Tetrahedron Letters,Vol.24,No.44,pp 4855-4858,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

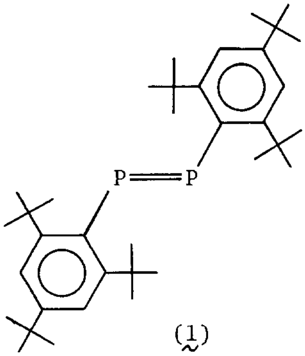
REACTION OF A DIARYLDIPHOSPHENE WITH HEXACARBONYLCHROMIUM(0): FORMATION OF (ARENE)TRICARBONYLCHROMIUM(0) COMPLEXES

Masaaki Yoshifuji* and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of
Tokyo, Hongo, Tokyo 113, Japan

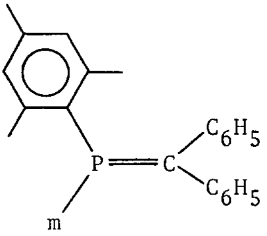
1,2-Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (1) reacts with hexacarbonylchromium(0) to give mono and bis π-chromium(0) tricarbonyls (3 and 4) as stable complexes.

Organochromium complexes have been widely used in organic syntheses.[1-3] Various phosphine ligands have been useful in transition metal chemistry.[4,5]

Recently we were successful in preparation and characterization of a sterically protected diphosphene, *E*-1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (1),[6] and since then such compounds with a phosphorus-phosphorus double bond have been of current interest.[7-11] Bickelhaupt et al.[12] and Nixon et al.[13] reported the syntheses of some mesityldiphenylmethylenephosphine - transition metal complexes and found that only phosphorus σ-co-ordinated complexes are formed.

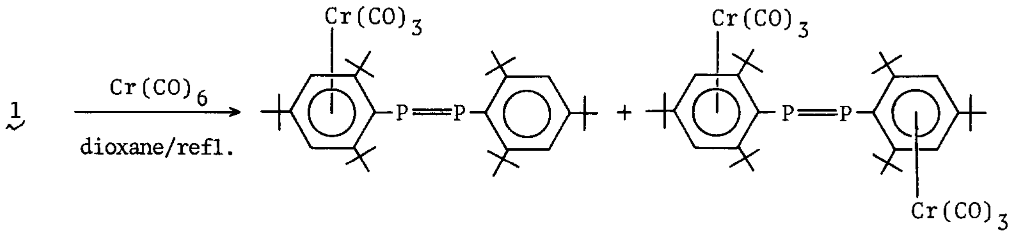


(1)



(2) m = cr, mo, w

We now report the reaction of the diphosphene (1) with hexacarbonylchromium(0) in an attempt to prepare and characterize diphosphene - chromium complexes.



(3) (4)

The diphosphene (1) was refluxed in 1,4-dioxane in the presence of an excess of hexacarbonylchromium(0) to give stable π-(arene)tricarbonylchromium(0) complexes (3) and/or (4), depending on the amount of chromium carbonyl employed and the reaction time. A mixture of the diphosphene (1) (224 mg, 0.406 mmol) and $Cr(CO)_6$ (413 mg, 1.88 mmol) in 20 ml of dioxane was refluxed under argon for 12 h to give a red homogeneous solution. The solvent was removed by rotary-evaporation and the residue was chromatographed on silica gel to give the recovered starting diphosphene (1) and the mono η^6-$Cr(CO)_3$ complex (3) (114 mg, 0.166 mmol; 72% yield based on 1 consumed). When a large excess amount of hexacarbonylchromium(0) was employed (567 mg, 2.58 mmol) with the diphosphene (1) (209 mg, 0.379 mmol) and the mixture was refluxed in dioxane for 2 days, the mixture turned dark red. After the usual workups the mono η^6-$Cr(CO)_3$ complex (3) (169 mg, 0.245 mmol; 65% yield based on 1 used) and the bis η^6-$Cr(CO)_3$ complex (4) (104 mg, 0.126 mmol; 33% yield) were obtained. 3: orange crystals, mp 203 - 205 °C, ^1H NMR ($CDCl_3$) δ 7.41 (s, 2H, arom.), 6.17 (s, 2H, arom.-Cr), 1.51 + 1.48 (s + s, 18H + 18H, o-Bu^t), and 1.36 + 1.33 (s + s, 9H + 9H, p-Bu^t), IR (KBr) ν_{CO} 1955 (s) and 1885 (br. s) cm^{-1}, UV (CH_2Cl_2) λ_{max} (ε) 304 (12300), 324 (12900), and 480 (757), MS m/e 688 (M^+). ^{31}P NMR (CH_2Cl_2, 85% H_3PO_4) appeared as an AB pattern centered at δ_P 503.2 and 475.6 ppm with $^1J_{PP} = 590.8$ Hz. 4: dark red crystals, mp > 300 °C, ^1H NMR (CD_2Cl_2) δ 6.26 (s, 4H, arom.-Cr), 1.56 (s, 36H, o-Bu^t), and 1.35 (s, 18H, p-Bu^t), IR (KBr) ν_{CO} 1950 (s), 1880 (s), and 1876 (s) cm^{-1}, UV (CH_2Cl_2) λ_{max} (ε) 328 (29800), 416 (3450), and 520 (903), MS (field desorption ionization) m/e 824 (M^+), ^{31}P NMR (CCl_4) δ_P 499.7 ppm.

However, attempts to prepare a phosphorus co-ordinated chromium complex failed; pentacarbonyl(tetrahydrofuran)chromium(0) was photochemically prepared[14] and was allowed to react with an equivalent amount of 1 under argon at room temperature, however, after the usual workups the starting diphosphene (1) was recovered; irradiation of a mixture of the diphosphene (1) and $Cr(CO)_6$ in tetrahydrofuran in a Pyrex NMR tube with a medium-pressure mercury lamp caused no signal change in $^{31}P\{^1H\}$ NMR spectrum of 1 (δ_P 491.9 ppm) at 36.3 MHz.[6]

These results indicate that the 2,4,6-tri-tert-butylphenyl-phosphorus is too crowded as a ligand to form σ-co-ordination with chromium, whereas there have been several recent reports on transition metal complexation with phosphorus atoms involving p_π-p_π bonding.[12,13,15-21]

TABLE I. Some $^{31}P\{^1H\}$ NMR Parameters of Diphosphenes and Related Compounds

Compound$^{a)}$	δ_P/ppm		$^1J_{PP}$/Hz	Solvent	Ref.
3	503.2	475.6	590.8	CH_2Cl_2	This work
ArP = PAr'	517.0	480.1	583.5	C_6D_6	7
ArP = P(S)Ar	255.8	247.8	629.9	Et_3N	22
ArP = P(O)Ar	206.5	69.8	683.6	$CDCl_3$	23

a) Ar = 2,4,6-$Bu^t_3C_6H_2$; Ar' = 2,4-Bu^t_2-6-MeC_6H_2

Table I shows some $^{31}P\{^1H\}$ NMR parameters at 36.3 MHz we have observed for diphosphenes and the related compounds with a phosphorus-phosphorus double bond. We recently reported the preparation and characterization of some unsymmetrical diaryldiphosphenes[7] for the spectrochemical studies, however, the π-complexation with the $Cr(CO)_3$ group described here would be an alternative facile method to prepare unsymmetrical diphosphenes. Quite large spin-spin coupling constants, $^1J_{PP}$, seem to be characteristic for the P = P bond.

Further studies on diphosphenes-transition metal complexations and X-ray crystallographic studies of 3 and 4 are in progress. We are indebted to Mr. Hiroaki Shiraishi at the National Institute for Environmental Research, Japan, for obtaining the field desorption ionization mass spectrum of 4. This work was supported in part by the Scientific Research Grant-in-Aid from the Ministry of Education, Science and Culture of Japan (No. 543008, 57540276, and 58840023).

REFERENCES

1) M. F. Semmelhack, Ann. N. Y. Acad. Sci., 295, 36 (1977); M. F. Semmelhack, H. T. Hall,

Jr., R. Farrina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, J. Am. Chem. Soc., 101, 3535 (1979).

2) G. Jaouen, Ann. N. Y. Acad. Sci., 295, 59 (1977).

3) R. P. A. Sneeden, "Organochromium Compounds," Academic Press, New York (1975).

4) R. F. Heck, "Organotransition Metal Chemistry," Academic Press, New York (1974).

5) G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry," Mathuen, London (1971).

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

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

8) G. Bertrand, C. Couret, J. Escudié, S. Majid, and J.-P. Majoral, Tetrahedron Lett., 23, 3567 (1982); C. Couret, J. Escudié, and J. Satgé, ibid., 23, 4941 (1982); J. Escudié, C. Couret, J. D. Andriamizaka, and J. Satgé, J. Organomet. Chem., 228, C76 (1982).

9) B. Çetinkaya, A. Hudson, M. F. Lappert, and H. Goldwhite, J. Chem. Soc., Chem. Commun., 1982, 609; B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, ibid., 1982, 691.

10) A. H. Cowley, J. E. Kilduff, M. Pakulski, and C. A. Stewart, J. Am. Chem. Soc., 105, 1655 (1983); A. H. Cowley, J. E. Kilduff, S. K. Mehrotra, N. C. Norman, and M. Pakulski, J. Chem. Soc., Chem. Commun., 1983, 528.

11) C. N. Smit., Th. A. van der Knaap, and F. Bickelhaupt, Tetrahedron Lett., 24, 2031 (1983).

12) Th. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, A. van Herk, J. Organomet. Chem., 210, 211 (1981); Th. A. van der Knaap, F. Bickelhaupt, H. van der Poel, G. van Koten, and C. H. Stam, J. Am. Chem. Soc., 104, 1756 (1982).

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

14) W. Strohmeier and F.-J. Müller, Chem. Ber., 102, 3608 (1969).

15) B. Deppisch and H. Schäfer, Z. anorg. allg. Chem., 490, 129 (1982).

16) K. M. Flynn, M. M. Olmstead, and P. P. Power, J. Am. Chem. Soc., 105, 2085 (1983).

17) H. Vahrenkamp and D. Wolters, Angew. Chem. Int. Ed. Engl., 22, 154 (1983).

18) P. S. Elms, M. L. Scudder, and B. O. West, J. Organomet. Chem., 122, 281 (1976).

19) E. Niecke, M. Engelmann, H. Zorn, B. Krebs, and G. Henkel, Angew. Chem. Int. Ed. Engl., 19, 710 (1980).

20) A. H. Cowley, R. A. Jones, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H.-M. Zhang, J. Am. Chem. Soc., 105, 3737 (1983).

21) J. C. T. R. B.-St. Laurent, P. G. Hitchcock, H. W. Kroto, and J. F. Nixon, J. Chem. Soc., Chem. Commun., 1981, 1141.

22) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Chem. Soc., Chem. Commun., 1983, in press.

23) M. Yoshifuji, K. Ando, K. Toyota, I. Shima, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1983, 419.

(Received in Japan 21 July 1983)