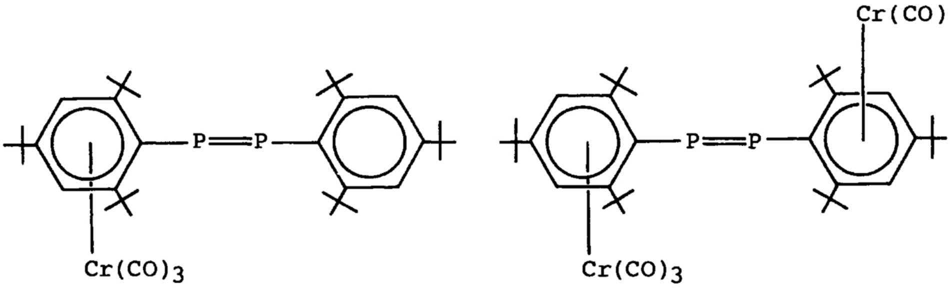
CHEMISTRY LETTERS, pp. 287 - 290, 1985.

PREPARATION OF THE P-COORDINATED GROUP VIB METAL PENTACARBONYL COMPLEXES OF DIARYLDIPHOSPHENES

Masaaki YOSHIFUJI,* Takashi HASHIDA, Katsuhiro SHIBAYAMA, and Naoki INAMOTO
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113

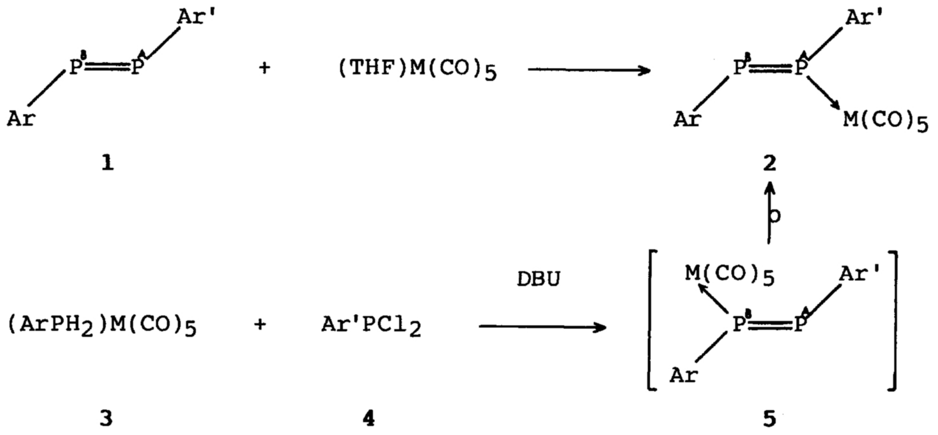
The Group VIB metal(0) carbonyl complexes of diaryldiphosphenes at the phosphorus atom were prepared by two different methods and characterized : A novel migration reaction of the metal carbonyl groups is described.

Strong attention has recently been drawn to the compounds containing phosphorus-phosphorus double bond from the view points of chemical reactivities and physicochemical properties, since we reported the isolation of sterically protected bis(2,4,6-tri-t-butylphenyl)diphosphene (**1C**) for the first time.1) We were also successful in preparation of less hindered diaryldiphosphenes, such as mesityl- (**1A**) and phenyl-(2,4,6-tri-t-butylphenyl)diphosphenes (**1B**).2) The very bulky **1C** failed to react with (THF)$Cr(CO)_5$ at 0 - 25 °C but **1C** reacted with $Cr(CO)_6$ on heating in dioxane to afford arene-complexes, (Ar-P=P-Ar)$[Cr(CO)_3]_n$ (n=1,2),3) where Ar=2,4,6-$Bu^t{}_3C_6H_2$ instead of P-coordinated complexes as shown below.



These results indicated that two 2,4,6-tri-t-butylphenyl groups in **1C** are too bulky to permit the phosphorus atom to coordinate directly with the chromium atom giving rise to an expected complex with five CO groups and suggested that less hindered diphosphenes could form complexes at the phosphorus atom.

We now report here the preparation of phosphorus-coordinated group VIB metal(0) carbonyl complexes of diaryldiphosphenes by two different methods as shown in the following scheme.



Ar=2,4,6-$Bu^t_3C_6H_2$. **A:** Ar'= 2,4,6-$Me_3C_6H_2$; **B:** Ar'=C_6H_5; **C:** Ar'=Ar.
a: M=Cr; **b:** M=Mo; **c:** M=W.

The first reaction sequence for the preparation of these complexes employed here was straightforward and almost the same as that described for phosphaalkene-transition metal carbonyl complexes.[4,5] The typical procedure is as follows: the tetrahydrofuran complex, $(THF)Cr(CO)_5$, was allowed to react with an equivalent amount of **1A** (235 mg, 0.522 mmol) in THF (50 mL) at 0 °C for 2 h in dark under argon. The product was chromatographed (silica gel) at room temperature and was recrystallized from pentane (yield, 49%). The complex **2Aa** is an orange red solid, which displays a remarkable stability to atmospheric oxygen and moisture. **2Aa:** FD-MS m/z 618 (M^+). The fundamental structure of **2** might be very similar to those for the 1-sulfide[6] and the tetracarbonyliron(0) complex[7] of **1C**. As for the structure of the group VIB metal complexes, Power[8] and Huttner[9] have recently reported dialkyldiphosphene chromium complexes and a diaryldiphosphene bis(pentacarbonylchromium(0)) complex such as $[(Me_3Si)_2CH\text{-}P{=}P\text{-}CH(SiMe_3)_2][Cr(CO)_5]$ and $[PhP{=}PPh][Cr(CO)_5]_2$, respectively.

Very similarly, molybdenum(0) and tungsten(0) carbonyl complexes (**2Ab** and **2Ac**) were prepared in 60 and 68% yields, respectively. Both complexes thus obtained were also stable. The NMR parameters and some physical properties are listed in Table 1. Each complex appeared as an AB pattern with large coupling constant, $^1J_{PP}$, in its ^{31}P NMR spectrum.

Table 1. Some Selected Physical Data of **2Aa-c**

Compd. (Mp/°C)	^{31}P NMR parameter (CDCl$_3$) δ_P/ppm		$^1J_{PP}$/Hz	^{1}H NMR a) δ(CDCl$_3$) Ar/Ar'	o/p-Me	o/p-Bu^t	IR (KBr) ν(CO)/cm^{-1}	UV (c-HexH) b) λ_{max}
2Aa	500.9	412.3	517.6	7.50	2.52	1.57	2060(s) 1990	460
(166)				7.10	2.34	1.33	1950(vs) 1940(vs)	
2Ab	486.3	395.0	518.8	7.53	2.51	1.58	2080(s) 2000	435
(163)				7.01	2.35	1.35	1960(vs) 1950(vs)	
2Ac	461.9	352.4	528.8	7.50	2.52	1.58	2080(s) 2000	436
(177)				7.00	2.35	1.34	1950(vs) 1940(vs)	

a) Ar=2,4,6-$Bu^t{}_3C_6H_2$, Ar'=2,4,6-$Me_3C_6H_2$. b) c-HexH = cyclohexane.

Secondly, when the pentacarbonylchromium complex of 2,4,6-tri-t-butylphenylphosphine (**3a**, 30.9 mg, 0.0746 mmol) was allowed to react with **4A** (0.112 mmol) in the presence of a base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.201 mmol) in THF (9 mL) at 0 °C for 5 h, the product obtained was identical with **2Aa** (70 % yield). Attempts to prepare the diphosphene complexes coordinated at the more crowded phosphorus atom (**5**) by the latter method failed, however, we have found interesting reactions which might involve a novel migration of the metal carbonyl group from the more crowded phosphorus atom (P^B) to the less hindered phosphorus atom (P^A).10) It should be noted that the migration process of the metal carbonyl group may proceed via π-complex on the P=P double bond. This novel method was applied for the preparation of complexes of the phenyl derivatives **2Ba-c**,11) starting from **3a-c**12) and **4B**. A similar chromatographic treatment for the purification, however, failed to permit isolation of **2Ba-c**, probably because of the insufficient steric protection.

This work was supported in part by the Scientific Research Grant-in-Aids from the Ministry of Education, Science and Culture (Nos. 57540276 and 58840023) and the Kurata Research Grant from the Kurata Foundation. The authors thank Mr. Hiroaki Shiraishi at the National Institute for Environmental Studies for obtaining the FD-MS of complexes **2** and **3**.

References

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

2) M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, J. Am. Chem. Soc., 105, 2495 (1983).

3) M. Yoshifuji and N. Inamoto, Tetrahedron Lett., 24, 4855 (1983).

4) T. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, and A. van Herk, J. Organomet. Chem., 210, 211 (1981).

5) H. E.-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, and M. J. Taylor, J. Chem. Soc., Chem. Commun., 1981, 199.

6) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Chem. Soc., Chem. Commun., 1983, 862.

7) A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, and T. C. Wright, J. Am. Chem. Soc., 105, 7751 (1983).

8) K. M. Flynn, B. D. Murray, M. M. Olmstead, and P. P. Power, J. Am. Chem. Soc., 105, 7460 (1983); K. M. Flynn, H. Hope, B. D. Murray, M. M. Olmstead, and P. P. Power, J. Am. Chem. Soc., 105, 7750 (1983).

9) J. Borm, L. Zsolnai, and G. Huttner, Angew. Chem., Int. Ed. Engl., 22, 977 (1983).

10) The X-ray analysis of a **2Aa** derivative will be published elsewhere; M. Yoshifuji, T. Hashida, N. Inamoto, K. Hirotsu, T. Horiuchi, T. Higuchi, K. Ito, and S. Nagase, to be submitted.

11) $^{31}P\{^1H\}$ NMR data (in THF); **2Ba:** δ_P 498.9 and 415.7 ppm (J_{PP} 503.5 Hz); **2Bb:** δ_P 484.1 and 399.5 ppm (J_{PP} 500.5 Hz); **2Bc:** δ_P 458.8 and 359.0 ppm (J_{PP} 498.1 Hz).

12) The arylphosphine complexes **3a-c** were prepared by the usual method from 2,4,6-tri-*t*-butylphenylphosphine and the corresponding group VIB metal complexes, (THF)M(CO)$_5$, generated photochemically in THF. Some physical data and ^{31}P NMR data: **3a:** mp 104-107 °C, δ_P (CDCl$_3$) -59.4 ppm, J_{PH} 329.4 Hz; **3b:** mp 96-98 °C, δ_P -90.2 ppm, J_{PH} 322.6 Hz; **3c:** mp 117-118 °C, δ_P -106.1 ppm, J_{PH} 337.1 Hz (satellite $^1J_{PW}$ 227.1 Hz).

(Received November 20, 1984)