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Preparation of Diethylaluminium Chelates, $R_2P(S)$-X-$AlEt_2$ (X=NMe, S) and Some Reactions with Carbonyl Compounds

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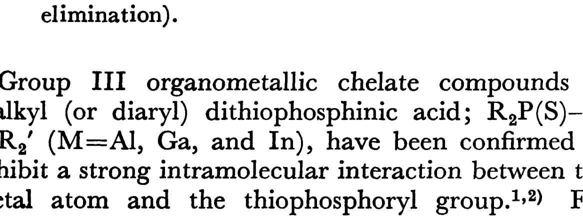
New monomeric organoaluminium chelate compounds; *N*-diethylaluminium *N*-methyl dialkylthiophosphinic amide and dialkyldithiophosphinate; $R_2P(S)$–X–$AlEt_2$ (X=NMe, S), were prepared. Spectroscopic results of these compounds indicate an intramolecular coordination of sulfur atom of P=S bond to the organoaluminium moiety. Addition reactions of $Me_2P(S)$–NMe–$AlEt_2$ and $Et_2P(S)$–S–$AlEt_2$ with phenyl isocyanate gave the corresponding 1/1 adducts and only small amount of elimination product was obtained. A reaction of $Me_2P(S)$–NMe–$AlEt_2$ with benzaldehyde gave $Me_2P(S)$–NMe–CH(Et)Ph and PhCH=NMe (by two ways of addition-elimination).

Group III organometallic chelate compounds of dialkyl (or diaryl) dithiophosphinic acid; $R_2P(S)$–S–MR_2' (M=Al, Ga, and In), have been confirmed to exhibit a strong intramolecular interaction between the metal atom and the thiophosphoryl group.[1,2] For instance, Coates prepared two dimethylaluminium derivatives of dimethyl(or diphenyl)dithiophosphinic acid; $R_2P(S)$–S–$AlMe_2$ (R=Me, Ph) and claimed an intramolecular coordination based on their infrared spectra.

The corresponding *N*-alkyl dialkylthiophosphinic organoaluminium amides; $R_2P(S)$–NR′–AlR_2'', have not been reported,[3] and the chemical behavior of these class of organoaluminium chelate compounds; $R_2P(S)$–X–$AlEt_2$ (X=NMe, S), has been unexplored. In our former paper,[4] diethylaluminium dialkyl *N*-methylphosphoramidates; $(RO)_2P(O)$–NMe–$AlEt_2$ (R=Me, Et), were found to react with carbonyl compounds giving the corresponding imino compounds by way of an addition and subsequent elimination reactions as Eq. (1).



(1)

Therefore, *N*-diethylaluminium *N*-methyl dialkylthiophosphinic amide; $R_2P(S)NMeAlEt_2$, and dialkyldithiophosphinate; $R_2P(S)SAlEt_2$, are expected to react with carbonyl compounds analogously affording the corresponding >C=NMe or >C=S compounds.

We describe here the preparation of chelate compounds of type $R_2P(S)$–X–$AlEt_2$ (X=NMe, S) and their reactions with carbonyl compounds.

Results and Discussion

Preparation of $R_2P(S)$–X–$AlEt_2$ Compounds. *N*-Diethylaluminium *N*-methyl dialkylthiophosphinic amides; $R_2P(S)$–NMe–$AlEt_2$ (Ia—d) were prepared from the reactions between $R_2P(S)NHMe$ (IIIa—d) and Et_3Al in refluxing benzene in 60—80% yields (Eq. (2)).

$$\underset{\text{(IIIa—d)}}{R_2P(S)NHMe} + Et_3Al \xrightarrow[80^\circ C]{\text{benzene}} \underset{\text{(Ia—d)}}{R_2P(S)NMeAlEt_2} + C_2H_6 \qquad (2)$$

(R; a=Me, b=Et, c=*i*-Pr, d=*t*-Bu)

The corresponding three dithiophosphinic acid derivatives; $R_2P(S)$–S–$AlEt_2$ (IIa—c) were prepared analogously from the reactions of $R_2P(S)SH$ (IVa—c) with Et_3Al. These new compounds are distillable and their physical, analytical results are summarized in Table 1.

The cryoscopic molecular weight determination in benzene shows that these compounds have monomeric structure in consistent with an intramolecular coordination.

Infrared and NMR Spectra. In Table 2 $\nu_{P=S}$ absorptions of (Ia—d, IIa—c) were compared with those of the parent organophosphorus compounds (IIIa—d, IVa—c) (in the range of 650—550 cm^{-1}).[5] The lower frequency shift of the $\nu_{P=S}$ absorptions in

Table 1. Physical and analytical data of $R_2P(S)$–X–AlE_2 (Ia—d, IIa—c)

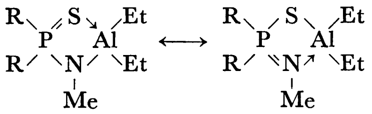
Compound	R	X	Yield (%)	Bp (°C/mmHg)	Found (%) C	H	Al	Calcd (%) C	H	Al	Mol. wt. Found (Calcd)	Concn (wt%)
Ia	Me	NMe	79	87—89 (0.06)	40.26	9.00	12.57	40.57	9.24	13.02	191 (207)	1.80
Ib	Et	NMe	69	94—97 (0.06)	45.44	9.85	11.81	45.94	9.85	11.49	220 (235)	2.52
Ic	*i*-Pr	NMe	66	80—111 (0.33)	50.34	10.18	10.62	50.17	10.33	10.25	239 (264)	2.82
Id	*t*-Bu	NMe	60	116—126 (0.33)	53.50	10.65	10.08	53.58	10.72	9.26	262 (291)	2.62
IIa	Me	S	71	65—68 (0.18)	34.41	7.56	13.10	34.27	7.67	12.83	188 (210)	2.73
IIb	Et	S	67	90—100 (0.25)	40.49	8.29	10.60	40.32	8.46	11.32	246 (238)	2.49
IIc	*i*-Pr	S	85	86—96 (0.20)	44.72	8.85	10.99	45.09	9.08	10.13	232 (266)	2.52

Table 2. Infrared spectra of $R_2P(S)$–X–$AlEt_2$(Ia—d, IIa—c) and $R_2P(S)XH$(IIIa—d, IVa—c) (cm^{-1})a,b)

Compounds		R	X	$\nu^A_{P=S}$ of (Ia—d, IIa—c)	$\nu^B_{P=S}$ of (IIIa—d, IVa—c)	$\Delta\nu_{P=S}=\nu^A_{P=S}-\nu^B_{P=S}$	$\nu_{P=N}$ of (Ia—d)
Ia,	IIIa	Me	NMe	622 vs, 524 w	652 vs, 588 w	−30, −64	1187 m
Ib,	IIIb	Et	NMe	624 vs	651 vs, 569 w	−27	1186 m
Ic,	IIIc	*i*-Pr	NMe	622 vs, 543 w	654 vs, 565 w	−32, −22	1186 m
Id,	IIId	*t*-Bu	NMe	620 vs	652 vs, 626 w	−32	1192 m
IIa,	IVa	Me	S	610 vs, 543 w	650 vs, 602 w	−40, −59	
IIb,	IVb	Et	S	570 vs, 548 w	592 vs, 573 w	−22, −25	
IIc,	IVc	*i*-Pr	S	623 vs, 543 w	647 vs, 594 w	−24, −51	

a) In 2% benzene solution. b) vs, very strong; m, medium; w, weak.

organoaluminium chelates (−20——60 cm^{-1}) may be explained in terms of the intramolecular coordination of the sulfur atom of thiophosphoryl group to organoaluminium moiety. The appearance of new absorption bands around 1190—1200 cm^{-1} (assignable to $\nu_{P=N}$[6,7]) indicates the contribution of a resonance form (B), in which (p—d)π interaction between phosphorus and nitrogen atom is involved.

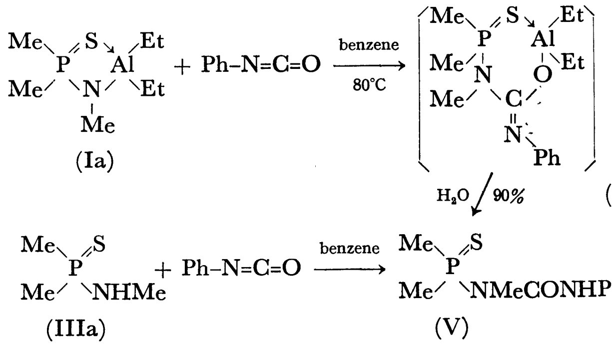


(A) (B)

NMR results are summarized in Table 3. The internal chemical shifts in NMR spectra; $\Delta=\delta AlCH_2-\delta AlCH_2CH_3$ (ppm); are larger ($\Delta=-0.90$——1.10 ppm) than that of Et_3Al ($\Delta=-0.75$ ppm). Narashimhan[8,9] correlated the electronegativity of the metal (x_M) with internal chemical shifts (Δ) of the ethyl group of ethylmetalloids as $x_M=0.62\Delta+2.07$. The apparent electronegativity values of the aluminium atom (x_{Alapp}) in Ia—d and IIa—c are calculated as 1.39—1.49 (Table 3). This means the aluminium atom in the chelate compounds has more negative charge than that in Et_3Al ($x_{Al}=1.60$, $\Delta=-0.75$ ppm).

The J_{PNCH} values of $R_2P(S)NMeAlEt_2$ (Ia—d) are 17—20 Hz, whereas those of parent compounds $R_2P(S)NHMe$ (IIIa—d) are apparently smaller (11—15 Hz). This indicates the significant contribution of a (p—d)π overlap between phosphorus and nitrogen atoms in (Ia—d) (*cf.* P^V=N–CH; J_{PNCH}=20—30 Hz[10,11]). An increase of (p—d)π bonding between phosphorus and nitrogen atoms by diethylaluminium moiety was reported in the case of $Y_2P(O)NMeAlEt_2$ (Y=RO, NR_2).[4]

Reactions of (Ia) and (IIb) with Carbonyl Compounds. The reaction of (Ia) with phenyl isocyanate at 80 °C for 15 hr and subsequent hydrolysis gave only the 1/1 insertion product (V) in 90% yield as Eq. (3). No elimination product (Ph–N=C=N–Me) was obtained.



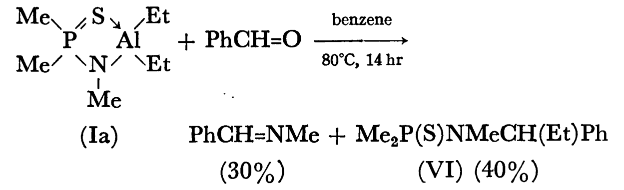
(3)

A reaction of Ia with benzaldehyde gave both *N*-benzylidenemethylamine (30%) and *N*-dimethylthiophosphinyl-*N*-phenylethylcarbinylmethylamine; $(CH_3)_2P(S)$–NCH_3–$CH(C_2H_5)C_6H_5$ (VI) (40%).

Table 3. NMR data (τ in benzene)

Compound	R	X	P–N–CH_3	J_{PNCH}a)	$AlCH_2$	$AlCH_2CH_3$	J_{HCCH}	χ_{Al}b)	P–R	J_{PCH}	J_{PCCH}
Ia	Me	NMe	7.51	19.1 (14.6)	9.79	8.69	8.3	1.39	8.74d	12.8	
Ib	Et	NMe	7.68	18.7 (12.8)	9.64	8.57	8.3	1.41	9.05t, 8.65t 8.05∼8.90m		22.5
Ic	*i*-Pr	NMe	7.74	17.3 (11.0)	9.71	8.65	8.3	1.41	9.17d, 8.90d 8.20m		18.0
Id	*t*-Bu	NMe	7.55	16.5 (11.5)	9.63	8.60	8.3	1.43	8.87d		15.0
IIa	Me	S			9.70	8.71	8.3	1.46	8.52d	13.2	
IIb	Et	S			9.64	8.67	8.3	1.47	9.23t, 8.86t 8.01—8.88m		22.5
IIc	*i*-Pr	S			9.59	8.66	8.0	1.49	9.21d, 8.87d 8.30m		21.0

a) Values in parentheses shows J_{PNCH} of the parent Al-free compound (IIIa—d). b) Apparent electronegativity of aluminium atom calculated by Narashimhan's equation; $\chi_{Alapp}=0.62\Delta+2.07$ ($\Delta=\tau AlCH_2CH_3-\tau AlCH_2$).



Evidence for the structure of (VI) are as follows; (i) the NMR spectrum (Fig. 1) and analyses were consistent with (VI). (ii) The reaction of an analogous dimethylaluminium compound; $\mathrm{Me_2P(S)}$–NMe–$\mathrm{AlMe_2}$ (VII), affords $\mathrm{Me_2P(S)}$–NMe–CH(Me)Ph (VIII, 40%) along with 30% of PhCH=NMe. The NMR spectrum of (VIII) showed a similar spectrum pattern with an analogous known phosphorus compound; $\mathrm{Ph_2P{-}NCH_3{-}CH(CH_3)C_6H_5}$.[12)]

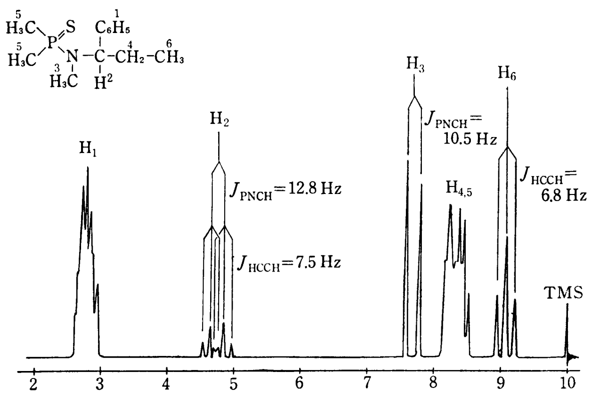
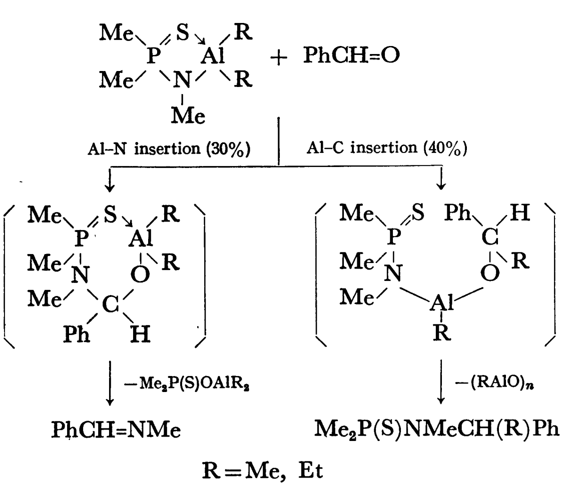
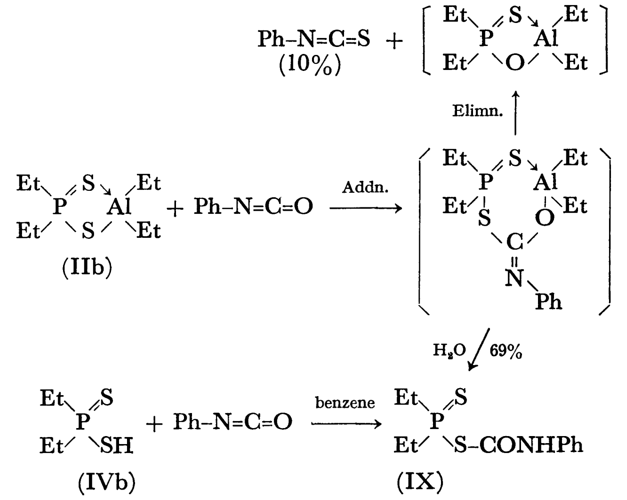


Fig. 1. NMR spectrum of $\mathrm{Me_2P(S)}$-NMe-CH(Et)Ph (VI) (in $\mathrm{CCl_4}$).

The formation of $\mathrm{Me_2P(S)}$–NMe–CH(R)Ph (VIII for R=Me and VI for R=Et) is explained in terms of an insertion of benzaldehyde into the Al–C bond of (Ia) followed by an elimination of the R–Al–O unit. Plausible mechanism was shown as follows.



The reaction of IIb with Ph–N=C=O at 80 °C for 12 hr and subsequent distillation gave Ph–N=C=S (in only 10% yield). Major product was a 1/1 insertion product, $\mathrm{Et_2P(S)}$–S–CONHPh (IX) in 69%, which was obtained by hydrolytic demetallation of the residue.



In conclusion, the insertion reactions of carbonyl compounds into an Al–N or an Al–S bond in Ia or IIb take place readily, whereas the subsequent elimination process proceeded to a less extent than the case of $\mathrm{(RO)_2P(O)NMeAlEt_2}$ which induced exclusively iminocarbonylation reactions by an addition-elimination process.[4)] This difference in reactivity of the elimination process may be due to the acidity of the phosphorus atom.

Experimental

Elemental analyses of organoaluminium compounds were carried out by Alfred Bernhardt Microanal. Lab. in West Germany. Aluminium content was analysed gravimetrically. Molecular weight determination and spectral measurement were carried out under dry nitrogen or argon atomosphere. Molecular weights in benzene solution were determined cryoscopically. Infrared and NMR spectra were recorded with a JASCO IR-S, DG-403G, and JEOL C-60HL spectrometers, respectively.

Commercial $\mathrm{Et_3Al}$ and $\mathrm{Me_3Al}$ (Ethyl. Corp.) were used without further purification. Organic solvents were thoroughly dried over sodium wire or molecular sieve. Starting phosphorus compounds were redistilled before use. The organophosphorus compounds except *N*-methyl diisopropylthiophosphinic amide (IIIc) and *N*-methyldi-*tert*-butylthiophosphinic amide (IIId), were prepared by the methods of literatures.[13–15)]

Preparation of IIIc. A benzene (20 ml) solution of 6.2 g (27.1 mmol) of diisopropylphosphinothioic bromide, prepared from diisopropylphosphinous bromide and sulfur, and $\mathrm{Et_3N}$ were added to $\mathrm{MeNH_2}$ (10 ml) in 20 ml of benzene at 0 °C. Then the mixture was refluxed for 30 min. After removal of the precipitated ammonium salt, distillation of the filtrate gave liquid product (IIIc) (4.2 g, 23.3 mmol) in 86% yield. Bp 85—88 °C/0.2 mmHg. Found: C, 46.76; H, 9.83; N, 7.97%. Calcd for $\mathrm{C_7H_{18}NPS}$: C, 46.90; H, 10.12; N, 7.81%.

Preparation of IIId. A benzene (30 ml) solution of 13.7 g (78.2 mmol) of *N*-methyl amino di-*tert*-butylphosphine[10)] was added dropwise to 2.51 g (78.2 mmol) of sulfur suspended in 30 ml of benzene. After refluxing for 6 hr and removal of the solvent, liquid (IIId) (8.5 g, 40.7 mmol) was obtained in 52% yield. Mp 115—117 °C. Found: C, 52.19; H, 10.37; N, 7.07%. Calcd for $\mathrm{C_9H_{22}NPS}$: C, 52.14; H, 10.90; N, 6.76%.

Preparation of $R_2P(S)NMeAlEt_2$ (Ia—d). The preparation of *N*-diethylaluminium *N*-methyl dimethylthiophosphinic amide Ia is shown here as an example. Others (Ib—d) were prepared analogously. 5.62 g (45.6 mmol) of IIIa was added slowly to 3.22 g (45.7 mmol) of Et_3Al in 8 ml of benzene at room temperature. During the addition of IIIa, an evolution of gas was observed. The reaction mixture was heated up to 80 °C and refluxed for 1 hr. After the gas evolution had completely stopped, the solvent was removed. The product Ia was distilled under reduced pressure. Ia: bp 87—89 °C/0.06 mmHg (7.51 g, 36.0 mmol, 79% yield based on used Et_3Al). The data are shown in Tables 1—3.

Preparation of $R_2P(S)$–S–$AlEt_2$ (IIa—c). As an example, preparation of diethylaluminium dimethyldithiophosphinate (IIa) is described. 1.3 g (10.5 mmol) of IVa in 10 ml of benzene was added dropwise to 1.2 g (10.5 mmol) of Et_3Al in 10 ml of benzene at room temperature. Gas evolution was observed. The reaction mixture was heated up to 80 °C and refluxed for 1 hr. The distillation gave the liquid product IIa (bp 67 °C/0.13 mmHg) (1.6 g, 7.67 mmol, 73% yield based on used Et_3Al). The data are shown in Table 1—3.

Preparation of $Me_2P(S)$–NMe–$AlMe_2$ (VII). The reaction between 2.4 g (33.3 mmol) of Me_3Al and 4.1 g (33.3 mmol) of IIIa in 25 ml of benzene afforded VII (4.0 g, 23.3 mmol) as white crystals in 70% yield based on used Me_3Al. Mp 132—136 °C. Found: Al, 15.05%; active methyl groups, 2.08 per mol. Calcd for $C_5H_{15}AlNPS$: Al, 15.81%; active methyl groups, 2.00 per mol. IR (in benzene) 1300 (m), 1290 (m), 940 (s), and 925 (s) cm^{-1}. NMR (in benzene) τ 10.22 ($AlCH_3$, 6H, s), 8.75 (6H, double doublet, $J_{PCH}=12.8$ Hz), and 7.55 (3H, d, $J_{PNCH}=18.8$ Hz).

Reaction of Ia with Phenyl Isocyanate. An equimolar mixture of 0.845 g (4.08 mmol) of Ia and 0.486 g (4.08 mmol) of phenyl isocyanate in 20 ml of benzene was held at room temperature for 1 day. An absorption band at 2250 cm^{-1} ($\nu_{N=C=O}$) disappeared completely while instead a new band in the range of 1450—1550 cm^{-1} appeared. Then the reaction mixture was heated to 80 °C and refluxed for 15 hr. Hydrolysis of the mixture with dilute hydrochloric acid solution gave a solid as the 1/1 insertion product (0.886 g, 90%). Mp 117°—119 °C. IR (in CCl_4) 3280 (m), 1680 (s), 1310 (s), 1300 (s), 1235 (s), 945 (s), 923 (s), and 690 (m) cm^{-1}. NMR (in $CDCl_3$) τ 7.86 (6H, d, $J_{PCH}=13.5$ Hz), 6.45 (3H, d, $J_{PNCH}=9.0$ Hz), 2.5—3.0 (5H, m), and 2.03 (1H, br. s). An authentic sample of the 1/1 insertion product was prepared by an equimolar reaction of phenyl isocyanate with IIIa in benzene. IR and NMR spectra of the obtained 1/1 insertion product were completely consistent with the authentic sample.

Reaction of Ia with Benzaldehyde. To a solution of 0.8 g (7.2 mmol) of benzaldehyde in 5 ml of benzene was added dropwise 1.5 g (7.2 mmol) of Ia in 5 ml of benzene at room temperature. After 18 hr an absorption band at 1700 cm^{-1} ($\nu_{C=O}$) slightly decreased and a new band at 1650 cm^{-1} ($\nu_{C=N}$) appeared. Then the reaction mixture was heated to reflux. Removal of the solvent and distillation under reduced pressure gave the liquid product, PhCH=NMe (0.54 g, 30%) and $Me_2P(S)NMeCH(Et)Ph$ (VI) (bp 90—100 °C/0.35 mmHg) (0.7 g, 40%). Found: C, 60.14; H, 8.55; N, 5.47%. Calcd for $C_{12}H_{20}NPS$: C, 59.92; H, 8.35; N, 5.80%. IR (in CCl_4) 1298 (s), 1288 (s), 1150 (m), 943 (s), 918 (s), and 710 (s) cm^{-1}. NMR (in CCl_4) τ 9.10 (3H, t, $J=6.8$ Hz), 8.00—8.55 (8H, m, P–CH_3+CH_2CH_3), 7.71 (3H, d, $J_{PNCH}=10.5$ Hz), 4.66, 4.88 (1H, double triplet, $J_{PNCH}=12.8$ Hz, $J_{HCCH}=7.5$ Hz), and 2.5—2.9 (5H, m).

Reaction of VII with Benzaldehyde. When the mixture of 0.8 g (7.3 mmol) of benzaldehyde and 1.3 g (7.3 mmol) of VII in 15 ml of benzene solution was kept at room temperature for 24 hr, and then heated to refluxing for 12 hr, an absorption band at 1700 cm^{-1} ($\nu_{C=O}$) disappeared completely and a new band at 1650 cm^{-1} ($\nu_{C=N}$) appeared. Removal of the solvent and distillation gave, PhCH=NMe (0.26 g, 30%) and $Me_2P(S)NMeCH(Me)Ph$ (VIII) (bp 95—100 °C/0.3 mmHg) (0.6 g, 40%). IR (in CCl_4) 1290 (s), 1280 (s), 1150 (m), 950 (s), 910 (s), and 705 (m) cm^{-1}. NMR (in CCl_4) τ 8.54 (3H, d, $J=6.0$ Hz), 8.28 (6H, d, $J_{PCH}=12.8$ Hz), 7.66 (3H, d, $J_{PNCH}=11.3$ Hz), 4.71, 4.48 (1H, double quartet, $J_{PNCH}=13.5$ Hz, $J_{HCCH}=6.0$ Hz), and 2.5—2.9 (5H, m).

Reaction of IIb with Phenyl Isocyanate. To a benzene solution (10 ml) of 0.61 g (5.12 mmol) of phenyl isocyanate was added a benzene solution (10 ml) of 1.05 g (4.43 mmol) of IIb at room temperature. After leaving the mixture for 18 hr, an absorption band at 2250 cm^{-1} ($\nu_{N=C=O}$) disappeared gradually, along with the appearance of a new band at 2050 cm^{-1} ($\nu_{N=C=S}$). Then the reaction mixture was heated to 80 °C and refluxed for 6 hr, resulting the complete disappearence of $\nu_{N=C=O}$. Removal of the solvent and distillation under reduced pressure gave the liquid product, Ph–N=C=S (bp 70—78 °C/0.5 mmHg) (Ph–N=C=S: bp 95 °C/12 mmHg) (0.16 g, 10%). Hydrolytic demetallation of the residue gave an oil of a derivative of the insertion product (IX) (0.770 g, 69%). IR (in CCl_4) 3260 (m), 1705 (s), 1243 (m), 1154 (m), 1028 (s), and 693 (s) cm^{-1}. NMR (in CCl_4) τ 8.95, 8.58 (6H, double triplet, $J_{PCCH}=22.2$ Hz, $J_{HCCH}=6.8$ Hz), 7.50—8.20 (4H, m), 2.33—3.33 (5H, m), and 1.86 (1H, br. s). The authentic sample of the 1/1 insertion product was prepared by an equimolar reaction of Ph–N=C=O with IVb in benzene. The 1/1 insertion product obtained showed the same IR and NMR spectra of the authentic sample.

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