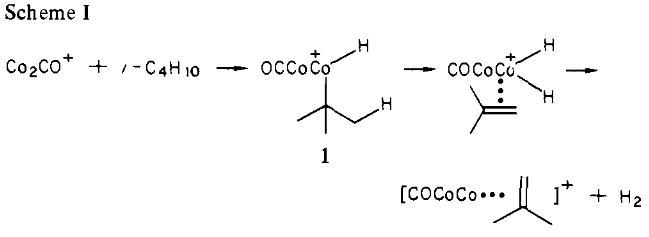
Scheme I



2-Methylpropane behaves in a similar way toward Co_2CO^+ and Co_2^+. Co_2CO^+ readily eliminates H_2 from 2-methylpropane (reaction 2), and Co_2^+ is unreactive. Reaction 2a accounts for

$$Co_2CO^+ + i\text{-}C_4H_{10} \rightarrow Co_2COC_4H_8^+ + H_2 \quad (2a)$$

$$Co_2CO^+ + i\text{-}C_4H_{10} \rightarrow Co_2C_4H_8^+ + H_2 + CO \quad (2b)$$

64% of the overall reaction. The overall rate constant is approximately the same as for reaction 1.

This behavior of Co_2^+ and Co_2CO^+ is markedly different from the behavior of Co^+ and $CoCO^+$. Co^+ reacts with n-butane to form $CoC_2H_4^+$, $CoC_3H_6^+$, and $CoC_4H_8^+$. With 2-methylpropane Co^+ reacts to form $CoC_3H_6^+$ and $CoC_4H_8^+$. $CoCO^+$ reacts with both C_4H_{10} isomers to form only $CoC_4H_{10}^+$.

Co_2^+ and Co_2CO^+ result from electron impact on $Co_2(CO)_8$,[9] and ion cyclotron resonance techniques identify their reactions.[10,11] Under the conditions of the ion cyclotron resonance experiment, only bimolecular gas-phase ion–molecule reactions can give rise to observable ionic products. Double resonance[11] and the pressure dependence of product peak intensities unambiguously identify the reactions. The products of reactions of 2-methylbutane-d_{10} and butane-d_{10} are consistent with the stoichiometries in reactions 1 and 2.

The reactivity of C–H bonds toward Co_2CO^+ is dramatically illustrated by its reaction with i-C_3H_7Br. The H_2 loss channel is 44% of the overall reaction.

$$Co_2CO^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_7Br^+ + CO \quad (3a)$$

$$Co_2CO^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_5Br^+ + H_2 + CO \quad (3b)$$

Furthermore, no HBr loss is observed. This is in contrast to Co_2^+, which breaks i-C_3H_7Br into HBr and C_3H_6 (reaction 4). Similarly, Co^+ reacts with i-C_3H_7Br to form only $CoC_3H_6^+$, and $CoCO^+$ reacts with i-C_3H_7Br to form $CoC_3H_6^+$, $CoCOC_3H_6^+$, and $CoC_3H_7Br^+$. The reactions of n-C_3H_7Br are similar to those of i-C_3H_7Br. The same products are formed in somewhat different proportions.

$$Co_2^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_6^+ + HBr \quad (4a)$$

$$Co_2^+ + i\text{-}C_3H_7Br \rightarrow Co_2HBr^+ + C_3H_6 \quad (4b)$$

A possible explanation for the effect of a CO ligand on Co_2^+ can be formulated in terms of the mechanism in Scheme I. Metal insertion into C–H and C–C bonds is quite well established as a critical feature of reactions of Fe^+, Co^+, and Ni^+ with alkanes.[1-8] If the formation of 1 is the critical step in the Co_2CO^+ reaction, then a minimal requirement is that the metal insertion is energetically feasible. While the thermochemical stability of 1 is not known, several pertinent bond strengths have been measured. These are $D°(Co^+–H) = 52 \pm 4$, $D°(Co–H) = 39 \pm 6$, $D°(Co^+–CH_3) = 61 \pm 4$, and $D°(Co–CH_3) = 41 \pm 10$ kcal/mol.[4] A striking feature of these bond strengths is that the bonds to Co^+ are much stronger than the corresponding bonds to Co. This indicates that 1 would be stabilized by concentrating positive charge on the Co that inserts into the C–H bond. The role of the CO ligand in 1 may be exactly that. Metals in zero or negative oxidation states tend to bind carbonyl ligands more strongly than metals in higher oxidation states. A structure such as 1 can strengthen the Co–CO bond as well as the Co–H and Co–R bonds by concentrating positive charge on the Co interacting with the alkane. The effect of a CO ligand on the reactivity of Co_2^+ may thus originate in the ability of the ligand to stabilize an asymmetric distribution of charge between the two Co atoms.

There is very little additional reliable thermochemical data to either support or disprove this hypothesis. Bond strengths between CoH^+ and alkyl radicals or between CoR^+ and H are not known. Essentially no bond strengths involving Co_2^+ are known. It is therefore difficult to address such questions as why C–H bonds add to Co_2CO^+ more readily than C–C bonds, while the opposite is true for Co^+. It is not inconsistent with our hypothesis that Co_2CO^+ reacts somewhat differently than Co^+. Even if one of the Co atoms in Co_2CO^+ carries most of the charge, its electronic environment will still not be identical with a free Co^+ ion.

If the hypothesis that CO activates Co_2^+ by polarizing the charge between the two Co atoms is correct, other ligands should have a similar effect. In particular, ligands that form stable complexes with metals in the zero oxidation state might be expected to have the same effect as CO. It is significant then that the product of (4a) reacts as in reaction 5. The two products

$$Co_2C_3H_6^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_7Br + C_3H_6 \quad (5a)$$

$$Co_2C_3H_6^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_6H_{11}Br^+ + H_2 \quad (5b)$$

of (5) are formed in equal amounts. The elimination of H_2 (channel 5b) indicates that $Co_2C_3H_6^+$ has a reactivity similar to Co_2CO^+. Since propene forms stable complexes with metals in the zero oxidation state, this reactivity of $Co_2C_3H_6^+$ lends support to the hypothetical explanation of the reactivity of Co_2CO^+.

Acknowledgment. The National Science Foundation provided partial support of this work (CHE 8110516).

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[9] Johnson, B. F. G.; Lewis, J.; Williams, J. G.; Wilson, J. M. *J. Chem. Soc. A* **1967**, 341–344. The electron energy was 70 eV, which probably produced Co_2CO^+ ions in a broad distribution of vibrational states. Most electronic excited states and metastable ions should disappear before reaction since the time between collisions is several milliseconds. The large rate constant implies that nearly all the Co_2CO^+ ions are reactive. If the reactions were characteristic of highly excited ions, only a fraction of the ions should react. In addition, Co_2CO^+ can have internal energy no greater than $D(Co_2^+–CO)$ so it is necessarily always less energetic than Co_2^+. For example, reaction of Co_2^+ with i-C_4H_{10} to give $Co_2C_4H_8^+$, which is not observed, must be more exothermic than (2b) regardless of the internal energy of the Co_2CO^+ reactant in (2b). The reactivity of Co_2CO^+ relative to that of Co_2^+ is thus not the result of internal energy effects.

(10) For reviews of ion cyclotron resonance techniques, see: Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527–560. Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley: New York, 1971.

(11) The particular double-resonance techniques used are described in: Wronka, J.; Ridge, D. P. *Int. J. Mass Spectrosc. Ion Phys.* **1982**, *43*, 23–30.

Stabilization of 2*H*-Phospholes by Complexation. A Phosphorus–Carbon Double Bond Acting as a Four-Electron Donor

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We have previously demonstrated[2-5] that the P substituents of tervalent 1*H*-phospholes easily migrate from phosphorus to carbon and yield 2*H*-phospholes. These 2*H*-phospholes are unstable species and spontaneously dimerize. They can be trapped by various reagents but have never been observed as such. Thus, in order to stabilize these species in their monomeric state, we decided to study the same type of migrations in 1*H*-phosphole P complexes. Our basic approach included a preliminary P complexation of phospholyl anion followed by protonation and H migration in the coordination sphere of the metal. In a first attempt, we reacted

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(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.

(2) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595.

(3) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 511.

(4) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1272.

(5) Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871.

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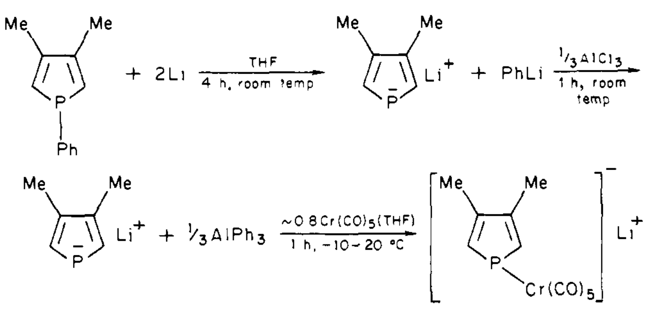
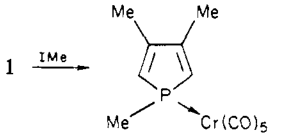
(3,4-dimethylphospholyl)lithium with $Cr(CO)_5(THF)$.

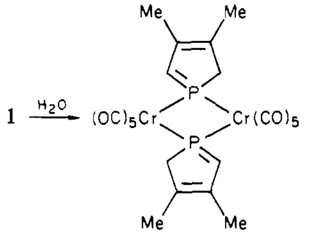


1

The reaction is best performed by pouring slowly the $Cr(CO)_5(THF)$ solution into a slight excess of phospholyllithium. The ^{31}P resonance of the complexed phospholyllithium **1** appears at −30 ppm in THF. Its reaction with methyl iodide yields (1,3,4-trimethylphosphole)pentacarbonylchromium **2** as the main product, thus establishing its formula unambiguously. The protonation of **1** by deoxygenated water probably occurs at phosphorus but a [1,5]H shift instantly takes place and the 2*H*-phosphole complex **3**[6] is obtained as the sole detectable product.



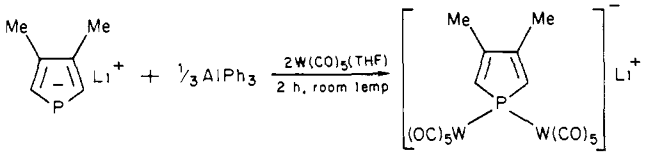
2 (^{31}P 34.4 ppm in $CDCl_3$)



3 (overall yield up to 55%)

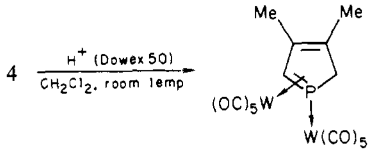
Unfortunately, we have been unable to obtain good crystals of **3** for X-ray analysis, probably because the two possible isomers syncrystallize. Nevertheless, extensive spectral and analytical data leave practically no doubt about the formula of **3**. Very recently, a two-coordinate aminoiminophosphane was shown to act as a 2-electron μ^2 bridging ligand through its phosphorus atom[7] but such behavior for a phosphaalkene is demonstrated here for the first time.

In another series of experiments, we reacted (3,4-dimethylphospholyl)lithium with $W(CO)_5(THF)$ and first obtained complex **4**.[8]



4

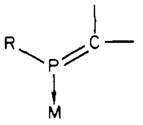
The anion **4** is much more stable toward water than anion **1** so that it can be purified by chromatography although with some loss. Its structure is related to that of $[Ph_2PW_2(CO)_{10}]^-$ which has been described in the literature very recently.[9] When crude complex **4** is protonated by a sulfonic resin, it gives complex **5**[10] in good yield.



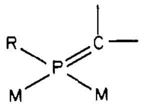
5 (overall yield ~60%)

The formula of **5** was unambiguously established by X-ray crystal structure analysis. Its metalation by butyllithium in hexane, NaH in THF, or *t*-BuOK in THF at room temperature gives back the anion **4**.

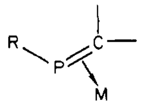
There are five possible coordination modes for a phosphaalkene A–E but almost all the complexes described so far in the literature belongs to type A.[11]



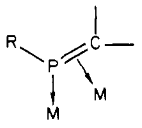
A



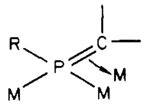
B



C



D



E

However, spectral evidences favoring an equilibrium A ⇄ C have been presented recently in one case,[12] and, even more recently, a C type complex has been characterized by X-ray crystal structure analysis.[13] On the contrary, the synthesis of bimetallic complexes such as B and D supposes that the steric hindrance of the phosphaalkene is sufficiently low and such is not the case with the currently available species. In that respect, the obtention of the first complexes belonging to types B and D with the 2*H*-phosphole ligand is quite logical.

In order to fully establish the formula of **5**, we decided to perform its X-ray crystal structure analysis, which gave the following crystal data: $C_{16}H_9O_{10}PW_2$, *Mr* 759.92; monoclinic;

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[6] Complex **3** is purified by chromatography on silica gel with toluene–hexane (1:9): yellow crystals, mp 187 °C dec. Correct C. H. P elemental analysis. ^1H NMR (C_6D_6) δ 1.25 (s, Me), 1.51 (d, $^4J(H\text{-}CH_3)$ = 0.7 Hz, Me), 2.20 (*A*BX, $^2J(A\text{–}B)$ = 17.6 Hz, CH_2P), 2.56 (A*B*X, CH_2P), 6.06 (pseudo t, =CHP); ^{31}P NMR ($CDCl_3$) δ 45.71 and 45.93; ^{13}C NMR ($CDCl_3$) δ 15.63 (pseudo t, Me), 17.20 (pseudo t, Me), 41.38 (pseudo t, CH_2), 128.55 (pseudo t, CH), 131.16 (s, Csp^2), 151.88 (pseudo t, Csp^2), 215.4 (pseudo t, CO); IR (decalin) ν (CO) 2070 w, 2058 w, 1955 vs, 1945 vs, 1940 s, 1930 s; mass spec (chemical ionization with CH_4), *m/e* 608 (M, 100%), 417 (66%), 305 (M/2 + H, 92%).

[7] Scherer, O. J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 297.

[8] According to the ^{31}P NMR spectrum of the reaction mixture, the synthesis of **4** appears to be almost quantitative. But chromatography on silica gel with ethyl acetate–acetone affords **4** as an orange oil in only 21% yield due to extensive decomposition on the column. Further purification is achieved by slow crystallization from a 1:1 mixture of CH_2Cl_2 and C_6H_6: ^1H NMR (CD_3OCD_3) δ 2.20 (s, 6 H, Me), 6.95 (d, $^2J(H\text{–}P)$ = 39.8 Hz, 2 H, CH–P); ^{31}P NMR (THF) δ −99.7 ($^1J(^{31}P\text{–}^{183}W)$ = 141.6 Hz); ^{13}C NMR (CD_3COCD_3) δ 15.62 (d, $^3J(C\text{-}P)$ = 8.5 Hz, Me), 137.8 (d, $^2J(C\text{–}P)$ = 3.6 Hz, c-Me), 147.21 (d, $^1J(C\text{–}P)$ = 15.8 Hz, CH–P), 200.07 (d, $^2J(C\text{–}P)$ = 4.9 Hz, eq CO); IR (CH_2Cl_2) ν CO 2065 w, 2045 w, 1966 m, 1932 vs, 1866 m.

[9] Keiter, R. L.; Madigan, M. J. *Organometallics* **1982**, *1*, 409.

[10] Complex **5** is purified by chromatography on silica gel with hexane–CH_2Cl_2 (90:10): orange crystals, mp 112 °C (CH_2Cl_2); ^1H NMR (C_6D_6) δ 1.40 (Me), 1.66 (Me), 2.62 (CH_2), 5.33 (d, $^2J(H\text{–}P)$ = 27.8 Hz, CH–P); ^{13}C NMR (C_6D_6) δ 15.05 (d, $^3J(C\text{–}P)$ = 3.7 Hz, Me), 15.90 (d, $^3J(C\text{–}P)$ = 6.1 Hz, Me), 52.16 (d, $^1J(C\text{–}P)$ = 4.9 Hz, CH_2P), 81.80 (d, $^1J(C\text{–}P)$ = 23.2 Hz, CHP), 134.38 (s, *C*-Me), 146.25 (s, *C*-Me), 196.59 (d, $^2J(C\text{–}P)$ = 4.9 Hz, CO); ^{31}P NMR (C_6D_6) δ −31.9; IR (decalin) ν (CO) 2088 w, 2067 m, 1992 s, 1983 s, 1975 vs, 1950 sh, 1947 s, 1943 s; ms (^{184}W, chemical ionization with CH_4), *m/e* 760 (M, 97%), 732 (M − CO, 46%), 705 (M − 2CO + H, 100%).

[11] Eshtiagh-Hosseini, H.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, 199. Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* **1982**, *1*, 89. Klebach, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; Van Herk, A. *J. Organometal. Chem.* **1981**, *210*, 211.

[12] Van der Knaap, Th. A.; Bickelhaupt, F.; Van der Poel, H.; Van Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1756.

[13] Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3737.

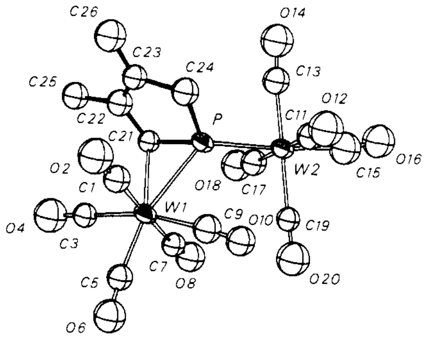

Figure 1. Structure of complex **5**. The heavy atom ellipsoids are scaled to enclose 50% of the electron density; hydrogen atoms are omitted. Principal bond distances (Å): W_1–C_{21}, 2.46 (1); W_1–P, 2.607 (4); P–C_{21}, 1.78 (1); P–C_{24}, 1.81 (2); C_{21}–C_{22}, 1.49 (2); C_{22}–C_{23}, 1.21 (2); C_{23}–C_{24}, 1.54 (2); P–W_2, 2.490 (4). Selected bond angles (deg): W_1–P–W_2, 125.3 (1); W_1–P–C_{21}, 65.2 (4); W_1–C_{21}–P, 73.8 (5); C_{21}–P–C_{24}, 93.2 (8); P–C_{21}–C_{22}, 105 (1); C_{21}–C_{22}–C_{23}, 121 (2); C_{22}–C_{23}–C_{24}, 113 (1); P–C_{24}–C_{23}, 106 (1); W_2–P–C_{21}, 128.3 (5); W_2–P–C_{24}, 108.6 (6).

$a = 15.063$ (6) Å, $b = 7.306$ (3) Å, $c = 19.903$ (8) Å, $\beta = 104.56$ (2)°, $U = 2120$ Å^3, $d_{obsd} = 2.33 \pm 0.03$ g cm^{-3}, $d_{calcd} = 2.381$ g cm^{-3}, $Z = 4$, space group $P2_1/C$ (N° 14); because of very low diffraction power and very bad crystals, CuK_α (1.5418 Å) radiation was used for cell dimension determination and intensity measurements; $\mu = 212.0$ cm^{-1} $F_{000} = 1392$.

Diffraction data were collected in the $\theta/2\theta$ flying step–scan mode using a Philips PW 1100/16 automatic diffractometer, graphite monochromated CuK^{-}_{α} radiation, and a crystal of dimensions 0.018 × 0.025 × 0.080 cm. Absorption corrections were applied using the numerical integration method (transmission coefficients 0.03–0.26). The structure was solved by the heavy-atom method using the Enraf-Nonius SDP/V + 1[14] package on a PDP 11/60 computer. Full matrix refinement using 2074 reflections having $I > 3\,\sigma\,(I)$ converged to conventional agreement factors R_1 and R_2 of 0.089 and 0.109 with anisotropic temperature factors for the two tungsten atoms and the phosphorus atom and isotropic ones for all other atoms. Hydrogen atoms were introduced by their computed coordinates but not refined.

The structure (Figure 1)[15] consists of discrete molecules linked only by Van der Waals contacts and hydrogen bonds. Selected geometrical details are given in the caption of Figure 1.

As already stated, the P–C_{21} double bond acts as a 4-electron donor towards two $W(CO)_5$ units in that complex.

Within experimental error, the P–C_{21} bond length (1.78 (1) Å) agrees with the only other value reported for an η^2-phosphaalkene (1.773 (8) Å in ref 13). The P–C_{24} single bond is logically longer (1.81 (2) Å) than the P–C_{21} double bond but the difference is perhaps not significant in view of the poor data.

The C═C double bond is well localized between C_{22} and C_{23} and, quite predictably, C_{21}–C_{22} is slightly shortened with respect to the normal C–C bond found between C_{23} and C_{24}.

Registry No, 1, 88296-54-2; **2**, 83576-94-7; **3**, 88296-55-3; **4**, 88296-56-4; **5**, 88296-57-5; $Cr(CO)_5(THF)$, 15038-41-2; $W(CO)_5(THF)$, 36477-75-5; (3,4-dimethylphospholyl)lithium, 67918-40-5.

Supplementary Material Available: Listings of the atomic coordinates and B_{eqv} (Table I) and the observed and calculated structure factors (× 10) for all observed reflections (Table II) (11 pages). Ordering information is given on any current masthead page.

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[14] Frenz, B. A. "The Enraf-Nonius CAD4-SDP. Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Ed.; Delft University Press: Delft, Holland, **1978**; p 64.

[15] Drawing performed by using program ORTEP: Johnson, C. K.; Report ORNL 3794; Oak Ridge, TN, 1965.

Additions and Corrections

Radiation-Induced Reduction of Thymidine in Aqueous Solution: Isolation and Characterization of a Novel Dimeric Product [*J. Am. Chem. Soc.* **1983**, *105*, 6740]. SEI-ICHI NISHIMOTO, HIROSHI IDE, KIKUMI NAKAMICHI, and TSUTOMU KAGIYA*

Page 6740, the caption to Figure 1 should read: ^{13}C NMR (25 MHz) spectra of 5,5′-bi-5,6-dihydrothymidine (**2**) with (a) complete decoupling and (b) off-resonance decoupling in D_2O at 20 °C. CD_3CN (δ_{CN} 119.5 ppm,*) was used as an internal standard and the signal of the CD_3 (δ 1.7 ppm) is omitted in a and b.