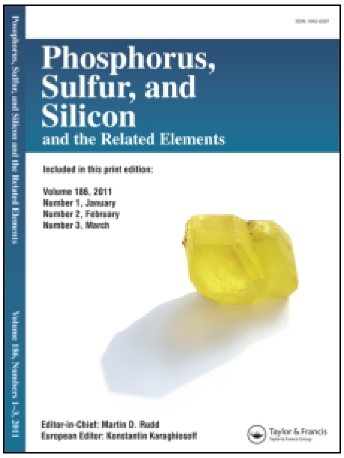

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# ESCA STUDIES OF A DIPHOSPHENE

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# ESCA STUDIES OF A DIPHOSPHENE

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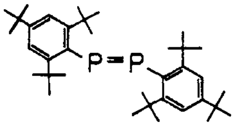
The nature of the P=P bond in *E*-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene was studied by means of ESCA, indicating that the phosphorus 2*p* binding energy is the lowest among those for common organophosphorus compounds.

We have succeeded in preparing *E*-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**) as a stable compound by introducing bulky *tert*-butyl groups at ortho positions of the phenyl rings.[1] Since there have been no reports on such phosphobenzene type of compounds, it is of interest to investigate the nature of the bonding properties of the double bond of third-row elements.



**1**

X-Ray analysis of the compound **1** showed that the bond length (2.034 Å) is considerably shorter than the normal P—P single bond indicating that it has double-bond character to some extent.[1] Therefore, we were interested in ESCA (X-ray photoelectron spectroscopy) studies of the diphosphene (**1**).

## RESULTS AND DISCUSSION

Figure 1 illustrates an ESCA spectrum of the P 2*p* region obtained from a freshly deposited film of compound **1**. The narrow linewidth observed (full width at half maximum 1.8 eV) indicates that no serious decomposition occurred during the evaporation process. Table I shows the P 2*p* binding energy ($E_b$) and $^{31}$P NMR chemical shift ($\delta_P$) of compound **1** together with those of some common phosphorus compounds. The P 2*p* binding energy for **1** was very low (130.4 eV), indicating that the phosphorus atoms in **1** are electron rich.[2] Indeed, this value is the lowest among those for common organophosphorus compounds.[3-5] As was suggested by Gelius *et al.*,[7] no apparent relationship was observed between $^{31}$P NMR chemical shifts and P 2*p* ESCA chemical shifts in contrast to that found in a series of phosphorus ylids.[8] The very low $E_b$(P 2*p*) thus observed for **1** indicates an unusual electronic environment around the phosphorus atoms in the P=P bond. Further theoretical studies are in progress.

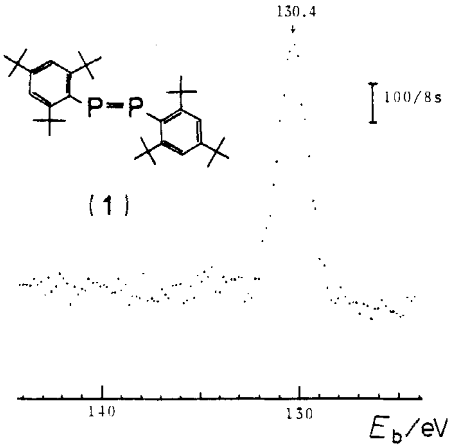


FIGURE 1 Phosphorus $2p$ spectrum of freshly evaporated film of diphosphene (**1**).

TABLE I

Phosphorus $2p$ binding energies [$E_b$(P $2p$)] and $^{31}$P NMR chemical shifts [$\delta_P$] of some phosphorus compounds

| Compound | $E_b$(P $2p$)[a]/eV This work | $E_b$(P $2p$)[a]/eV Ref. 5 | $E_b$(P $2p$)[a]/eV Ref. 4 | $\delta_P$/ppm (CDCl$_3$) |
|---|---|---|---|---|
| **1** | 130.4 | | | 489.8 |
| Phosphorus | 130.1[b] (red) | 130.1 (red) | | −461.3 (white, neat)[c] |
| Ph$_3$P | 130.9 | 130.6 | 131.3 | −5.3 |
| Ph$_3$P(O) | 132.5 | 132.7 | 132.8 | 28.9 |

[a] Binding energies are referenced to the C $1s$ peak (285.0 eV).

[b] Another peak due to oxidized phosphorus was observed at 134.5 eV as in Ref. 5.

[c] Taken from Ref. 6.

TABLE II

Binding energies [$E_b$] of core peaks for compound **1** referenced to Au $4f_{7/2}$ and C $1s$

| Sample | $E_b$ rel. to Au $4f_{7/2}$[a]/eV P $2p$ | $E_b$ rel. to Au $4f_{7/2}$[a]/eV C $1s$ | $E_b$ rel. to C $1s$[b]/eV P $2p$ | $E_b$ rel. to C $1s$[b]/eV Au $4f_{7/2}$ | $I$(Au $4f_{7/2}$)[c]/s$^{-1}$ |
|---|---|---|---|---|---|
| Freshly evaporated film | | | 130.4 | | |
| After exposure to air[d] | | | 130.3[e] | | |
| First gold evaporation | 129.5 | 284.2 | 130.4 | 84.7 | 230 |
| Second gold evaporation | 129.9 | 284.5 | 130.4 | 84.3 | 880 |
| Third gold evaporation | ~ 130.1[f] | 284.7 | ~ 130.5[f] | 84.1 | 1530 |

[a] $E_b$(Au $4f_{7/2}$) = 83.8 eV.

[b] $E_b$(C $1s$) = 285.0 eV.

[c] Intensity of the Au $4f_{7/2}$ line was taken as a peak height measured from peak maximum to a background.

[d] The vacuum of the sample chamber was broken in order to replace an evaporator filament.

[e] Another peak due to oxidized product was observed at about 133.9 eV. Enhanced reactivity toward oxygen might be due to the radiation damage during the first ESCA measurement.

[f] Because of reduced intensity and poor S/N of the P $2p$ peak, precise energy could not be determined.

The 4*f* lines from vacuum-deposited gold on the specimen surface are widely utilized as a binding-energy standard. However, in the case of compound **1**, the gold deposition technique did not give reliable core-level binding-energy values. With successive deposition of gold, we examined the variation of core-electron binding energies referenced to Au $4f_{7/2}$ and C 1*s* (Table II). As the intensity of Au $4f_{7/2}$ peak increases, $E_b$ (P 2*p*) and $E_b$ (C 1*s*) relative to Au $4f_{7/2}$ become larger, whereas P 2*p* binding energies relative to C 1*s* stay nearly constant throughout the experiment. These results suggest that deposited gold reacts with the specimen and that it is not present in metallic form. A similar reaction between deposited gold and a specimen was reported for some phosphorus(III) compounds by Matienzo and Grim.[9]

## ACKNOWLEDGMENTS

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## EXPERIMENTAL

*E-Bis(2,4,6-tri-tert-butylphenyl)diphosphene* **1** was prepared as reported previously.[1] The other commercially available organophosphorus compounds were purified by the usual methods before the spectral analyses.

*$^{31}$P NMR spectra* were recorded on a Jeol JNM-FX-90Q spectrometer using 85% $H_3PO_4$ as an external standard at 36.28 MHz.

*ESCA spectra* were recorded with a McPherson ESCA 36 electron spectrometer by using Mg $K_\alpha$ radiation (1253.6 eV). Powdered samples were mounted on double-sided adhesive tape and/or rubbed directly onto an aluminum plate. Films of compound **1** prepared in the ESCA spectrometer by sublimation were also examined. Because of the high vapor pressure of triphenylphosphine at room temperature, it was deposited onto a cooled aluminum plate (at *ca.* −40°C) and was analyzed at that temperature. Since gold deposition technique could not be adopted to calibrate the ESCA spectra of compound **1**, binding energies of core level were referenced to the C 1*s* line (285.0 eV) which derives from the contamination carbon layer and/or from carbon atoms in a sample. The P 2*p* binding energies thus obtained were independent of the preparative methods of specimens within ±0.2 eV.

## REFERENCES AND NOTES

1. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); **104**, 6167 (1982).
2. E. Fluck and D. Weber, *Pure Appl. Chem.*, **44**, 373 (1975).
3. B. J. Lindberg and J. Hedman, *Chimica Scripta*, **7**, 155 (1975).
4. W. E. Morgan, W. J. Stec, R. G. Albridge and J. R. Van Wazer, *Inorg. Chem.*, **10**, 926 (1971).
5. M. Pelavin, D. N. Hendrickson, J. M. Hollander and W. L. Jolly, *J. Phy. Chem.*, **74**, 1116 (1970).
6. V. Mark, C. H. Dungan, M. M. Crutchfield and J. R. Van Wazer, *Topics in Phosphorus Chemistry* (Interscience Publishers, New York, 1967) M. Grayson and E. J. Griffith, eds., Vol. 5, p. 239.
7. U. Gelius, G. Johansson, H. Siegbahn, C. J. Allan, D. A. Allison, J. Allison and K. Siegbahn, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 285 (1972/73).
8. M. Seno, S. Tsuchiya, H. Kise and T. Asahara, *Bull. Chem. Soc. Jpn.*, **48**, 2001 (1975).
9. L. J. Matienzo and S. O. Grim, *Anal. Chem.*, **46**, 2052 (1974).