

Preliminary communication

P-COORDINATED GROUP VI METAL(0) PENTACARBONYL COMPLEXES OF MULTIPLE-BOND ORGANOPHOSPHORUS COMPOUNDS IN THE LOW COORDINATION STATE

MASAAKI YOSHIFUJI *, KATSUHIRO SHIBAYAMA, TAKASHI HASHIDA, KOZO TOYOTA, TAKASHI NIITSU, IKUMI MATSUDA, TAKAHIRO SATO and NAOKI INAMOTO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113 (Japan)

(Received May 15th, 1986)

Summary

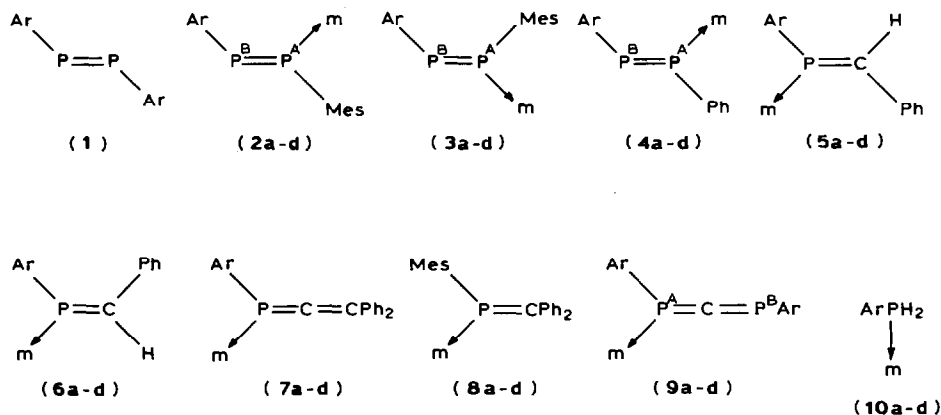
Group VI metal(0) carbonyl complexes of diphosphenes, phosphoethylenes, 1-phosphaallene, and 1,3-diphosphaallene with the phosphorus atom in the low coordination state were prepared, and the ^{31}P chemical shifts of these complexes were found to correlate to one another: the structures in solution could be determined by taking into account the correlation and phosphorus–tungsten coupling constants in ^{31}P NMR.

After we reported the sterically protected *E*-bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1**) for the first time [1], much attention has recently been drawn to multiple-bond compounds containing phosphorus atom(s) in the low coordination state, for their chemical reactivities and physico-chemical properties. We were also successful in the preparation of less-hindered and unsymmetrical diaryldiphosphenes such as **2d** and **4d** [2], *E*- and *Z*-phosphoethylenes (**5d** and **6d**) [3], 1-phosphaallene (**7d**) [4], and 1,3-diphosphaallene (**9d**) [5].

TABLE 1

$^1\text{J}(\text{PW})$ OBSERVED IN THE TUNGSTEN(0) PENTACARBONYL COMPLEXES

| Complex | $^1\text{J}(\text{PW})$ (Hz) | Complex | $^1\text{J}(\text{PW})$ (Hz) |
|-----------|------------------------------|------------|------------------------------|
| 5c | 271.0 | 3c | 231.9 |
| 6c | 273.4 | 7c | 268.6 |
| 4c | 244.1 | 9c | 271.0 |
| 2c | 238.0 | 10c | 227.1 |



(Ar = 2, 4, 6-Bu^t₃C₆H₂; Mes = 2, 4, 6-Me₃C₆H₂)

(a : m = Cr(CO)₅ ; b : m = Mo(CO)₅ ; c : m = W(CO)₅ ; d : m = none)

We now report interesting ³¹P NMR chemical shift correlations among the phosphorus-coordinated Group VI metal(0) carbonyl complexes of multiple-bond phosphorus compounds as described previously [3-7]. The ³¹P NMR spectra were recorded on a JEOL FX-90Q multinuclear spectrometer at 36.3 MHz using 85% H₃PO₄ as an external standard.

Figure 1 shows the plots of ³¹P NMR chemical shifts (in THF) of the complexes 2a-2c and 4a-4c against those for 8a-8c, or equivalent, as reported by Bickelhaupt [8] and Nixon [9]. It is of interest to note that the δ(P) values of the complexes

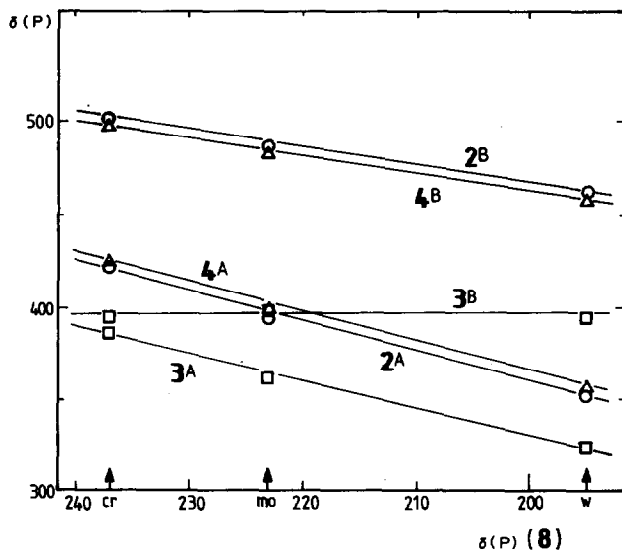


Fig. 1. Plots of $\delta(\text{P})$ values (2a-2c, 3a-3c, and 4a-4c) against $\delta(\text{P})$ (8a-8c); $r(2^{\text{A,B}}, 4^{\text{A,B}}) = 0.999$, $r(3^{\text{A}}) = 0.996$.

TABLE 2

 $^1J(\text{PP})$ (OR $^2J(\text{PP})$ ^a) OBSERVED AS AN AB PATTERN OF ^{31}P NMR

| Compound | $J(\text{PP})$ (Hz) | Compound | $J(\text{PP})$ (Hz) |
|----------|---------------------|----------|---------------------|
| 2d | 573.7 | 3c | 579.8 |
| 4d | 548.7 | 4a | 503.5 |
| 2a | 518.8 | 4b | 500.5 |
| 2b | 518.8 | 4c | 498.1 |
| 2c | 518.8 | 9a | 39.1 ^a |
| 3a | 518.8 | 9b | 36.6 ^a |
| 3b | 585.9 | 9c | 36.6 ^a |

^a $^2J(\text{PP})$ (Hz).

(2a–2c and 4a–4c) are found on the graph with a correlation coefficient of $r = 0.999$. The two sets of $\delta(\text{P})$ values at higher field may be assigned to P^{A} because the slope is steeper than for the other (P^{B}). In addition, for tungsten(0) carbonyl complexes 2c and 4c, the peaks at the high-field position were accompanied by satellite peaks due to coupling by the directly bonded ^{183}W ; with a 14.4% natural abundance ($S = 1/2$), $^1J(\text{PW})$ (Table 1).

We have reported that complexes 2a–2c isomerize to 3a–3c on irradiation with a mercury lamp [7]. The ^{31}P chemical shifts of P^{A} for 3a–3c also correlate to those of 8a–8c ($r = 0.996$), whereas those of the uncoordinated P^{B} remained almost constant. Again the higher peaks of the tungsten complex 3c were accompanied by satellites caused by ^{183}W .

The $^{31}\text{P}\{-^1\text{H}\}$ NMR of complexes 2, 3, 4, and 9 (a–c) appeared as an AB pattern. The coupling constants, $^1J(\text{PP})$ (for 2–4) and $^2J(\text{PP})$ (for 9a–9c), are listed in Table 2.

Figure 2 shows the plots of ^{31}P NMR chemical shifts of 6a–6c and 7a–7c against those of 5a–5c in chloroform-*d*. The correlation factors for 6a–6c and for 7a–7c were good ($r = 0.999$), whereas those for the mesityl derivatives (8a–8c) were not. The Group VI metal carbonyl complexes of 9d, 9a–9c, were also obtained by a method similar to that for 7a–7c and the chemical shifts were plotted as shown in Fig. 2. The plots were classified according to their correlation and slope, as shown in Fig. 2. The correlation factor of the plot owing to the coordinated phosphorus (P^{A}) was 0.999, whereas the plots due to the uncoordinated phosphorus (P^{B}) stayed almost constant. Thus the ^{31}P NMR spectrum of 9a–9c was assigned by this correlation. The chemical shifts of (2,4,6-tri-*t*-butylphenylphosphine)metal complexes 10a–10c [6] correlate less well ($r = 0.980$), probably because hybridization of the phosphorus atom in the phosphine 10 is different to that of the low coordinated phosphorus atoms in 2–7. The same is true for the poor correlation of 5–7 with 8a–8c.

The chemical shifts are governed by diamagnetic, paramagnetic, neighboring-atom, and steric effect terms [10]. The main contributor to ^{31}P shielding might be the paramagnetic term; however, the mechanism as to how the different metal atoms, (i.e., Cr, Mo, or W) directly change these parameters is not clear.

A similar trend of coordination chemical shifts for phosphine complexes of Group VI metal carbonyls has been found and occurs in the order $\text{Cr} > \text{Mo} > \text{W}$ [10,11].

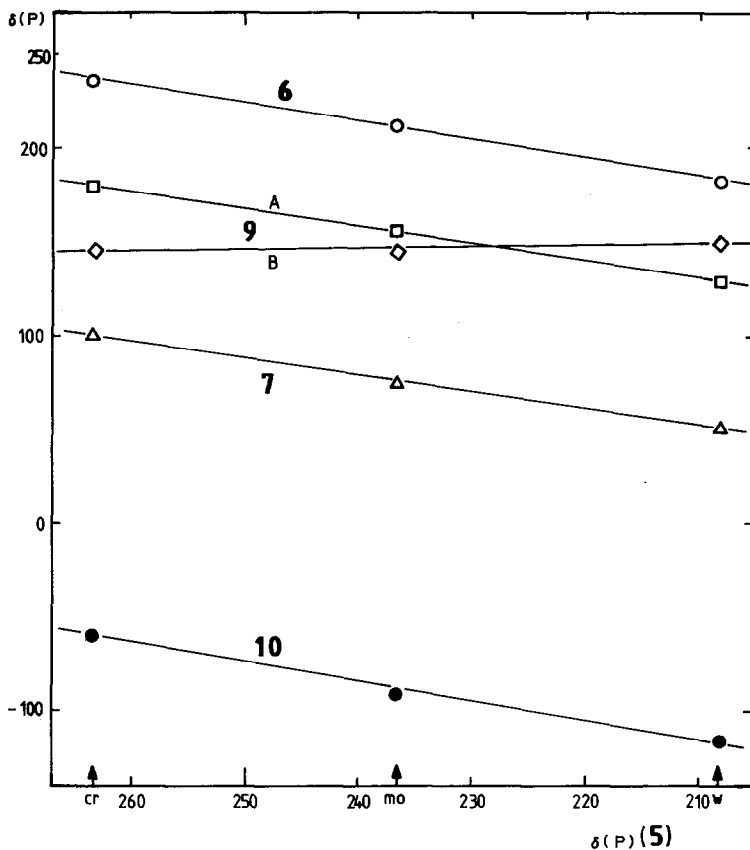


Fig. 2. Plots of $\delta(P)$ values (6a-6c, 7a-7c, 9a-9c, and 10a-10c) against $\delta(P)$ (5a-5c); $r(6, 7, 9^A) = 0.999$, $r(10) = 0.980$.

As for the metal coordination of multiple-bond systems, there are many possible types [8,9,12,13]. It seems likely that all the complexes described here are of the type with terminal-P coordination; even when in solution, the chemical shift correlation and the observed $^1J(PW)$ give a value which could be ascribable to a σ -type complex.

There is no apparent $^1J(PP)$ correlation with the different Group VI metals, Cr, Mo, and W; the same is true for the chemical shifts of uncoordinated ligands ($m = \text{none}$) with 2a-2c. Further theoretical studies on these complexes are in progress.

This work was supported in part by the Scientific Research Grant-in-Aids from the Ministry of Education, Science and Culture of Japan and the Kurata Research Grant from the Kurata Foundation.

References

- 1 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 103 (1981) 4587; 104 (1982) 6167.

- 2 M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita and K. Nishimoto, *J. Am. Chem. Soc.*, 105 (1983) 2495.
- 3 M. Yoshifuji, K. Toyota and N. Inamoto, *Tetrahedron Lett.*, 26 (1985) 1727; M. Yoshifuji, K. Toyota, N. Inamoto, K. Hirotsu and T. Higuchi, *ibid.*, 26 (1985) 6443.
- 4 M. Yoshifuji, K. Toyota, K. Shibayama and N. Inamoto, *Tetrahedron Lett.*, 25 (1984) 1809; M. Yoshifuji, K. Toyota, N. Inamoto, K. Hirotsu, T. Higuchi and S. Nagase, *Phosphorus and Sulfur*, 25 (1985) 237.
- 5 M. Yoshifuji, K. Toyota and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, (1984) 689.
- 6 M. Yoshifuji, T. Hashida, K. Shibayama and N. Inamoto, *Chem. Lett.*, (1985) 287.
- 7 M. Yoshifuji, T. Hashida, N. Inamoto, K. Hirotsu, T. Horiuchi, T. Higuchi, K. Ito and S. Nagase, *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 211.
- 8 T.C. Klebach, R. Lourens, F. Bickelhaupt, C.H. Stam and A. van Herk, *J. Organomet. Chem.*, 210 (1981) 211.
- 9 H.E.-Hosseini, H.W. Kroto, J.F. Nixon, M.J. Maah and M.J. Taylor, *J. Chem. Soc., Chem. Commun.*, (1981) 199.
- 10 S.O. Grim, D.A. Wheatland and W. McFarlane, *J. Am. Chem. Soc.*, 89 (1967) 5573.
- 11 J.F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectrosc.*, 2 (1969) 345.
- 12 T.A. van der Knaap, F. Bickelhaupt, J.G. Kraaykamp, G. van Koten, J.P.C. Bernards, H.T. Edzes, W.S. Veeman, E. de Boer and E.J. Baerends, *Organometallics*, 3 (1984) 1804.
- 13 O.J. Scherer, *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 924.