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Ylide-Metal Complexes. X.[1] An X-Ray Photoelectron Spectroscopic Study of Triphenylmethylenephosphorane and Gold- and Copper-Phosphorane Complexes

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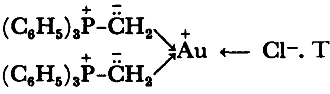
Triphenylmethylenephosphorane, the bis(triphenylmethylenephosphorane)gold chloride and the corresponding copper chloride have been studied by X-ray photoelectron spectroscopy. For the phosphorane, the binding energies, E_B, for P 2s and P 2p peaks were observed at 190.1 and 132.6 eV, respectively. The E_B value for the P 2p peak agrees with that (132.6 eV) for the phosphonium ion in triphenylmethylphosphonium bromide. The C 1s spectrum was separated into two peaks at E_B=285.0 and 283.9 eV, assuming a ratio of 18:1. The peak at 285.0 eV corresponds to the phenyl carbons, and that at 283.9 eV can be assigned to the electron-rich methylene carbon. Thus, the structure of the phosphorane is considered to be an ylide formula, $(C_6H_5)_3\overset{+}{P}-\overset{-}{\ddot{C}}H_2$. In gold phosphorane complexes, E_B of the C 1s, P 2s, and P 2p peaks were close to those for the phosphorane. The E_B of the Cl $2p_{3/2}$, Au $4f_{7/2}$, and Au $4f_{5/2}$ peaks coincided with those for bis(triphenylphosphine)gold chloride. These results indicate the structure of the gold complex to be



$$\left.\begin{matrix}(C_6H_5)_3\overset{+}{P}-\overset{-}{\ddot{C}}H_2\\(C_6H_5)_3\overset{+}{P}-\overset{-}{\ddot{C}}H_2\end{matrix}\right\rangle\overset{+}{Au}\longleftarrow Cl^-$$

The XPS results also indicate that the structure of the copper complex is similar to that of the gold complex.

Previously, we have been concerned with the preparation and properties of metal complexes with unstable triphenylmethylenephosphorane,[2] $(C_6H_5)_3P=CH_2$, and unstable triphenylmethylenearsorane[3] $(C_6H_5)_3As=CH_2$.

Many investigations regarding the XPS of metal complexes have been reported, especially, halogen complexes,[4] e.g., K_2MCl_6 (M: W, Re, Os, Ir, Pt); coordinated nitrogen-type complexes,[5] e.g., $[Co(NH_3)_5(NO_2)]Cl_2$; phosphine complexes,[6] e.g., $[(C_6H_5)_3P]_2CdCl_2$; olefine complexes,[7] e.g., $[(C_6H_5)_3P]_2Pt(CH_2=CH_2)$; metallocene,[8] e.g., $(\pi\text{-}C_5H_5)_2M$ (M: V, Cr, Mn, Fe, Co, Ni); carben complexes,[9] e.g., $(CO)_5CrC(OCH_3)CH_3$; and metal–carbonyl complexes,[10] e.g., $Fe(CO)_5$. However, the XPS study of ylide-metal complexes has not been reported so far, since preparation of complexes with unstable ylide was difficult.

The present paper deals with XPS measurements and the structure of triphenylmethylenephosphorane and its gold and copper complexes.

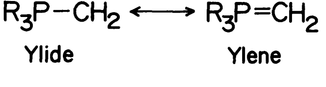
Experimental

XPS Measurements. Sample handling was always carried out in a 99.9995% pure nitrogen atmosphere to prevent possible decomposition. Samples were placed on a gold or nickel mesh holder and introduced into a spectrometer with a 99.9995% pure nitrogen atmosphere. After evacuating to better than 7×10^{-7} Pa (5×10^{-9} Torr†), the sample was cooled to 200 K, and irradiated with Mg $K\alpha$ X-ray (120 W). The instrument used was a VG ESCA 3 electron spectrometer. Analyzer energy was set to give a half width at half maximum [FWHM] of Au $4f_{7/2}$ peak of 1.18 eV. Peak separation of the spectra was made by the Gauss–Newton least-squares method, where a mixed Gaussian–Lorentzian curve shape having a fixed FWHM was utilized. The electron binding energies were calibrated by assigning 285.0 eV to the C 1s peak of the normal phenyl carbon.

Preparation of Phosphorane and Metal-Phosphorane Complexes. Triphenylmethylenephosphorane (**1**) was prepared from the triphenylmethylphosphonium bromide by the sodium amide method.[11] Bis(triphenylmethylenephosphorane)gold chloride (**6**), (triphenylmethylenephosphorane)(triphenylphosphine)gold chloride (**7**), and bis(triphenylmethylenephosphorane)copper chloride (**9**) were prepared by the method of the previous paper.[3b,11] Bis(triphenylphosphine)gold chloride (**8**) was prepared by the method of Baenziger.[12]

Results and Discussion

XPS of Triphenylmethylenephosphorane (1): The structure of phosphorane has been given in two formulae,[13] the ylide formula and the ylene formula as Scheme 1. The ylide formula shows a dipolar zwitterionic nature involving a carbanionic function and an onium center at the phosphorus element. In



Scheme 1.

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† 1 Torr=133.322 Pa.

the ylene formula, a true double bond is postulated between the onium center and the phosphorane carbon. Although the P–C bond length of **1** was determined to be 1.66 Å by X-ray analysis[14](suggesting a double-bond character), the assignment of ylide or ylene formula for the phosphorane (**1**) remains unsolved so far.

The results by the XPS measurements of phosphorane (**1**) and the corresponding phosphonium salts are summarized in Table 1 with some reference values. The binding energy, E_B, value (132.6 eV) of the P 2p peak for triphenylmethylphosphonium bromide, $[(C_6H_5)_3\overset{+}{P}CH_3]Br^-$ (**2**), is in good agreement with that (132.5 eV) for phosphonium ion in benzyltriphenylphosphonium chloride,[15] $[(C_6H_5)_3\overset{+}{P}CH_2(C_6H_5)]Cl^-$ (**3**). In reference 16, the E_B of P 2p peak for **3** and methyltriphenylphosphonium chloride, $[(C_6H_5)_3\overset{+}{P}CH_3]$-$Cl^-$ (**4**), are reported. However, those values are different from our results and also from those in reference 15. The E_B in reference 16, however, are somewhat ambiguous, because only E_B of the P 2p peak are given and there is no description of a calibration method. Therefore, the measured E_B for **2** is regarded as reasonable. Other reference values for **2** or **4** were not found by our literature survey. The E_B of the P 2p peak of **2** is different from that[6,15,17] for triphenylphosphine, $(C_6H_5)_3P$ (**5**), as is shown in Table 1. The E_B of **5** measured by different investigators show fairly large scattering, but the highest value is still lower than 132.6 eV of **2**.

In the XPS for phosphorane (**1**), the E_B of the P 2p peak was observed at 132.6 eV; i.e., phosphorus element in **1** can be assigned to the phosphonium ion. This suggests the ylide formula, $(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}H_2$. The C 1s spectrum for **1** showed a slightly distorted shape, a tailing at the lower binding-energy side and with a separate very weak satellite peak at the higher binding-energy side. The peak binding energy, E_B, was set at 285.0 eV as due to phenyl carbons. Assuming an 18:1 intensity ratio between phenyl carbons and a methylene carbon, the C 1s peak can be separated to two peaks at 285.0 eV and 283.9 eV. The E_B of the latter peak indicates an electron-rich carbon and is favorable to the ylide formula, but the results must be evaluated with caution since a few arbitrary factors are involved in the peak separation.

XPS of Bis(triphenylmethylenephosphorane)gold Chloride, $[(C_6H_5)_3PCH_2]_2AuCl$ (6), (Triphenylmethylenephosphorane)(triphenylphosphine)gold Chloride, $[(C_6H_5)_3PCH_2][(C_6H_5)_3P]AuCl$ (7), Bis(triphenylphosphine)gold Chloride (8) and Bis(triphenylmethylenephosphorane)copper Chloride, $[(C_6H_5)_3PCH_2]_2CuCl$ (9): The results of XPS for metal phosphorane and metal phosphine complexes are summarized in Table 2. The E_B of Au 4f and Cl $2p_{3/2}$ peaks for both gold complexes **6** and **7** are in good agreement with those for **8**. The E_B values for **8** coincide with those reported by others[18]: E_B[C 1s]=284.9 eV, E_B[P 2p]=131.8 eV, E_B[Cl $2p_{3/2}$]=197.5 eV, and E_B[Au $4f_{7/2}$]=85.2 eV, where oxidation number of gold has been assigned to +1. In addition, the structure of **8** has been found to be essentially trigonal planar by X-ray diffraction.[12] Therefore, the structure of **6** and **7** can be analogous to **8**, and the chloride in **6** and **7** can bond to Au(I). The E_B of C 1s, P 2s, and P 2p peaks for bonded phosphorane in **6** and **7** are very close to those for **1**, but are different from those for the coordinated phosphine. This suggests that the phosphorane in gold complexes can be the ylide formula; i.e., phosphorane-gold bonds are formed from the electron-pair in the carbanion and empty orbitals (sp^2) of gold. Then, the structure of **6** can be expressed as Scheme 2.

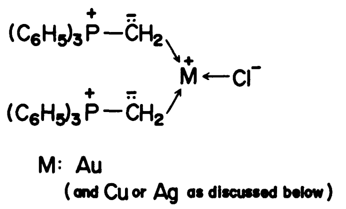
For copper complex **9**, the Cu 2p spectra showed no satellite peaks; thus the copper is monovalent

Table 1. Binding Energies Observed in the XPS of Phosphorane and Phosphonium Bromide, and Some Reference Values

No.	Compound	Binding energies of electrons, E_B/eV C 1s		P 2s	2p	Ref.
1	$(C_6H_5)_3P{=}CH_2$	283.9	285.0	190.1	132.6	
2	$[(C_6H_5)_3PCH_3]Br$		285.0		132.6	
3	$[(C_6H_5)_3PCH_2(C_6H_5)]Cl$		285.0		132.5	15)
		(E_B[P 2p]=133.3 eV for $Na_4P_2O_7$)			130.5	16)
4	$[(C_6H_5)_3PCH_3]Cl$	(E_B[P 2p]=133.3 eV for $Na_4P_2O_7$)			130.2	16)
5	$(C_6H_5)_3P$		285.0		131.3	6a)
			285.0		131.9	6b)
			285.0		131.3	6c)
			285.0		130.6	15)
			285.0		130.9	17)

Table 2. Binding Energies Observed in the XPS of Metal Complexes with Phosphorane and Phosphine

No.	Complex	Binding energies of electrons, E_B/eV								
		C 1s		P		Cl	Au		Cu	
				2s	2p	$2p_{3/2}$	$4f_{7/2}$	$4f_{5/2}$	$2p_{3/2}$	$2p_{1/2}$
6	$[(C_6H_5)_3PCH_2]_2AuCl$	283.8	285.0	189.6	132.4	197.5	84.9	88.6		
7	$[(C_6H_5)_3PCH_2]$-		285.0	189.8	132.9	197.7	85.0	88.7		
	$[(C_6H_5)_3P]AuCl$			189.3	131.6					
8	$[(C_6H_5)_3P]_2AuCl$		285.0	189.3	131.8	197.8	85.2	88.8		
9	$[(C_6H_5)_3PCH_2]_2CuCl$	283.6	285.0	189.5	132.4	197.8			933.5	953.3



Scheme 2.

(3d^{10}) or metallic.[19)] The E_B of the Cu 2p peaks are much higher than those for commonly known complexes of Cu(I) or Cu(0),[19)] but are in good agreement with those for triphenylphosphinecopper(I) chloride,[19a)] $(C_6H_5)_3PCuCl$ (**10**), and tris(triphenylphosphine)copper(I) chloride, $[(C_6H_5)_3P]_3CuCl$ (**11**): $E_B[\text{Cu } 2p_{3/2}]=933.5$ eV, and $E_B[\text{Cu } 2p_{1/2}]=953.2$ eV assuming $E_B[\text{C 1s}]=285.0$ eV for phenyl carbons. The values for bis(triphenylphosphine)copper chloride, $[(C_6H_5)_3P]_2CuCl$ (**12**), were not found. Further, to distinguish the Cu(I) and Cu(0) Auger parameter, α, is known to be useful. It is defined as the kinetic energy of an intense Auger line minus that of an intense photoelectron line.[20)] The measured $E_K[\text{Cu}_{LMM}]-E_K[\text{Cu } 2p_{3/2}]$ for copper in **9** was 361.3 eV. This value is very close to $\alpha=361.0$ eV for CuCl and CuCN, but different from $\alpha=364.6$ eV for metallic Cu.[20)] Thus, the oxidation number of copper in **9** is one (or +1). Since other E_B values for **9** coincide with gold complex **6**, and the structure of **12**[21)] is confirmed to be similar to that of **8**, the structure of **9** is as in Scheme 2. The XPS results strongly suggest that gold and copper complexes have the structure of Scheme 2. However, as a matter of course, X-ray diffraction may provide indisputable conclusions. So far, the diffraction is not conducted due to the difficulties of sample preparation, handling, and facilities.

The similarity of copper and gold complexes leads to a conclusion that the corresponding silver complex $[(C_6H_5)_3PCH_2]_2AgCl$ (**13**)[11)] may have the same structure as is shown in Scheme 2.

Referenses

1) Part IX: Ref. 3a.

2) Y. Yamamoto, *Chem. Lett.*, **1980**, 311; Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 3025 (1982); **56**, 1772 (1983); **57**, 43 (1984).

3) a) Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **57**, 2835 (1984); b) Y. Yamamoto and Z. Kanda, *Bull. Chem. Soc. Jpn.*, **52**, 2560 (1979); c) W. Richter, Y. Yamamoto, and H. Schmidbaur, *Chem. Ber.*, **110**, 1312 (1977).

4) G. J. Leigh, and W. Bremser, *J. Chem. Soc., Dalton Trans.*, **1972**, 1216.

5) M. V. Zelber and R. G. Hayes, *J. Am. Chem. Soc.*, **95**, 3855 (1973); K. L. Cheng, J. C. Carver, and T. A. Carlson, *Inorg. Chem.*, **12**, 1702 (1973); P. Finn and W. L. Jolly, *Inorg. Chem.*, **11**, 893 (1972); G. J. Leigh, J. N. Murrell, W. Bremser, and W. G. Proctor, *J. Chem. Soc., Chem. Commun.*, **1970**, 1661; D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

6) a) P. A. Grutsh, M. V. Zeller, and T. P. Fehlner, *Inorg. Chem.* **12**, 1431 (1973); b) J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *ibid.*, **9**, 2374 (1970); c) W. E. Morgan, W. J. Stec, R. G. Albridge, and J. R. Van Wazer, *ibid.*, **10**, 962 (1971).

7) R. Mason, D. M. P. Mingos, G. Russi, and J. A. Connor, *J. Chem. Soc., Dalton Trans.*, **1972**, 1729.

8) M. Barber, J. A. Connor, L. M. R. Derrick, M. B. Hall, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **1973**, 559.

9) W.B. Perry, T. F. Schaaf, W. L. Jolly, L. J. Todd, and D. L. Cronin, *Inorg. Chem.*, **13**, 2038 (1974).

10) M. Barber, J. A. Connor, M. F. Guest, M. B. Hall, I. H. Hillier, and W. N. E. Meredith, *Faraday Discuss. Chem. Soc.*, **54**, 219 (1972); M. Barber, J. A. Connor, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc., Chem. Commun.*, **1971**, 682.

11) Y. Yamamoto and H. Schmidbaur, *J. Organomet. Chem.*, **96**, 133 (1975).

12) N. C. Baenziger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, **13**, 805 (1974).

13) A. W. Johnson "Ylide Chemistry," Academic Press, New York, N. Y.(1966).

14) J. C. J. Bart, *J. Chem. Soc. (B).*, **1969**, 350.

15) M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

16) W. E. Swartz, Jr., and D. M. Hercules, *Anal. Chem.*, **43**, 1066 (1971).

17) C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, **12**, 2770 (1973).

18) A. McNeillie, D. H. Brown, W. E. Smith, M. Gibson, and L. Watson, *J. Chem. Soc., Dalton Trans.*, **1980**, 767.

19) a) D. C. Frost, A. Ishitani, and C. A. McDowell, *Mol. Phys.*, **24**, 861 (1972); b) P. E. Larson, *J. Electron Spectrosc.*, **1**, 251 (1972/73); c) B. Folkesson, P. Sundberg, L. Johansson, and R. Larson, *J. Electron Spectrosc. Relat. Phenom.*, **32**, 245 (1983).

20) C. D. Wagner, *Faraday Discuss. Chem. Soc.*, No. 60, 291 (1975).

21) P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **12**, 213 (1973).