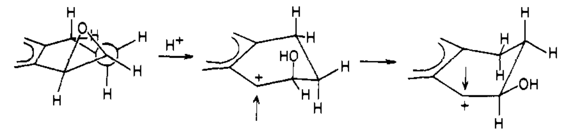
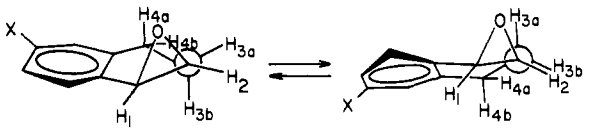
Scheme II



10 11 12

Inspection of molecular models leads to the prediction that **4a** and **4b** can exist in two possible conformations, a staggered conformation **8** and an eclipsed conformation **9**. The 250-MHz spectra of **4a** and **4b** were recorded, and the resonances due to the six hydrogens of the reduced ring (labeled H_1–H_{4b} in **8** and **9**) were separated and essentially first order in nature. From decoupling experiments, resonances were assigned and coupling constants determined.[7a] The small couplings $J_{2,3a}$ (2.8–3.0 Hz) and $J_{2,3b}$ (0.8–1.0 Hz) for both **4a** and **4b** are consistent with structure **8**, in which H_2 is staggered between H_{3a} and H_{3b}, but not with structure **9**. In **9**, a larger coupling would be expected due to the dihedral angle of ca. 0° for H_2–H_{3b}.[7b]



8 **9**

A rationale for the product distributions from acid-catalyzed hydrolyses of **4a** and **4b** is outlined in Scheme II.[8] Ionization of **4a** and **4b** from their ground-state conformations via A1 mechanisms lead to intermediate benzyl cations **11**.[9] Unsubstituted cyclohexenyl cations are known to undergo preferential pseudoaxial attack by solvent at a rate faster than conformational isomerization of the ion,[10] and therefore the unstabilized ion **11a** derived from **4a** might be expected to undergo a similar attack by solvent to yield the trans-diol **4a**. For more stabilized ions such as that derived from **4b**, however, conformational isomerization of the initially formed ion might be expected to compete with solvent attack of **11b**. Product would then be derived from the more stable ion **12b**, which should undergo stereoselective axial attack by solvent to give preferential cis hydration. Therefore, as the ability of the aryl group to stabilize positive charge at the benzyl position increases, cis hydration will be favored.

The predominant trans hydration throughout the trans-diol epoxide series (2a–2c) has been rationalized by assuming that ionization occurs from the favored ground-state conformation with the hydroxyl groups equatorial, leading directly to the more stable cation with the newly formed hydroxyl group in an axial position.[8] Axial collapse of solvent with this intermediate leads to trans hydration.

The mechanisms of the spontaneous reactions are discussed in detail in the following paper.[11]

Acknowledgment. This investigation was supported by Public Health Service Grants No. CA-17278 and CA-26086 with the National Cancer Institute. We thank Dr. David L. Harris, NMR Facilities Director of the University of North Carolina Chemistry Department, for providing 250-MHz ^1H NMR spectra of **4a** and **4b**.

Registry No. 3a, 36504-68-4; **3b**, 67694-88-6; **3c**, 56179-80-7; **3d**, 2461-34-9; **4b**, 82167-70-2; **5b**, 16821-34-4; **6b**, 65272-94-8; **7b**, 24722-22-2; 3,4-dihydro-6-methoxynaphthalene, 52178-91-3; 3,4-dihydro-6-methoxynaphthalene bromohydrin, 82167-71-3.

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[7] (a) The 250-MHz spectra of **4a** and **4b** in $CDCl_3$ solutions were recorded. Coupling constants (Hz) assigned for **4a** were as follows: $J_{1,2}$ = 4.4, $J_{2,3a}$ = 3.0, $J_{2,3b}$ = 0.8, $J_{2,4b}$ = 1.3, $J_{3a,3b}$ = 14.6, $J_{3a,4a}$ = 6.5, $J_{3a,4b}$ = 1.6, $J_{3b,4a}$ = 13.4, $J_{3b,4b}$ = 5.8, $J_{4a,4b}$ = 15.7. Coupling constants (Hz) assigned for **4b** were as follows: $J_{1,2}$ = 4.4, $J_{2,3a}$ = 2.8, $J_{2,3b}$ = 1.0, $J_{2,4b}$ = 1.5, $J_{3a,3b}$ = 14.3, $J_{3a,4a}$ = 6.6, $J_{3a,4b}$ = 1.5, $J_{3b,4a}$ = 13.1, $J_{3b,4b}$ = 5.5, $J_{4a,4b}$ = 15.5. Assignments were made with the aid of decoupling experiments. (b) Couplings between eclipsed hydrogens in compounds with conformations similar to **9** are ca. 5.0 Hz: Yagi, H.; Thakker, D. H.; Lehr, R. E.; Jerina, D. M. *J. Org. Chem.* **1979**, *44*, 3439.

[8] This mechanism has been proposed to explain product distributions from bay-region diol epoxides of polycyclic aromatic hydrocarbons: Sayer, J. M.; Yagi, H.; Silverton, J. V.; Friedman, S. L.; Whalen, D. L.; Jerina, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 1972.

[9] Evidence for an A1 mechanism in the acid-catalyzed hydrolysis of **4a** has been provided by the fact that in solutions containing chloride ion, the product distribution is different than when chloride ion is absent despite the fact that there is no kinetic dependence on chloride ion at sufficiently low pH. Therefore, an intermediate must be trapped by chloride ion subsequent to the rate-limiting step (ref 4).

[10] Goering, H. L.; Josephson, R. R. *J. Am. Chem. Soc.* **1962**, *84*, 2779.

[11] Gillilan, R. E.; Pohl, T. M.; Whalen, D. L. *J. Am. Chem. Soc.*, the following paper in this issue.

"α" and "β" Deuterium Isotope Effects in the Hydrolysis of Naphthalene Tetrahydro Epoxides: Rate-Limiting Hydrogen Migration in the Spontaneous Hydrolysis of 6-Methoxy-1,2,3,4-tetrahydronaphthalene Oxide

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The mechanism by which an epoxide undergoes hydrolysis is a function of the pH of the solution. In addition to hydronium ion and hydroxide ion catalyzed hydrolyses, many epoxides undergo spontaneous reactions with solvent within certain pH limits.[1] The products from the spontaneous reaction of simple epoxides are usually diols or carbonyl compounds, formed in ratios dependent on the structure of the epoxide.[2–6] Spontaneous reactions of arene oxides usually yield phenolic products.[7]

The mechanism proposed for the spontaneous reaction of benzene oxide is outlined in Scheme I and involves the intermediacy of a zwitterionic species **2**. Formation of the intermediate **2** was proposed to be the rate-limiting step due to the lack of a significant kinetic deuterium isotope effect on the migrating hydrogen.[7b] The isomerization of aryl and vinyl epoxides to ketones via spontaneous reaction with solvent is formally similar to the spontaneous isomerization of arene oxides to phenols and presumably also occurs with 1,2-hydrogen migration.[8] In this paper, we report that 6-methoxy-1,2,3,4-tetrahydronaphthalene oxide **5b** (Scheme II) undergoes a spontaneous reaction to yield mostly (ca. 76%) 6-methoxy-2-tetralone **8b**, *and that this reaction proceeds with rate-limiting hydrogen migration.*

The rates of reaction of **5a** and **5b** (at pH <10) were fit to $k_{obsd} = k_{H^+}a_{H^+} + k_0$. Values of k_{H^+} and k_0 are provided in the previous paper,[9] along with product distributions from both acid-catalyzed

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[1] (a) Bronsted, J. N.; Kilpatrick, M.; Kilpatrick, M. *J. Am. Chem. Soc.* **1929**, *51*, 428. (b) Long, F. A.; Pritchard, J. G. *Ibid.* **1956**, *78*, 2663.

[2] Becker, A. R.; Janusy, J. M.; Bruice, T. C. *J. Am. Chem. Soc.* **1979**, *101*, 5679.

[3] (a) Whalen, D. L. *J. Am. Chem. Soc.* **1973**, *95*, 3432. (b) Ross, A. M.; Pohl, T. M.; Piazza, K.; Thomas, M.; Fox, B.; Whalen, D. L. *Ibid.* **1982**, *104*, 1658.

[4] Whalen, D. L.; Ross, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 7859.

[5] Whalen, D. L.; Ross, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 3678.

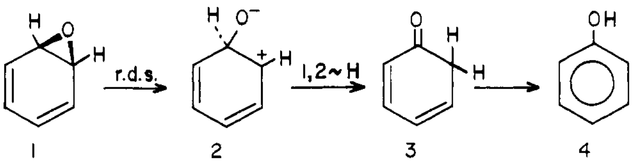
[6] (a) Whalen, D. L.; Montemarano, J. A.; Thakker, D. R.; Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 5522. (b) Whalen, D. L.; Ross, A. M.; Yagi, H.; Karle, J. M.; Jerina, D. M. *Ibid.* **1978**, *100*, 5218.

[7] (a) Kasperek, G. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 198. (b) Kasperek, G. J.; Bruice, T. C.; Yagi, H.; Jerina, D. M. *J. Chem. Soc., Chem. Commun.* **1972**, 784. (c) Bruice, T. C.; Bruice, P. Y. *Acc. Chem. Res.* **1976**, *9*, 378. (d) Bruice, P. Y.; Bruice, T. C.; Dansette, P. M.; Selander, H. G.; Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 2965.

[8] The isomerization of 1,3-cyclopentadiene oxide to 3-cyclopentenone occurs via hydride migration; ref 5.

0002-7863/82/1504-4482$01.25/0

Scheme I



Scheme II

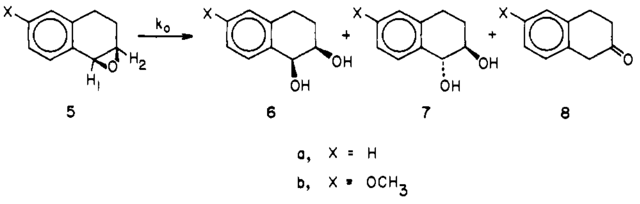
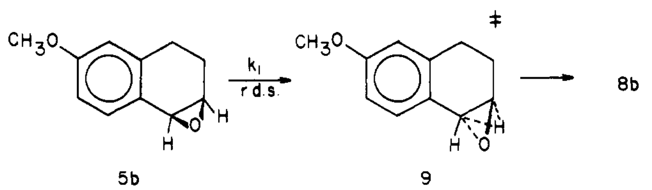


Table I. Kinetic Deuterium Isotope Effects on k_{H^+} and k_0 for the Hydrolysis of 5a and 5b at 25 °C, $\mu = 0.1$ (NaClO$_4$)[a]

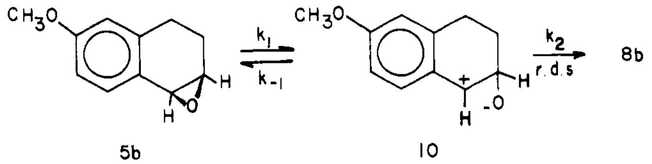
compd	rate constant	k_{H_1}/k_{D_1}	k_{H_2}/k_{D_2}
5a	k_{H^+}	1.08 ± 0.02[b]	0.93 ± 0.01[c]
	k_0	1.05 ± 0.01[d]	1.00 ± 0.03[e]
5b	k_{H^+}[f]	1.05 ± 0.01	0.94 ± 0.01
	k_0[f]	1.15 ± 0.02	1.59 ± 0.03

[a] Monitored spectrophotometrically at 232-235 nm on a Gilford 2400 spectrophotometer. The pH was maintained by 10^{-3} M buffer solution (HOAc, Tris, or cacodylic acid). Rate constants were determined by nonlinear regression analysis of the data on a Wang 700 B desk calculator, and internal errors for individual rate constants were generally 0.3-0.6%. All infinity absorbances were found to be stable. [b] Average of six determinations between pH 4.21 and 5.85. [c] Average of four determinations at pH 5.55. [d] Calculated from four determinations: pH 7.78, 8.24, 8.51 (twice). Corrections were made at each pH value for that fraction of the reaction occurring by the acid-catalyzed process. At pH 8.5, ca. 90% of the reaction takes place by the spontaneous mechanism. [e] Calculated from four determinations at pH 8.5. Corrections were made for that fraction of the reaction (ca. 10%) occurring by the acid-catalyzed process. [f] A total of 14 determinations of $(k_{obsd})_H/(k_{obsd})_D$ were determined between pH 6.2 ($t_{1/2}$ = ca. 6 s) and 8.8 ($t_{1/2}$ = ca. 80 s). Weighted least-squares plots of $[(k_{obsd})_H - (k_{obsd})_D]$ vs. a_{H^+} yielded slopes of $[(k_{H^+})_H - (k_{H^+})_D]$ and intercepts of $[(k_0)_H - (k_0)_D]$. The isotope effects listed were calculated from the slopes and intercepts.

Scheme III



Scheme IV



and spontaneous processes. In particular, the spontaneous reaction of **5a** yields exclusively the diol **7a**,[2] but its methoxy derivative **5b** yields 76% of the β-tetralone **8b**, 17% of cis-diol **6b**, and only 7% of trans-diol **7b**. We have labeled **5a** and **5b** at the 1- and 2-positions with deuterium and have determined the kinetic deuterium isotope effects on both k_{H^+} and k_0. These data are tabulated in Table I.

The "α" deuterium[10] isotope effects (k_{H_1}/k_{D_1}) on k_{H^+} for both **5a** and **5b** are normal (1.08 ± 0.02 and 1.05 ± 0.01, respectively) and are somewhat larger than that reported for the acid-catalyzed methanolysis of *p*-nitrostyrene oxide (1.02 ± 0.03).[11] An A2-like mechanism has been postulated for this latter case, whereas A1 mechanisms are postulated for acid-catalyzed hydrolysis of both **5a** and **5b**.[9] The "β" deuterium[10] isotope effects (k_{H_2}/k_{D_2}) on k_{H^+} for **5a** and **5b** were found to be significantly inverse (ca. 0.93). Similar "β" effects in the acid-catalyzed methanolysis of *p*-nitrostyrene oxide[11] were attributed to rehybridization of the β-CH bonds from their ground-state configurations to transition states that possess greater sp^3 character.[12]

From the data in Table I, it can be seen that the kinetic isotope effect k_{H_2}/k_{D_2} for the spontaneous reaction of tetrahydronaphthalene oxide **5a** (which yields exclusively the trans 1,2-diol) is very close to unity. On the other hand, k_{H_2}/k_{D_2} for the spontaneous reaction of **5b** (which yields ca. 76% of ketone **6b**) is equal to 1.59 ± 0.03. This value is too large to be a secondary effect and must therefore reflect a primary isotope effect associated with at least partially rate-limiting hydrogen migration from C$_2$ to C$_1$. If it is assumed that the kinetic isotope effect for diol formation is unity, as in the hydrolysis of **5a**, then the isotope effect on ketone formation for **5b** can be calculated from the product partitioning ratio and the observed kinetic isotope effect. The value of 2.0 calculated is close to the expected isotope effect of ca. 2-3 for 1,2-hydrogen migration.[13] The product distribution from **5b**-2-*d* (36% of **6b**, 12% of **7b**, and 51% of **8b**) is in agreement with these assignments.

Several mechanisms are consistent with the rate-limiting hydrogen migration for spontaneous reaction of **5b**, either a one-step reaction with concurrent C-O bond cleavage and hydrogen migration (Scheme III) or reversible C-O bond cleavage followed by rate-limiting hydrogen migration (Scheme IV). Although no clear-cut distinctions between the mechanisms outlined in Schemes III and IV can be made, the fact that the cis/trans hydration ratio is similar for both acid-catalyzed and spontaneous hydrolyses of **5b** suggests a common benzyl cation intermediate in the diol-forming reaction.[9] This intermediate could be formed either by a competing reaction involving general acid-catalyzed ring opening of ground-state epoxide **5b** by water (if Scheme III is correct) or by partitioning of the intermediate **10** between hydrogen migration to yield ketone **8b** and protonation by water to yield a benzyl cation (if Scheme IV is correct).

The mechanism for hydrolysis of **5b** by the spontaneous route is clearly different from that of **5a**, as reflected by both product ratios and isotope effects. The fact that the only product from **5a** is the trans diol suggests that addition of water is very nearly synchronous with C-O bond cleavage, and a relatively small "α" effect for this reaction is consistent with this interpretation.[14]

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(9) Gillilan, R. E.; Pohl, T. M.; Whalen, D. L. *J. Am. Chem. Soc.*, preceding paper in this issue.

(10) The "α" and "β" notations are put in quotation marks to distinguish them from their normal usuage in describing isotope effects, since the "β" isotope effects referred to in this paper are not true β-isotope effects in the usual definition of the term.

(11) Hanzlik, R. P.; Westkaemper, R. B. *J. Am. Chem. Soc.* **1980**, *102*, 2464.

(12) A reviewer suggested that the inverse isotope effects on k_{H^+} for the **5a** and **5b** provided support for Scheme III of the previous paper,[9] in which **5a** and **5b** react to yield intermediates **13a** and **13b** with "β" C-H bonds essentially orthogonal to the vacant p orbital. For example, in the solvolysis of a tertiary bicyclooctyl chloride, containing a β C-H(D) bond that is forced to be orthogonal to the developing p orbital at the reaction center and not undergoing change in hybridization, a β-isotope effect k_H/k_D of 0.985 was observed: Shiner, V. J., Jr.; Humphrey, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 2416. This inverse effect was attributed to the inductive effect of deuterium. Therefore, the inverse "β" effects for **5a** and **5b** (ca. 0.93) might be attributed to both rehybridization of the β carbon and the inductive effect of deuterium.

(13) (a) Collins, C. J.; Rainey, W. T.; Smith, W. B.; Kaye, I. A. *J. Am. Chem. Soc.* **1959**, *81*, 460. (b) Winstein, S.; Takahashi, J. *Tetrahedron* **1958**, *2*, 316.

(14) (a) Shiner, V. J. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Ed.; Van Nostrand-Reinhold Princeton, NJ, 1970; Chapter 2. (b) Vitullo, V. P.; Grabowski, J.; Sridharan, S. *J. Chem. Soc., Chem. Commun.* **1981**, 737.

Additional experiments are now in progress in an effort to distinguish between the possible spontaneous reaction mechanism for **5b**.

Acknowledgment. This investigation was supported by Public Health Service Grants No. CA-17278 and CA-26086 from the National Cancer Institute.

Registry No. 5a, 2461-34-9; **5b**, 82167-70-2; **8b**, 2472-22-2; deuterium, 16873-17-9.

Generation and Trapping of Terminal Phosphinidene Complexes. Synthesis and X-ray Crystal Structure of Stable Phosphirene Complexes

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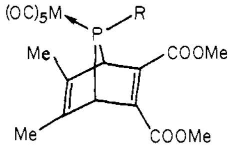
Received February 26, 1982

Phosphinidenes (RP) are known to act as μ^2-, μ^3-, and μ^4-bridging ligands in their transition-metal complexes.[1] No complex such as **1** including a terminal phosphinidene unit with a dicoordinated phosphorus atom and a formal phosphorus–metal double bond has ever been described in the literature up to now. We report here on the generation and trapping of such species.

$R{-}P{=}ML_n$

1

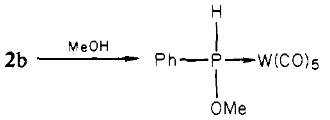


2a, M = Cr; R = Ph
b, M = W; R = Ph
c, M = W; R = Me

$R{-}P{=}M(CO)_5$

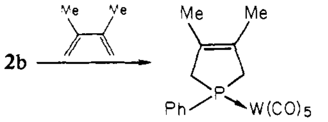
3a–c

In a previous communication,[2] we described the synthesis of stable 7-phosphanorbornadiene complexes **2**. We also found that **2b** was able to generate the terminal phosphinidene complex **3b** upon pyrolysis in a mass spectrometer. Besides, the X-ray crystal structure of **2a** showed long (1.877 (2) Å) and weak intracyclic P–C bonds. These data strongly suggested that complexes such as **2** were ideal candidates for the generation of terminal phosphinidene complexes under standard experimental conditions. Thus we decided to study the thermolysis of complexes **2a–c** in the presence of trapping reagents. The preliminary experiments were carried out with **2b**. When heated in toluene at 150 °C for 16–17 h with an excess of methanol, 2,3-dimethylbutadiene, or tolane, **2b** yielded respectively **4**,[3] **5**,[4] or **6b** in good yield (eq 1–3).



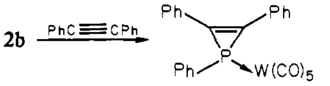
4, 87% yield

(1)



5, 63% yield

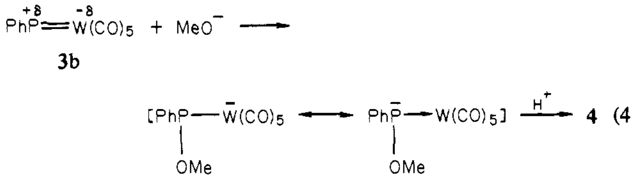
(2)



6b, 64% yield

(3)

The intermediacy of the terminal phosphinidene complex **3b** is thus firmly established. In the first case, the logical mechanism implies a nucleophilic attack of MeO⁻ on the positively charged phosphorus[5] (eq 4).



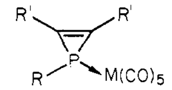
$$\underset{\mathbf{3b}}{\overset{+\delta}{\mathrm{PhP}}{=\!=}\overset{-\delta}{\mathrm{W}}(\mathrm{CO})_5} + \mathrm{MeO}^- \longrightarrow$$

$$[\underset{\mathrm{OMe}}{\mathrm{PhP}}-\overset{-}{\mathrm{W}}(\mathrm{CO})_5 \longleftrightarrow \mathrm{Ph}\underset{\mathrm{OMe}}{\overset{-}{\mathrm{P}}}-\mathrm{W}(\mathrm{CO})_5] \xrightarrow{\mathrm{H}^+} \mathbf{4} \quad (4)$$

The second reaction is just the reverse of the reaction generating **3b** itself and probably involves **3b** in its singlet state. The last reaction can be either a cheletropic reaction involving only phosphorus or a [2 + 2] cycloaddition giving transiently a four-membered carbon–phosphorus–tungsten ring.

Whatever the mechanism through which they are formed, the obtention of stable complexes such as **4** or **6b** is very exciting. Indeed, the corresponding free ligands are unknown. In the case of **4**, the free ligand probably loses spontaneously methanol to give the cyclopolyphosphine $(PhP)_n$. In the case of **6b**, the only literature report on a phosphirene oxide[6] was later shown to be wrong.[7] This type of ring is so extraordinary that we decided to perform a more systematic study of its synthesis. It appeared immediately that this synthesis was quite general (eq 5).

$$\mathbf{2}\ (\mathbf{a}, \mathbf{b} \text{ or } \mathbf{c}) \xrightarrow[\text{150 °C toluene}]{\Delta} \underset{\mathbf{3}\ (\mathbf{a}, \mathbf{b}, \text{ or } \mathbf{c})}{[\mathrm{RP}{=}\mathrm{M}(\mathrm{CO})_5]} \xrightarrow[\text{3- or 4-fold excess}]{\mathrm{R'C}\equiv\mathrm{CR'}}$$



(5)

6a, M = Cr; R = R′ = Ph; 15 h, 72%
b, M = W; R = R' = Ph; 17 h, 64%
c, M = W; R = Ph; R' = Et; 16 h, 50%
d, M = W; R = Me; R' = Ph; 17 h, 60%
e, M = W; R = Me; R' = Et; 5 h, 71%

---

[1] For the only well-characterized μ^2-phosphinidene complex, see: Huttner, G.; Muller, H. D.; Frank, A.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 705. For various recently described μ^3- and μ^4-phosphinidene complexes, see: Richter, F.; Beurich, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *166*, C5. Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Sartorelli, U. *Ibid.* **1981**, *204*, C10. Natarajan, K.; Zsolnai, L.; Huttner, G. *Ibid.* **1981**, *220*, 365. Natarajan, K.; Scheidsteger, O.; Huttner, G. *Ibid.* **1981**, *221*, 301. Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. Natarajan, K.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1981**, *209*, 85.

[2] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

[3] Complex **4** was purified by chromatography on a silica gel column under argon with hexane–toluene (90:10); mp 80 °C; ^{1}H NMR (C_6D_6) δ 2.76 (d, ^3J(H–P) = 12.5 Hz, 3 H, OMe), 7.15 (m, 5 H, Ph), 7.24 (d, ^1J(H–P) = 346 Hz, 1 H, P–H); ^{31}P NMR (toluene–methanol) δ +105.1 ppm; IR (Decalin) ν(CO) 2076 m, 1989 w, 1959 sh, 1950 vs cm^{-1}; IR (KBr) ν (PH) 2335, (POC) 1020 cm^{-1}; mass spectrum (70 eV, 100 °C, ^{184}W), *m/e* 464 (M, 30%), 436 (M–CO, 10%), 408 (M – 2CO, 14%), 380 (M – 3CO, 13%), 324 (M – 5CO, 100%) [*m/e* 28 (CO peak) excluded].

[4] Complex **5** was purified by chromatography on silica gel with hexane–toluene (90:10); mp 74 °C; ^{1}H NMR (C_6D_6) δ 1.25 (s, 6 H, Me), 2.67 (m, 4 H, CH_2P), 7.15 (m, 5 H, Ph); ^{31}P NMR (toluene) δ −3.2; IR (Decalin) ν(CO) 2070 m, 1976 w, 1945 sh, 1940 vs cm^{-1}; mass spectrum (70 eV, 100 °C, ^{184}W), *m/e* 514 (M, 40%), 486 (M – CO, 19%), 430 (M – 3CO, 75%), 402 (M – 4CO, 46%), 374 (M – 5CO, 100%) [CO peak excluded]; correct C, H, P elemental analysis.

[5] On the basis of the relative electronegativities of phosphorus and carbon and in view of the properties of methylenephosphines (see, for example: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731), it appears that the phosphinidene group is slightly more electropositive than the carbene group. Since in carbene–$W(CO)_5$ complexes the carbenic carbon bears a positive charge (see, for example: Casey, C. P.; Burkhardt, T. J.; Bunnel, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127), the same is very probably true for phosphorus in **3b** and in other similar complexes.

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