Pergamon

0277–5387(94)00177–4

*Polyhedron* Vol. 14, No. 2, pp. 277–283, 1995

0277–5387/95 $9.50+0.00

# SYNTHESIS, SOLUTION DYNAMICS AND X-RAY CRYSTAL STRUCTURES OF NEODYMIUM–YLIDE COMPLEXES, $[(C_5H_4R)_3NdCH_2P(Me)Ph_2]$ (R = H, $Bu^t$)

WAI-KWOK WONG*

Department of Chemistry, Hong Kong Baptist College, Kowloon, Hong Kong

and

JINGWEN GUAN, QI SHEN,* LILU ZHANG and YONGHUA LIN

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Academia Sinica, 109 Stalin Street, Changchun 130022, P.R.C.

and

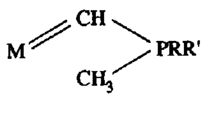
WING-TAK WONG*

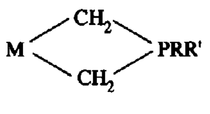
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

(*Received* 8 *March* 1994; *accepted* 20 *April* 1994)

**Abstract**—The interaction of $[(C_5H_4R)_2NdCl \cdot 2LiCl]$ (R = H, $Bu^t$) with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in refluxing tetrahydrofuran gave the purplish-blue complex $[(C_5H_4R)_3NdCH_2P(Me)Ph_2]$ in 50% yield. The compounds have been fully characterized by analytical, spectroscopic and X-ray diffraction methods. Variable temperature $^{31}P\{^1H\}$ NMR spectroscopy indicated the existence of the following equilibrium: $[(C_5H_4R)_3NdCH_2P(Me)Ph_2] + THF \rightleftharpoons (C_5H_4R)_3Nd(THF) + CH_2{=}P(Me)Ph_2$. At room temperature, the exchange between the coordinated and free ylide ligand is slow on the NMR time scale.

Phosphorus ylides have been shown to possess an extensive coordination chemistry with main group and transition metal atoms and to form metal–carbon σ-bonds of unusual stability.[1] Schumann *et al.*[2] and Gilje *et al.*[3] have extended the ylidic chemistry to lanthanide and actinide metals, respectively. Gilje and co-workers have further demonstrated that the phosphorus ylidic ligand, depending on the reaction conditions, can act either as a monodentate or a bidentate ligand, as shown below.[3a]





We are interested in examining the factors that affect the mode of coordination of the phosphorus ylidic ligand, particularly the steric and electronic effects of substituents of the cyclopentadienyl rings on the mode of coordination. Recently, we have shown that the interaction of $Cp'_2SmCl \cdot LiCl$ with $Li[(CH_2)(CH_2)PPh_2]$ gives the cyclic ylidic complex $Cp'_2Sm(CH_2)(CH_2)PPh_2$ when Cp′ is the sterically

---

* Authors to whom correspondence should be addressed.

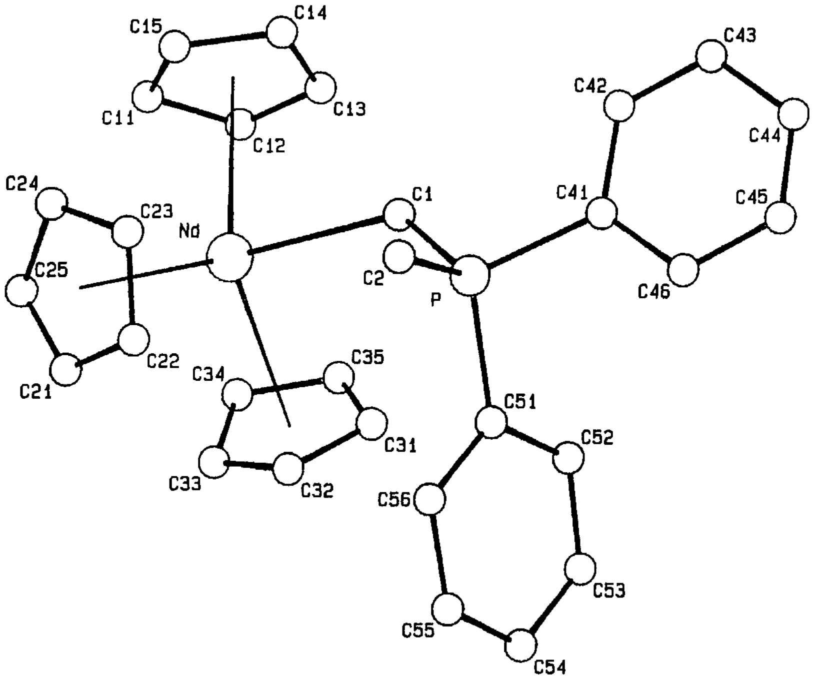


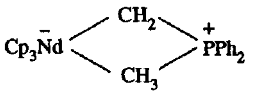
Fig. 1. A perspective drawing of I.

bulky $C_5Me_5$ ring[4] and the ylide complex $Cp'_3SmCH_2P(Me)Ph_2$ when Cp′ is the sterically less demanding $C_5H_5$ ring.[5] In this paper, we report the results of the reaction of $Cp'_2NdCl \cdot 2LiCl$ (Cp′ = $C_5H_5$, $Bu^tC_5H_4$) with $Li[(CH_2)(CH_2)PPh_2]$.

## RESULTS AND DISCUSSION

### *Preparation and crystal structure of* $[(C_5H_4R)_3NdCH_2P(Me)Ph_2]$

(i) R = H. Interaction of $(C_5H_5)_2NdCl \cdot 2LiCl$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in refluxing tetrahydrofuran for 16 h, after work up gave purplish-blue crystals of stoichiometry $(C_5H_5)_3NdCH_2(Me)PPh_2$ (**I**) in 50% yield after recrystallization from toluene solution. The structure of **I** was established by an X-ray diffraction study. Crystals suitable for X-ray diffraction study were grown from a solution in toluene. A perspective drawing of **I** is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 1. Compound **I** can be formulated as a ylide complex having structure A as shown below.



$$\overset{-}{\mathrm{Cp_3Nd}}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_3}\end{matrix}\overset{+}{\mathrm{PPh_2}}$$

*A*

The solid state structure of **I** can be described as a distorted tetrahedron if one considers that the metal is coordinated to the centroid of the cyclopentadienyl rings. The cyclopentadienyl rings are bonded in a $\eta^5$-fashion with Nd—C bond lengths ranging from 2.671(23) to 2.857(20) Å. The mean Nd—C distances for the three Cp rings are 2.76, 2.78 and 2.79 Å. The Nd—C(1) distance is 2.643(16) Å and is longer than the Nd—C terminal distance in $Cp'_2NdCH(SiMe_3)_2$ [$Cp'_2 = (C_5Me_5)_2$, 2.517(7) Å; $Cp'_2 = Me_2Si(C_5Me_4)_2$, 2.506(7) Å][6] and shorter than the long Nd—C bridging distance in the asymmetrical methyl bridged dimer $[(C_5H_4Bu^t)_2NdMe]_2$. [2.70(2) Å.[7] This is consistent with the fact that the Nd—C(1) bond is a dative bond which should be weaker than a Nd—C $\sigma$-bond as in $Cp'_2NdCH(SiMe_3)_2$ and stronger than an electron-deficient three centre-two electron Nd—C bridging bond as in $[(C_5H_4Bu^t)_2NdMe]_2$. The P—C distances for the P—$CH_2$ and P—$CH_3$ groups are 1.750(14) and 1.793(16) Å, respectively. These bond lengths are in very good agreement with comparable bond lengths in $(C_5H_5)_3SmCH_2P(Me)Ph_2$ [P—$CH_2$, 1.734(6) Å; P—$CH_3$, 1.811(6) Å[5] and $(C_5Me_5)_2U(Cl)[(CH_2)(CH_2)P(Me)Ph]$ [P—$CH_2$, 1.74(1) and 1.74(1) Å; P—$CH_3$, 1.77(1) Å].[3b]

(ii) R = t $Bu^t$. Interaction of $(C_5H_4Bu^t)_2NdCl \cdot 2LiCl$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in refluxing tetrahydrofuran for 16 h work up gave purplish-blue crystals of stoichiometry $[(C_5H_4Bu^t)_3NdCH_2P(Me)Ph_2]$ (**II**) in

Table 1. Selected bond distances (Å) and angles (°) for **I** and **II**

| | **I** | **II** |
|---|---|---|
| Nd—C(1) | 2.64(2) | 2.66(2) |
| Nd—C(11) | 2.79(2) | 2.909(9) |
| Nd—C12 | 2.79(2) | 2.745(8) |
| Nd—C13 | 2.79(2) | 2.72(1) |
| Nd—C14 | 2.86(2) | 2.89(2) |
| Nd—C15 | 2.72(2) | 3.014(9) |
| Nd—C21 | 2.79(2) | 2.89(2) |
| Nd—C22 | 2.77(2) | 2.82(2) |
| Nd—C23 | 2.84(2) | 2.780(9) |
| Nd—C24 | 2.80(3) | 2.864(9) |
| Nd—C25 | 2.71(4) | 2.991(8) |
| Nd—C31 | 2.82(2) | 2.842(9) |
| Nd—C32 | 2.67(2) | 2.75(1) |
| Nd—C33 | 2.76(2) | 2.778(9) |
| Nd—C34 | 2.76(2) | 2.866(9) |
| Nd—C35 | 2.80(2) | 2.881(9) |
| P—Cl | 1.75(1) | 1.71(1) |
| P—C2 | 1.79(2) | 1.81(1) |
| P—C41 | 1.83(1) | 1.83(2) |
| P—C51 | 1.81(1) | 1.80(2) |
| C15—C16 | — | 1.56(1) |
| C25—C26 | — | 1.51(2) |
| C35—C36 | — | 1.55(2) |
| Nd—Cl—P | 138.1(7) | 136.2(4) |
| Cl—P—C2 | 111.0(7) | 113.3(6) |
| Cl—P—C41 | 113.5(6) | 114.9(5) |
| Cl—P—C51 | 112.9(7) | 109.2(5) |
| C2—P—C41 | 103.7(7) | 104.1(5) |
| C(2)—P—C(51) | 107.7(6) | 109.0(4) |

50% yield after recystallization from a toluene solution. The structure of **II** was established by X-ray crystallography. Crystals suitable for X-ray diffraction study were grown from a toluene solution. A perspective drawing of **II** is shown in Fig. 2. Selected bond lengths and bond angles are listed in Table 1.

The solid state structure of **II** can be described as a distorted tetrahedron if one considers that the metal is coordinated to the centroid of the t-butylcyclopentadienyl rings. The cyclopentadienyl rings are bonded in a $\eta^5$-fashion with Nd—C (ring) distances ranging from 2.72(1) to 3.014(9) Å with the longest distances being those carbon atoms bonded to tert-butyl groups. A similar observation has been reported for $[(C_5H_4Bu^t)_2NdMe]_2$.[7] The mean Nd—C distances for the three Cp rings are 2.82, 2.86 and 2.87 Å. These values are slightly longer than that of **I** (2.76, 2.78 and 2.79 Å), and similar to that of $[(C_5H_5)_3Nd(\mu\text{-}H)Nd(C_5H_5)_3]^-$ (2.81 Å).[8] This is consistent with the fact that tert-butyl is an electron donating group and in agreement with structure A, where a negative charge is delocalized on to the neodymium metal. The Nd—C(1) distance is 2.66(2) Å and is comparable to the Nd—C(1) distance of **I**.

In contrast to $(C_5Me_5)_2NdCl \cdot LiCl$, which reacted with $Li[(CH_2)(CH_2)PPh_2]$ to give the expected cyclic ylidic complex $(C_5Me_5)_2Nd(CH_2)(CH_2)PPh_2$,[4] interaction of $(C_5H_4R)_2NdCl \cdot 2LiCl$ ($R = H$, $Bu^t$) gives the unexpected ylide complex $[(C_5H_4R)_3NdCH_2P(Me)Ph_2]$. A similar observation has also been reported for the samarium analogy.[5] A possible mechanism for the formation of the ylide complex is shown in Scheme 1. Compounds **I** and **II** are probably formed via the cyclic ylidic intermediate **III**, which may either undergo dimerization to give **IV** and CpH or undergo rearrangement to give **V** which then undergoes an addition reaction with CpH to give the ylide complex. Uranium compounds analogous to the dimerization intermediate **IV**[9] and the rearrangement intermediate **V**[10] have been isolated. However, the dimerization process and the addition reaction will be disfavoured by steric bulky cyclopentadienyl ligands. Thus, in the case of the bulky $C_5Me_5$ ligand, where steric hindrance probably prevents the dimerization and addition process, the cyclic ylidic complex $[(C_5Me_5)_2M(CH_2)(CH_2)PPh_2]$ ($M = Nd$, Sm) was obtained. These results suggest that the nature of the products of the above reaction may be influenced by the substituents of the Cp rings. We are in the process of examining this effect.

### *Solution dynamics of I and II*

In THF-$d_8$, both **I** and **II** exhibit very complex $^1H$ NMR spectra, which are difficult to interpret, but rather simple temperature-dependent $^{31}P\{^1H\}$ NMR spectra. The ambient temperature $^{31}P\{^1H\}$ NMR spectrum of **I** exhibits a broad singlet centred at $\delta$20.08 ppm and a sharp singlet at $\delta$25.15 ppm. The chemical shift of the resonance at $\delta$25.15 ppm is consistent with the chemical shift of a free ylide.[11] Thus, the resonances at $\delta$20.08 and 25.15 ppm can be assigned to the coordinated ylide of the complex and the uncoordinated ylide $Ph_2(Me)P{=}CH_2$, respectively. On lowering the temperature, the resonance at $\delta$20.08 sharpens and shifts upfield, whereas the resonace at $\delta$25.15 ppm remains relatively unchanged. At $-60$°C, the broad signal at $\delta$20.08 ppm becomes a sharp singlet and shifts upfield to $\delta$10.05 ppm, whereas the sharp singlet shifts only slightly to $\delta$25.93 ppm. As the temperature of the solution is raised to 50°C, both signals broaden and tend to coalesce. The variable temperature $^{31}P\{^1H\}$ NMR spectra of **I** in THF-$d_8$

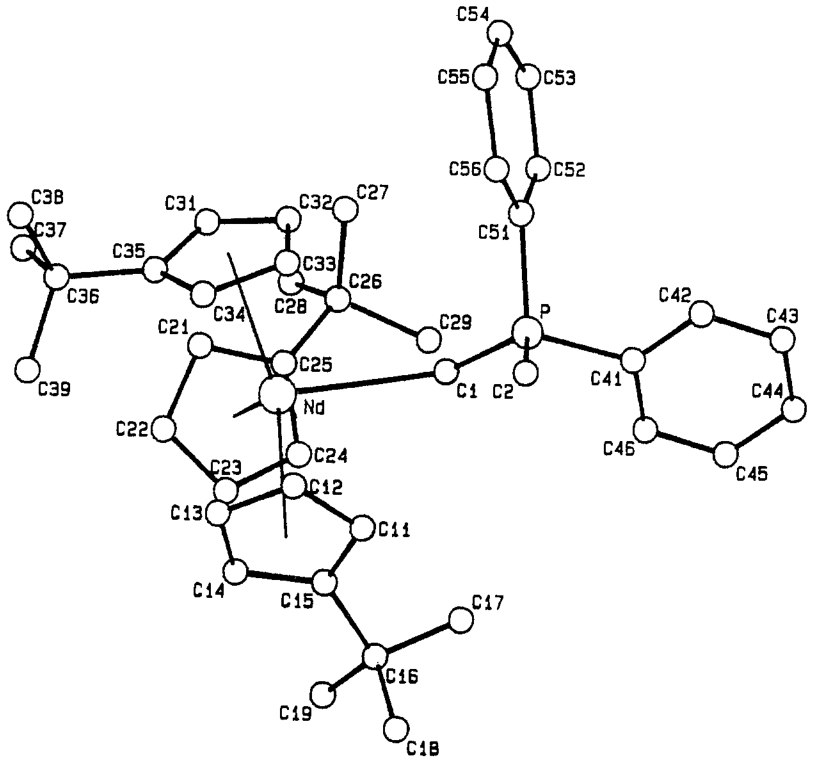
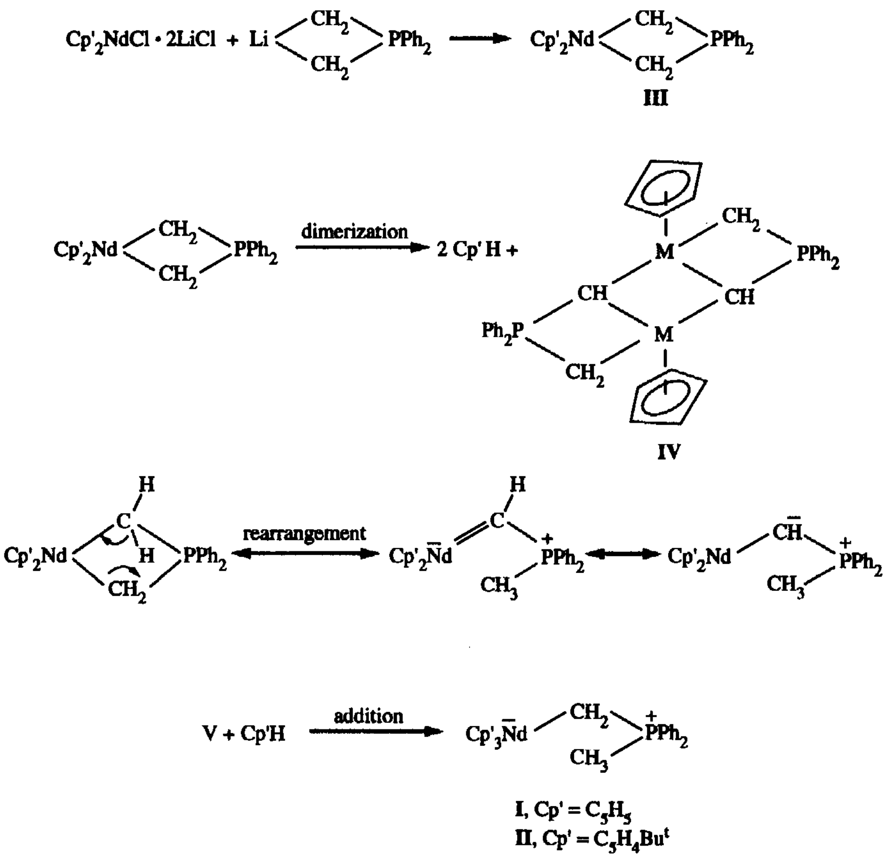


Fig. 2. A perspective drawing of **II**.



Scheme 1. A possible mechanism for the formation of **I** and **II**.

are shown in Fig. 3. This suggests that the following equilibrium exists in solution:

$$\mathrm{Cp'_3Nd \leftarrow CH_2P(Me)Ph_2 + THF \rightleftharpoons Cp'_3Nd(THF) + CH{=}P(Me)Ph_2 \quad (Cp' = C_2H_2,\ C_5H_4Bu^t)}$$

At room temperature, the exchange between the coordinated and uncoordinated ylide is slow on the NMR time scale and becomes more rapid as the temperature increases. Compound **II** exhibits similar dynamic behaviour in solution. Temperature-dependent NMR spectra are also observed for **II**. The ambient temperature $^{31}P\{^1H\}$ NMR spectrum of **II** in THF-$d_8$ exhibits a sharp single at $\delta$25.04 ppm for the free ylide and a broad singlet at $\delta$32.02 ppm for the coordinated ylide. On lowering the temperature to −60°C, the broad signal at $\delta$32.02 ppm becomes a sharp singlet and shifts downfield to $\delta$39.25 ppm, whereas the sharp singlet at $\delta$25.04 ppm shifts slightly to $\delta$25.71 ppm.

## EXPERIMENTAL

Analysis of neodymium was carried out by complexometric titration of chloride by Volhard's method. Carbon and hydrogen analysis were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Science, China. IR spectra (KBr pellets) were recorded on a Hitachi 270–30 IR spectrometer: data are given in cm$^{-1}$.

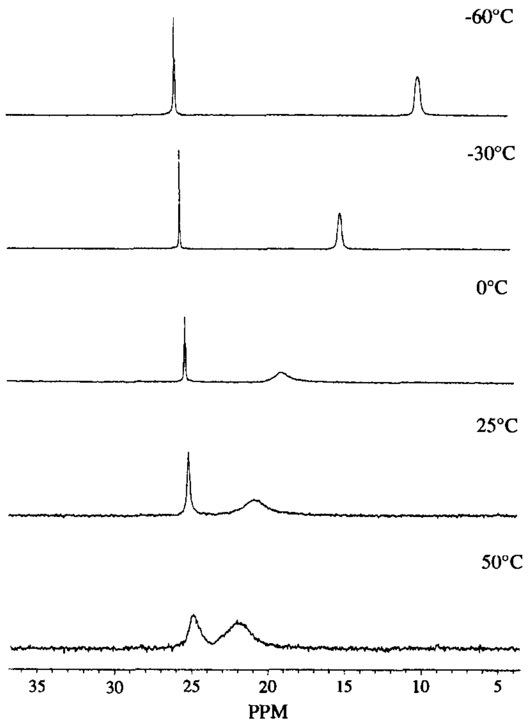


Fig. 3. Variable temperature $^{31}P\{^1H\}$ NMR spectra of [$Cp_3NdCH_2P(Me)Ph_2$].

NMR spectra were recorded on a JEOL EX270 spectrometer. Chemical shifts of $^1H$ NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS = $\delta$ 0.0 ppm. $^{31}P$ NMR spectra were referenced to external 85% $H_3PO_4$.

All operations were performed under nitrogen or *in vacuo*. All chemicals used were of reagent grade. Solvents were dried by standard procedures, distilled and deaerated prior to use. Melting points were taken in sealed capillaries and are uncorrected. $Li[(CH_2)(CH_2)PPh_2]$[12] and $(C_5H_4R)_2NdCl\cdot 2LiCl$ (R = H, Bu$^t$)[13] were prepared according to literature methods.

### *Preparation of* [$(C_5H_4R)_3NdCH_2P(Me)Ph_2$]

(i) R = H (**I**). A solution of $(C_5H_5)_2NdCl\cdot 2LiCl$ (2.21 g, 5.6 mmol) and $Li[(CH_2)(CH_2)PPh_2]$ (1.41 g, 6.4 mmol) in THF (15 cm$^3$) was refluxed for 16 h to give a purplish-green solution. The solvent of the resultant solution was removed *in vacuo*. Toluene (60 cm$^3$) was then added to the residue and stirred at 80°C for 60 h to give a purplish-green solution. The solution was filtered, concentrated to *ca* 15 cm$^3$, and then cooled to −20°C to give purple crystals which were filtered, washed with cold toluene (5 cm$^3$) and dried *in vacuo*. Yield: 1.65 g, 53%; m.p. 221–223°C. Found: Nd, 25.9; Cl, <0.1; C, 62.8; H, 5.5. Calc. for $C_{29}H_{30}PNd$: Nd, 26.1; Cl, 0.0; C, 62.9; H, 5.4%. IR (KBr): 3055 m, 2960 m, 2890 m, 1437 s, 1298 w, 1180 m, 1160 m, 1120 s, 1011 s, 958 w, 932 m, 868 w, 745 vs, 691 s, 570 w, 439 m cm$^{-1}$. $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$20.08 (br, s); 25.15 (s) ppm.

(ii) R = Bu$^t$ (**II**). Compound **II** was prepared according to the same procedure outlined above for **I** using $(C_5H_4Bu^t)_2NdCl\cdot 2LiCl$ (2.78 g, 5.5 mmol) and $Li[(CH_2)(CH_2)PPh_2]$ (1.34 g, 6.1 mmol). Purple crystals were obtained. Yield: 1.98 g, 50%; m.p. 176–178°C. Found: Nd, 20.4; Cl, <0.1; C, 68.1; H, 7.3. Calc. for $C_{41}H_{54}PNd$: Nd, 20.0; Cl, 0.0; C, 68.2; H, 7.5%. IR (KBr): 3060 w, 2962 s, 2902 m, 2868 w, 1591 m, 1541 m, 1481 m, 1438 m, 1363 s, 1303 m, 1158 s, 1120 s, 933 m, 899 w, 868 w, 745 s, 694 s, 629 m, 492 m cm$^{-1}$. $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$25.04 (s); 32.02 (br, s) ppm.

### *X-ray diffraction studies*

Crystals of **I** and **II** suitable for X-ray diffraction studies were grown from toluene solutions. Crystal data and data collection parameters for **I** and **II** are summarized in Table 2. Crystals of both **I** and **II** are exceedingly air-sensitive and were sealed in a Lindeman glass capillary in an argon atmosphere. The intensity data for **I** were collected at room

Table 2. Crystal data and data collection parameters for **I** and **II**

| | **I** | **II** |
|---|---|---|
| Formula | $C_{29}H_{30}PNd$ | $C_{41}H_{54}PNd$ |
| Colour, habit | Pale blue plates | Pale blue plates |
| Crystal size (mm) | 0.08 × 0.36 × 0.66 | 0.06 × 0.34 × 0.44 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1\ c$ (No.14) | $P1$ (No.2) |
| $a$ (Å) | 8.075(3) | 10.850(5) |
| $b$ (Å) | 16.571(9) | 11.961(4) |
| $c$ (Å) | 19.472(6) | 15.912(3) |
| $\alpha$ (°) | 90.0 | 86.08(1) |
| $\beta$ (°) | 101.04(2) | 85.41(2) |
| $\gamma$ (°) | 90.0 | 66.44(2) |
| $V$ (Å$^3$) | 2557.1 | 1885.4 |
| $Z$ | 4 | 2 |
| Formula wt. | 553.20 | 722.12 |
| Calc. density (g cm$^{-3}$) | 1.440 | 1.272 |
| Absorption coef. (cm$^{-1}$) | 21.2 | 14.4 |
| $F$ (000) | 1116 | 750 |
| $2\theta$ range (°) | 3–50 | 2–50 |
| Scan type | $\omega$ | $\omega$–$2\theta$ |
| Scan speed (deg min$^{-1}$) | 7.32 | 1.10–16.48 |
| Scan range (°) | 2.1 | $0.50 + 0.34 \tan\theta$ |
| Reflections collected | 5135 | 6766 |
| Unique reflections | 4928 | 6289 |
| Observed reflections [$I > 3\sigma(I)$] | 2470 | 5444 |
| Number of parameters | 280 | 388 |
| Weighting scheme | $[\sigma^2(F_o + 0.0002F_o^2]^{-1}$ | $4F_o^2[\sigma^2(F_o^2) + 0.02(F_o^2)^2]$ |
| $R$ | 0.060 | 0.056 |
| $R_w$ | 0.054 | 0.091 |

temperature on a Nicolet R3m/E four-circle diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71069 Å), while those for **II** were collected on an Enraf–Nonius CAD4 diffractometer using Mo-$K_\alpha$ radiation. Both sets of data were corrected for Lorentz and polarization effects, and absorption corrections by Ψ-scan method were also applied. Both structures were solved by the Patterson method and refined by full-matrix least-squares analysis, with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms were generated in their idealized positions (C—H bond fixed at 0.96 Å). For all calculations the SHELXTL-PLUS[14] and SDP[15] packages were used in **I** and **II**, respectively. Tables of bond lengths and angles, final atomic coordinates, thermal parameters and structure factors for both structures **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre.

*Acknowledgements*—W.-K. Wong thanks the Hong Kong Baptist College, the Hong Kong Research Grant Council and the Croucher Foundation for financial support. W.-T. Wong thanks the Hong Kong Research Grant Council and the University of Hong Kong for financial support.

## REFERENCES

1. H. Schmidbaur, *Accts Chem. Res.* 1975, **8**, 62 and refs therein.
2. (a) H. Schumann, I. Albrecht, F. W. Reier and E. Hahn, *Angew. Chem., Int. Edn Engl.* 1984, **23**, 522; (b) H. Schumann and F. W. Reier, *Inorg. Chim. Acta*, 1984, **95**, 43 and refs therein.
3. (a) J. W. Gilje, R. E. Cramer, M. A. Bruck, K. T. Higa and K. Panchanetheswaran, *Inorg. Chim. Acta* 1985, **110**, 139; (b) R. E. Cramer, S. Roth, F. Edelmann, M. A. Bruck, K. C. Cohn and J. W. Gilje, *Organometallics* 1989, **8**, 1192 and refs therein.
4. W. K. Wong, H. Chen and F. L. Chow, *Polyhedron* 1990, **9**, 875.
5. W. K. Wong, J. Guan, J. Ren, Q. Shen and W. T. Wong, *Polyhedron* 1993, **12**, 2749.
6. G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.* 1985, **107**, 8091, 8103.
7. Q. Shen, Y. Cheng and Y. Lin, *J. Organomet. Chem.* 1991, **419**, 293.

8. Y. Sun, Q. Shen, S. Jin and Y. Lin, *Yingyong Huaxue* 1991, **8**, 23.
9. R. E. Cramer, R. B. Maynard and J. W. Gilje, *Inorg. Chem.* 1980, **19**, 2564.
10. R. E. Cramer, R. B. Maynard, J. C. Paw and J. W. Gilje, *Organometallics* 1982, **1**, 869.
11. S. O. Grim, *Phosphorus*-31 *NMR Spectroscopy in Stereochemical Analysis*: *Unusual Ligation Modes of Phosphorus Compounds*: *Phosphorus Ylide* (Edited by J. G. Verkade and L. D. Quin), p. 645. VCH, Deerfield Beach, FL (1987).
12. L. E. Manzer, *Inorg. Chem.* 1976, **15**, 2567.
13. Y. Li, X. Xu, L. Zhu and G. Lu, *Chinese J. Appl. Chem.* 1987, **5**, 82.
14. G. M. Sheldrick, *Crystallographic Computing* 3: *Data Collection*, *Structure Determination*, *Proteins*, *and Databases* (Edited by G. M. Sheldrick, C. Kruger and R. Goddard), p. 175. Oxford University Press, New York (1985).
15. Enraf–Nonius Structure Determination Package. Enraf–Nonius, Delft (1985).