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Tungsten (*Z*)-1,2-Diphosphite−Alkene and (*E*)-Vinyl−Phosphite Complexes from Phosphite Fischer Carbene Complexes

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Summary: Pentacarbonyl acyl tungstates **1** *react with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane to give phosphite Fischer carbene complexes* **2**, *which in very mild conditions readily lead to the corresponding tungsten (Z)-1,2-diphosphite−alkene tetracarbonyl complexes* **3** *via a dimerization process (R = aryl) or tungsten (E)-vinyl−phosphite pentacarbonyl complexes* **4** *via a 1,2-hydrogen shift (R = alkyl), respectively.*

Since the discovery by Fischer[1] of stable carbene complexes for chromium, molybdenum, and tungsten, there has been widespread interest in their applications in organic synthesis.[2] In recent years, a variety of sililoxy,[3] titanoxy,[4] zirconoxy,[5] and boroxy[6] Fischer carbene complexes have been synthesized in order to modulate the carbene reactivity by steric and electronic variation of the metal or metalloid component bound to the heteroatom. On the other hand, heteroatom-stabilized metal carbenes, such as alkoxy carbenes, are thermally stable and only at relatively high temperatures react with alkenes that posses electron-withdrawing or electron-donating groups to give cyclopropane derivatives[2d,7] and in its absence undergo loss of the metal fragment affording mixtures either of dimerization products or enol ethers.[8] In the present communication we describe, for the first time, the preparation of phosphite Fischer carbene complexes and their easy transformation into (*Z*)-1,2-diphosphite−alkenes or (*E*)-vinyl−phosphites as tungsten complexes *via* a dimerization process or a 1,2-hydrogen shift, respectively.

The treatment of pentacarbonyl acyl tungstate intermediates **1**, formed by the reaction of tungsten hexacarbonyl and the corresponding organolithium compound,[9] with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane[10] in diethyl ether at temperatures ranging between −60 and −30 °C readily led to phosphite carbene complexes **2**, which could not be isolated and were detected by NMR. On warming to room temperature, the compounds **2a**−**c**, where R is an aryl group, underwent loss of the metal fragment affording the tungsten (*Z*)-1,2-diphosphite−alkene tetracarbonyl complexes **3** as a single diastereoisomer. The structure of these complexes was determined on the basis of their NMR spectra and the X-ray structural analysis of complex **3a**[11] (Figure 1). This transformation involves the dimerization of the carbene **2** in very mild conditions. On the contrary, starting from carbene complexes

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(1) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(2) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5, p 1065. (d) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 387. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 469. (f) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 549.

(3) (a) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275. (b) Fischer, E. O.; Selmary, T.; Kreissl, F. R.; Schubert, U. *Chem Ber.* **1977**, *110*, 2574. (c) Schubert, U.; Wiener, M.; Köhler, F. H. *Chem Ber.* **1979**, *112*, 708. (d) Balzer, B. L.; Cazanoue, M.; Finn, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 8735. (e) Gross, M. F.; Finn, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10921.

(4) (a) Fischer, E. O; Fontana, S. *J. Organomet. Chem.* **1972**, *40*, 159. (b) Raubenheimer, H. G.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *91*, C23. (c) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145. (d) Sabat, M.; Gross, M. F.; Finn, M. G. *Organometallics* **1992**, *11*, 745. (e) Balzer, B. L.; Cazanoue, M.; Sabat, M.; Finn, M. G. *Organometallics* **1992**, *11*, 1759.

(5) (a) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (c) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. (d) Erker, G.; Sosna, F.; Petersen, J. L.; Benn, R.; Grondey, H. *Organometallics* **1990**, *9*, 2462. (e) Erker, G.; Pfaff, R. *Organometallics* **1991**, *10*, 3559. (f) Erker, G.; Mena, M.; Hoffmann, U.; Menjón, B.; Petersen, J. L. *Organometallics* **1990**, *10*, 291.

(6) (a) Fischer, E. O.; Gibbins, S. G.; Kellerer, W. *J. Organomet. Chem.* **1981**, *218*, C51. (b) Petz, W. *Z. Naturforsch.* **1981**, *36b*, 335. (c) Barluenga, J.; Canteli, R. M.; Flórez, J.; García-Granda, S.; Gutiérrez-Rodríguez, A. *J. Am. Chem. Soc.* **1994**, *116*, 6949. (d) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F. J.; López-Ortiz, F. *J. Am. Chem. Soc.* **1996**, *118*, 6090.

(7) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Brookhart, M.; Studebaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(8) (a) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Müller, J. *J. Organomet. Chem.* **1969**, *16*, P29. (b) Fischer, E. O.; Plabst, D. *Chem Ber.* **1974**, *107*, 3326. (c) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (d) Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236.

(9) Fischer, E. O.; Maasböl, A. *Chem Ber.* **1967**, *100*, 2445.

(10) 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane has been prepared as described in the literature, see: Lucas, H. J.; Mitchell, F. W., Jr.; Scully, C. N. *J. Am. Chem. Soc.* **1950**, *72*, 5491.

(11) Crystal data for **3a**: Recrystallized from diethyl ether, $C_{28}H_{30}O_{10}P_2W$, $M_r = 772.31$, triclinic, space group $P\bar{1}$, $a = 10.758(2)$ Å, $b = 11.884(9)$ Å, $c = 13.328(4)$ Å, $\alpha = 79.71(4)°$, $\beta = 74.64(3)°$, $\gamma = 88.42(2)°$, $V = 1616.(1)$ Å^3, $Z = 2$, $D_x = 1.59$ Mg/m^3, Mo Kα radiation (graphite-crystal monochromator, $\lambda = 0.710\,73$ Å), $\mu = 3.72$ mm^{-1}, $F(000) = 764$, $T = 293(1)$ K, final conventional R1 = 0.052 and wR2 = 0.131 for 5667 "observed" reflections and 371 parameters. The structure was solved by Patterson interpretation using DIRDIF[12] and anisotropiclly refined on F^2 using SHELXL93.[13] The plot in Figure 1 was made by the EUCLID package[14]

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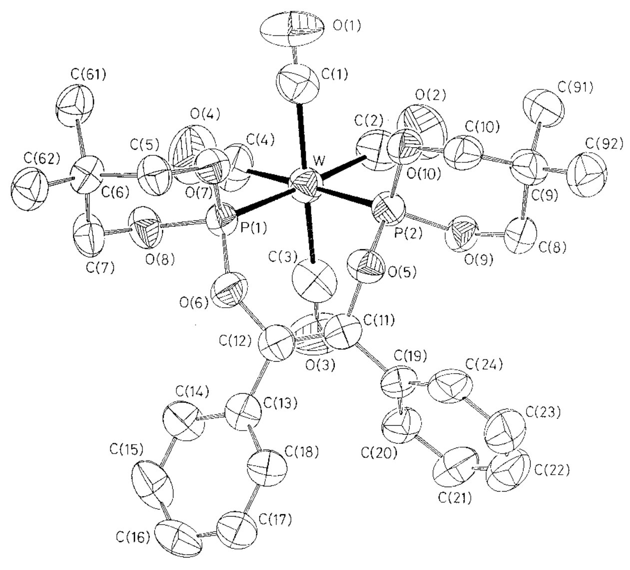


Figure 1. Molecular structure of **3a**.

Scheme 1

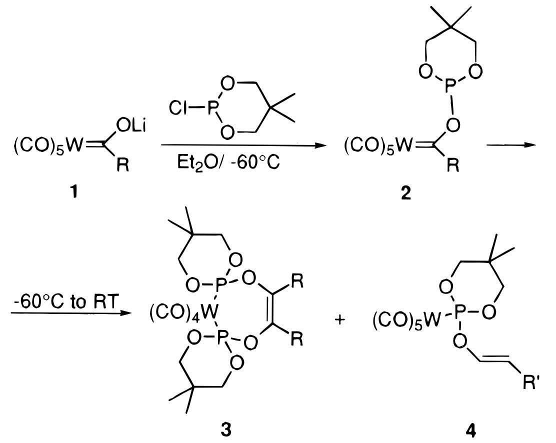
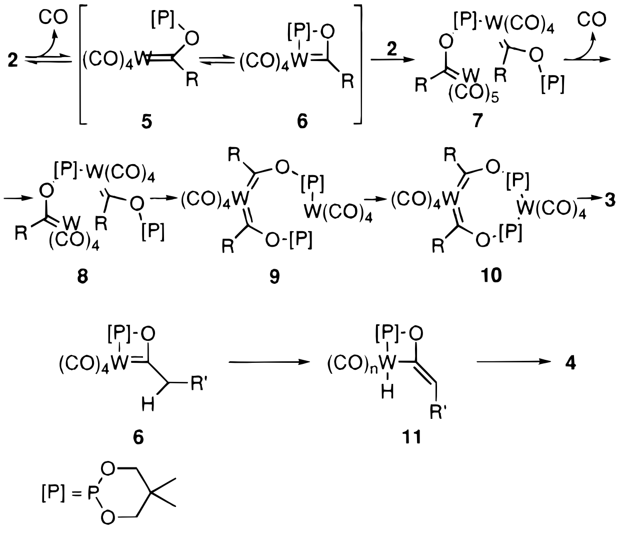


Table 1. Tungsten (*Z*)-1,2-Diphosphite–Alkene Tetracarbonyl and Tungsten (*E*)-Vinyl–Phosphite Pentacarbonyl Complexes 3 and 4 from Pentacarbonyl Acyl Tungstates 1 and 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane

starting acylate	R	R′	product		yield (%)[a]
1a	Ph		**3a**		57
1b	4-ClC$_6$H$_4$		**3b**		41
1c	4-CF$_3$C$_6$H$_4$		**3c**		62
1d	Et	Me	**3d**	**4d**	12/60[b]
1e	Bu	Pr	**3e**	**4e**	8/68[b]

[a] Isolated yield based on W(CO)$_6$. [b] First yield corresponds to product **3** and second to **4**.

Scheme 2



2d,**e**, which contain α-hydrogen atoms, formation of tungsten (*E*)-vinyl–phosphite pentacarbonyl complexes **4** along with a small amount of the carbene dimer complexes **3** was observed (Scheme 1 and Table 1). The *E* configuration of **4** was established by NOE experiments and the NMR coupling constants between the vinylic protons (12 Hz). The (*Z*)-isomers were not detected.

A reasonable mechanism that accounts for the formation of carbene dimer complexes **3** is outlined in Scheme 2 and involves first a CO dissociation[15] in complexes **2**, favored presumably by an interaction between the phosphorous atom and the tungsten of carbene complex, to give the tetracarbonyl complexes **5**, which are in equilibrium with the hexacoordinate complexes **6**. Further reaction of complexes **5** or **6** with **2** affords the intermediates **7**, *via* coordination to phosphorous. Subsequent loss of CO from **7** would produce **8**, which undergoes a carbene ligand transfer to form **9**. Further phosphite coordination would lead to biscarbene complexes **10**. Finally, decomposition of **10** leads to the carbene dimers **3**. According to this mechanism, the coordination of the unsaturated tungsten atom to the phosphorous in complexes **9** favors the *cis* arrangement in the carbene ligand transfer leading exclusively to the (*Z*)-diastereoisomers. The carbene transfer step could involve a dinuclear intermediate containing a μ-carbene ligand bridging both metal centers but not free carbenes since no formation of cyclopropanes was observed when the reaction was carried out in the presence of an excess amount of alkenes (cyclohexene, methyl acrylate, acrylonitrile, ethyl vinyl ether). On the other hand, the formation of vinylic phosphites **4** probably proceeds by a migration of the acidic proton α to the carbene carbon atom to the tungsten in metal carbene complexes **6** to give complexes **11**, followed by a reductive elimination furnishing the vinylic phosphites **4**. In contrast with the results reported in the literature[16] for the base-catalyzed decomposition of carbene complexes, in which mainly the (*Z*)-isomer was obtained, we have observed the stereoselective formation of the more stable (*E*)-isomer, likely due to the intramolecular coordination of the phosphorous atom to the tungsten in intermediates **6**.

In conclusion, we have described an efficient and diastereoselective conversion of phosphitecarbene com-

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(12) Beurskens, P. T.; Admiraall, G; Behm, H.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smykalla, C. DIRDIF User's guide. Technical Report. Crystallography Laboratory, University of Nijmegen: The Netherlands, 1992.

(13) Shedrick, G. M. SHELXL93. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, P., Simon, K., Eds.; IUCr/Oxford University Press: 1993, pp 111–122.

(14) Spek, A. L. The EUCLID package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528.

(15) Casey, C. P.; Cesa, N. C. *Organometallics* **1982**, *1*, 87.

(16) Casey, C. P.; Brunsvold, W. R. *J. Inorg. Chem.* **1977**, *16*, 391.

plexes to (*Z*)-1,2-diphosphite−alkene and (*E*)-vinyl−phosphite derivatives in very mild reaction conditions.

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Supporting Information Available: Text giving the synthetic procedures and spectral data for **3** and **4** and tables of the crystal data and structure refinement, atomic coordinates, bond lengths, bond angles, isotropic displacement parameters, hydrogen coordinates, and torsion angles of **3a** (18 pages). Ordering information is given on any current masthead page.

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