] and $SnCl_4 \cdot Ph_2PCH_2PPh_2$ ($\Gamma = 1.10$) [27]. In fact, by the appropriate point-charge equation for ΔE [2] and the p.q.s. above, it has been obtained (for regular octahedral $SnCl_4 \cdot (AlkPh_2P)_2$, *cis*-$P_2$) $\Delta E = -0.26$ mm s^{-1}, which is very probably too low to be detected, also employing fitting procedures with Lorentzian lineshapes. Calculations of $V_{\alpha\alpha}$ and diagonalizations of the e.f.g. tensor [2, 10, 25] have been then effected for $RSnCl_3 \cdot DPE$, structures I–III, obtaining the results shown in Fig. 3. Calculated V_{zz} being negative (as expected in view of the predominant concentration of electronic charge predicted to occur along Sn–C bonds), ΔE of $RSnCl_3 \cdot DPE$ (Table II) is positive [25]; the latter data (with their proper sign) have been then employed in calculating p.q.s.'s reported in Table II, using the suitable point-charge equations [2, 25] and tabulated p.q.s.'s for Ph_{oct} and Alk_{oct} [24, 25] (see also legend to Fig. 3).

It has been reported that p.q.s.'s obtained from different estimator compounds, concerning a ligand in a given configuration, may differ by ±0.2 mm s^{-1} according to the existing systematic [24]. Assuming as actual in our case the value −0.13 mm s^{-1}, p.q.s.'s from Bu^n, Oct^n and Ph derivatives pertaining to III (and consequently structure III itself) would be accordingly ruled out. Besides, positive p.q.s.'s ([P] − [X]) could be disregarded also on the basis of inconsistency with the sequence of σ-donor power of ligand atoms discussed in the preceeding. Structures I or II would be then assumed as the more probable for $RSnCl_3 \cdot DPE$, R being Bu^n, Oct^n and Ph. As far as the Me derivative is concerned, statements above would indicate configuration III as actual; on the other hand, if signs are ignored, p.q.s.'s for I–III are too similar to allow any choice of structure.

In conclusion, at least for Bu^n, Oct^n and Ph derivatives, the nature of the Sn environment in our solid state polymers remains unassigned for what concerns the possible *cis* or *trans* positions of P atoms. Previous reports indicate that both types of configurations may occur in octahedral species with two Sn–P bonds, as discussed in the preceding; it must be also recalled here that $Bu^nSnCl_3 \cdot (Ph_3P)_2$ (the only RSn^{IV} derivative, belonging to this class, so far reported) has been assumed as a *cis*-P_2 species [31].

Acknowledgments

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