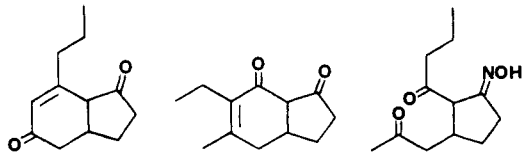
by trapping of the resulting enolate with butyryl cyanide[8,9] and then cyclization with glacial acetic acid gives **2**.

The scope of the method is evident from the entries in Table I. While the yields are not uniformly high,[10] this deficiency is more than offset by the facility with which a high degree of complexity can be straightforwardly assembled from quite simple starting materials. In particular, the method provides a means for assembling on a pyridine nucleus up to five different substituents in one operation with full regiochemical control. We note also that the regiospecific incorporation of the dimethylhydrazone unit as in **7** serves to avoid a number of competing[6b] side reactions (such as those leading to or passing through **8-10**)



8 **9** **10**

which could be anticipated to beset a synthesis of **2** proceeding via **4**. As is apparent from the first four entries in Table I, trapping of the initial Michael adduct with an acylating agent is optional, depending on the structure of the target molecule. A representative experimental procedure is provided.[11]

Acknowledgment. Support of this work by the National Institutes of Health (Grant GM30696) is gratefully acknowledged. We thank Dr. A. S. Magee and M. C. Connelly for ancillary studies, Professor R. E. Gawley[7] for sharing information, and Professor G. Stork for suggesting the use of acyl cyanides.[9]

Registry No. 2, 97235-08-0; **7**, 97235-13-7; $Me_2C{=}NNMe_2$, 13483-31-3; $MeC(O)CH{=}CH_2$, 78-94-4; $EtC(O)CH{=}CH_2$, 1629-58-9; $MeC(O)CH{=}CHPh$, 122-57-6; $MeC(O)C(CH_3){=}CH_2$, 814-78-8; $PrC(O)CN$, 38576-58-8; $MeC(O)CN$, 631-57-2; 2-methylcyclohexanone dimethylhydrazone, 5758-08-7; cyclopentanone dimethylhydrazone, 14090-60-9; acetophenone dimethylhydrazone, 13466-32-5; 2-cyclopentenone, 930-30-3; 6-methoxy-1,2,3,4-tetrahydronaphthan-1-one dimethylhydrazone, 16388-08-2; 2-cyclohexenone, 930-68-7; 5,5-dimethyl-2-cyclohexenone, 4694-17-1; 2,8-dimethyl-5,6,7,8-tetrahydroquinoline, 75031-41-3; 6,7-dihydro-2-ethyl-5*H*-1-pyrindine, 30564-54-6; 2,4-diphenyl-6-methylpyridine, 1912-16-9; 2,3-dimethyl-6-phenylpyridine, 27068-61-7; 1-propyl-3-methyl-8-oxoisoquinoline, 97235-09-1; 1,3-dimethyl-8-oxoisoquinoline, 97235-10-4; 1,3,6,6-tetramethyl-8-oxoisoquinoline, 55713-38-7; 4,6-dimethyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*c*]quinolin-3-one, 97235-11-5; 2-methoxy-6-methyl-10,11-dihydro-9*H*-benzo[*h*]cyclopenta[*c*]quinolin-7-one, 97235-12-6; 2-(2-oxobutyl)-6-methylcyclohexanone dimethylhydrazone, 58911-64-1; 2-(3-oxopentyl)cyclopentanone dimethylhydrazone, 97235-14-8; 2,6-dioxo-5,6-diphenylhexane dimethylhydrazone, 97235-15-9; 2,6-dioxo-3-methyl-6-phenylhexane dimethylhydrazone, 97235-16-0; 2-butanoyl-3-(2-oxopropyl)cyclohexanone dimethylhydrazone, 97235-17-1; 2-acetyl-3-(2-oxopropyl)cyclohexanone dimethylhydrazone, 97235-18-2; 2-acetyl-3-(2-oxopropyl)-5,5-dimethylcyclohexanone dimethylhydrazone, 97235-19-3; 2-methyl-6-(2-acetylcyclopentanon-3-yl)cyclohexanone, 97235-20-6; 2-(2-acetylcyclopentanon-3-yl)-6-methoxy-1-naphthalenone dimethylhydrazone, 97235-21-7.

(8) Normant, J. F.; Piechucki, C. *Bull. Soc. Chim. Fr.* **1972**, 2402-2403.

(9) Use of butyryl chloride gave O-acylation. For the use of acyl cyanides to circumvent this problem, see: Howard, A. S.; Meerholz, C. A.; Michael, J. P. *Tetrahedron Lett.* **1979**, 1339-1340 and references therein.

(10) In general the yield-limiting step is the ring closure (e.g., **7** → **2**). We believe this is partly due to the tautomeric composition of the diketone intermediate (e.g., **7**).

(11) Preparation of **2**:[12a] To a solution of 6.50 g (65.0 mmol) of acetone dimethylhydrazone in 130 mL of THF under Ar at −78 °C (Neslab cryocool) was added over ca. 40 min 68.2 mmol of *n*-butyllithium (~2.5 M in hexane). After stirring at −78 °C for another 30 min the milky white suspension was added dropwise over 20-30 min via cannula[12a] to a −78 °C solution of 11.2 g (65 mmol) of PhSCu[12b,13] in 180 mL of THF. The mixture was stirred at −78 to −65 °C until (ca. 3 h) a *clear* orange-red solution formed. To this was added over 30 min at −78 °C a solution of 4.2 mL (50 mmol) of cyclopent-2-enone in 15 mL of THF. The reaction was stirred at −70 °C for 12 h, gradually warmed to 0 °C over 8 h, and recooled to −78 °C. A precooled (−78 °C) solution of 6.3 mL (65 mmol) of butyryl cyanide[8] in 30 mL of THF was then added rapidly via cannula. After 0.5 h the cooling bath was removed and the reaction was allowed to warm to room temperature. Solvent and volatiles were removed under vacuum and the residue was suspended in 275 mL of glacial HOAc and heated at reflux for 4 h. The reaction was cooled to room temperature and solid material filtered off and washed with 10% HCl. The filtrate and wash were neutralized at 0 °C with 3 N NaOH, made basic with saturated aqueous $NaHCO_3$ and extracted 5× with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 10.4 g of a brown oil. Flash chromatography (45:55:3 EtOAc/petroleum ether/Et_3N) gave **2** in 31% overall yield based on cyclopentenone.

(12) (a) See ref 7b for experimental caveats. (b) In entries 2-4, 6-8, and 10 in Table I the homocuprate (from CuI and Me_2S) was used (see: Heathcock, C. H.; Kleinman, E. F.; Binkley, E. S. *J. Am. Chem. Soc.* **1982**, *104*, 1054-1068).

(13) Posner, G. H.; Brunelle, D. J.; Sinoway, L. *Synthesis* **1974**, 662-663.

(14) All new compounds gave satisfactory combustion analyses and spectra consistent with the structure assigned.

(15) For general method of preparation, see: Wiley, R. H.; Slaymayer, S. C.; Kraus H. *J. Org. Chem.* **1957**, *22*, 204-207. See also: Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337-1361. To simplify purification **14** was prepared in the absence of solvent; **17** was separated from unreacted tetralone by precipitation of its hydrochloride salt from ether.

(16) Cook, K. L.; Waring, A. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 529-537.

(17) Dauben, W. G.; Shaffer, G. W.; Vietmeyer, N. D. *J. Org. Chem.* **1968**, *33*, 4060-4069.

Synthesis of *sec*-Alkylacetylenes. Reduction of Cobalt Carbonyl Complexes of Acetylenic Alcohols

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Due to competition from elimination reactions, standard acetylene coupling methods are inefficient for the synthesis of secondary alkylacetylenes. Other methods for the preparation of such acetylenes suffer either from poor product yields or inconvenient large-scale preparations.[2] We present here a facile route to secondary alkylacetylenes on a preparative scale through the reduction of the corresponding cobalt complexed α-acetylenic alcohols with sodium borohydride and trifluoroacetic acid in dichloromethane.[3] This method, which takes advantage of the remarkable stability of propargyldicobalt hexacarbonyl cations,[4] is shown to be useful in the preparation of general building block acetylenes (e.g., diisopropylacetylene) as well as those of specific synthetic interest (e.g., 17-deoxy-17-ethynyl steroids).[7] Furthermore this procedure is readily adapted to allow incorporation of deuterium α to an acetylenic unit, the resulting products being

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(2) For excellent critiques of existing acetylene syntheses, see: Iverson, D. J. Ph.D. Dissertation, Princeton University, Princeton, NJ, 1981. Viehe, H. G. "Chemistry of Acetylenes"; Marcel Dekker: New York, 1969.

(3) Precedence for this method can be found in the report by Gribble et al. that benzyl alcohols that form stable carbenium ions[4] can be reduced with $NaBH_4$ in neat TFA.[5]

(4) Previously it has been shown that $Co_2(CO)_6{\cdot}R_2C(OH)C{\equiv}CC(OH)R_2$ complexes yield stable α-cations while retaining the integrity of the triple bond.[6]

(5) Gribble, G. W.; Leese, R. M.; Evans, B. E. *Synthesis* **1977**, 172.

(6) (a) Connor, R. E.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45. (b) Nicholas, K. M.; Pettit, R. *J. Organomet. Chem.* **1972**, *44*, C21. (c) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1977**, 3475.

(7) (a) Van Dijck, L. A.; Lankwerden, B. J.; Vermeer, J. G. C. M. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 200. (b) Krubiner, A. M.; Gottfried, N.; Oliveto, E. P. *J. Org. Chem.* **1969**, *34*, 3502.

0002-7863/85/1507-4999$01.50/0

Scheme I

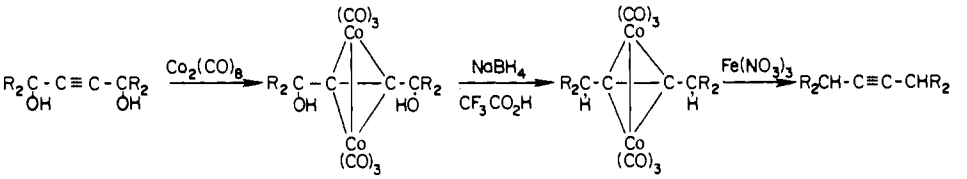


Table I

product[a] RC≡CR, R =	mp (bp), °C	^{1}H NMR ($CDCl_3$), δ	$^{13}C\{^1H\}$ NMR ($CDCl_3$), δ	M^+, m/z	yield[c]
i-Pr	(104–106)	(septet) 2.48, (d) 1.09	85.0, 23.5, 20.5	110	70%
i-Pr-d_7	(100–103)		(s), (septet), (t)	124	66%
sec-Bu	(50, 20 mm)	(m) 2.26, (m) 1.37, (m) 1.04	84.9, 30.4, 27.6, 21.2, 11.6	138	57%
Et_2CH	*b*	(m) 2.15, (m) 1.42, (t) 0.97	84.6, 35.3, 28.3, 11.8	166	46%
17-deoxymestranol (**3**)[e]	146–148[d]	see ref 17			85%

[a] Both dicyclopentyl and dicyclohexylacetylene were synthesized in about 40% yield but neither was pure enough to be fully characterized. [b] Purified by HPLC (one peak). [c] Isolated, not optimized. [d] Lit. mp 148–149 °C.[6a] [e] Demetalation effected with $Fe(NO_3)_3 \cdot 9H_2O$ in ethanol at 0 °C.[13]

useful in mechanistic and physical studies.[8,9]

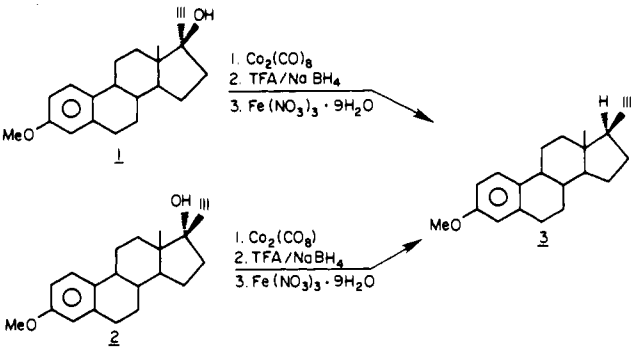
The method we have developed is outlined in Scheme I. α-Acetylenic alcohols[10] complex with dicobalt octacarbonyl smoothly and essentially quantitatively at room temperature in a variety of solvents.[11] We have found that addition of an excess of trifluoroacetic acid to a suspension of sodium borohydride in a dichloromethane solution of such a complex effects a reduction of the alcohol function without altering the triple bond.[4] Oxidation of the resulting complex with ferric nitrate frees the acetylene fragment which can then be purified by distillation.

A typical procedure for the preceding scheme is as follows.[12] A 1-L round-bottom flask is charged under argon with 17.0 g of 3,6-dimethyl-4-octyne-3,6-diol (0.1 mol) in 400 mL of dichloromethane. One equivalent (34.5 g/0.1 mol) of dicobalt octacarbonyl is then added and the solution is allowed to stir at room temperature for 5–6 h. During this time 2 equiv of carbon monoxide are given off. The flask is then chilled in an ice–salt–water bath and 11.1 g of sodium borohydride (0.3 mol) is added. To the resulting suspension, kept at 0 °C, is added 100 mL of trifluoroacetic acid over 10 min. The reaction is quenched by decanting the solution away from the residual sodium borohydride into about 300 mL of ice water slush. The organic layer is separated and washed again with water. The complex is then demetalated by the addition of 150 g of ferric nitrate nonahydrate to the dichloromethane solution over 2 h, followed by an additional 4 h of stirring.[13] The solution is decanted, dried, and distilled to give 7.8 g (57% yield) of 3,6-dimethyl-4-octyne ($bp_{20\,mm}$ 50 °C).

The yields (Table I) for this procedure are not optimized and range from moderate to good (45–70%). The reaction has been carried out on scales up to 0.5 mol.[14] Deuterium incorporation is effected by substituting $NaBD_4$/TFA-d_1 for $NaBH_4$/TFA in the above procedure. No loss in yield is seen by this substitution. In TFA-d_1 deuterium is also incorporated β to the acetylenic unit; $NaBD_4$/TFA may avert this.

The success of the reduction reaction can be traced to the facility with which the highly stable (propargyl)$Co_2(CO)_6$ cations are formed.[6] Support for the intermediacy of free or nearly free carbocationic species in these reactions was provided by reductions of the epimeric mestranols **1**[15] and **2**[16] (Scheme II). Thus subjection of *either* α-ethynyl derivative **1** or β-ethynyl species **2** to the complexation, reduction, and demetalation sequence produced stereoselectively the same β-ethynyl product **3** (>90% one epimer).[17] This result is consistent with the formation of a common metal-stabilized carbocation intermediate which is trapped by BH_4^- attack from the less hindered α-face. Indeed, the ready availability of 17α-ethynyl-17β-hydroxy steroids from the 17-keto derivatives[18] coupled with the above stereoselective conversion to the 17β-ethynyl-17-deoxy derivatives provides a novel and efficient route to these heretofore rather inaccessible compounds,[7b] prospective precursors to a variety of 17-β-side chain steroids.

Scheme II



The use of acetylene–metal complexes as reagents in organic synthesis is well documented.[19] Of particular interest to us is the use of dialkylacetylenes in the synthesis of compounds having adjacent secondary alkyl groups. Such compounds show a substantial conformational preference[8,20] (static gear effect) which has been exploited to alter the reactivity and physical properties of several molecular systems. Notable examples are the stability of tetraisopropylcyclopentadienone monomer[21] and the spectral properties of tetraisopropylcyclobutadiene radical cation[22] and hexaisopropylbenzene.[8,21]

(8) For an example of the use of this labeling in the conformational analysis of hexaisopropylbenzene, see: Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 7763.

(9) Chang, C.-A.; Cronin, K. G.; Crotts, D. D.; Duñach, E.; Gadek, T. R.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1545.

(10) (a) Zalkind, Yu, S.; Gverdtsiteli, I. M. *Dokl. Akad. Nauk.* **1939**, *9*, 855. (b) Nazarov, I. N.; Ivanova, L. N. *Dokl. Akad. Nauk.* **1956**, *26*, 78.

(11) Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 120.

(12) Commercial reagents were used as supplied. Solvents were not dried.

(13) For nonvolatile acetylenes demetalation in ethanol is probably preferable (see ref 6).

(14) Efficient cooling and stirring is very important in large-scale preparations.

(15) Obtained from Sigma Chemical Co.

(16) Westmijze, H.; Kleijn, H.; Vermeer, P.; van Dijck, L. A. *Tetrahedron Lett.* **1980**, *21*, 2665.

(17) These reductions were accompanied by formation of variable amounts of the enyne complex. Dehydration could be largely suppressed by rapid addition of CF_3CO_2H. **3** exhibited key ^{1}H NMR absorptions ($CDCl_3$) at δ 3.77 (s, OCH_3), 2.11 (s, C≡CH), and 0.85 (s, CH_3) (lit.[7a] δ 3.77, 2.10 and 0.83). The corresponding α-isomer exhibits resonances[7] at δ 3.77, 2.17, and 0.80. Less than 10% of the α-isomer was present in the demetalated crude product.

(18) Cotton, F. B. U.S. Patent 3 666 769, 1954.

(19) Nicholas, K. M.; Nestle, M. O.; Seyferth, D. "Transition Metal Organometallics in Organic Synthesis"; Halper, Ed.; Academic Press: New York, 1978; Vol. II, p 1.

(20) (a) Langler, R. F.; Tidwell, T. T. *Tetrahedron Lett.* **1975**, 777. (b) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 998.

(21) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729.

(22) Courtneidge, J. L.; Davies, A. G.; Lusztyk, E.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 155.

Acknowledgment. We thank Kurt Mislow for stimulating discussions and the National Science Foundation (CHE-8009670) and National Institutes of Health (GM 26760) for support of this work.

Registry No. 1, 72-33-3; **2**, 4502-08-3; *i*-PrC≡CPr-*i*, 927-99-1; *i*-Pr-(d_7)C≡CPr-*i*(d_7), 88158-48-9; *sec*-BuC≡CBu-*sec*, 69393-86-8; $Et_2CHC{\equiv}CCHEt_2$, 97253-87-7; $Me_2C(OH)C{\equiv}CC(OH)Me_2$, 142-30-3; $(CD_3)_2C(OH)C{\equiv}CC(OH)(CD_3)_2$, 62875-11-0; $Co_2(CO)_8$, 10210-68-1; EtC(OH)(Me)C≡CC(OH)(Me)Et, 78-66-0; $Et_2C(OH)C{\equiv}CC(OH)Et_2$, 2044-37-3; bis(17-deoxymestranol)-β-acetylene, 97253-88-8; dicyclopentylacetylene, 97253-89-9; dicyclohexylacetylene, 62371-39-5; 1,2-dicyclopentyl-1,2-dihydroxyacetylene, 5325-62-2; 1,2-dicyclohexyl-1,2-dihydroxyacetylene, 78-54-6; bis(17-deoxymestranol)-α-acetylene, 97334-56-0.

Carbonylation of a Strained Phosphorus–Carbon Bond. Conversion of Phosphirene into 2-Keto-1,2-dihydrophosphete Complexes: An Entry into the Chemistry of the Phosphorus Analogues of Unsaturated β-Lactams

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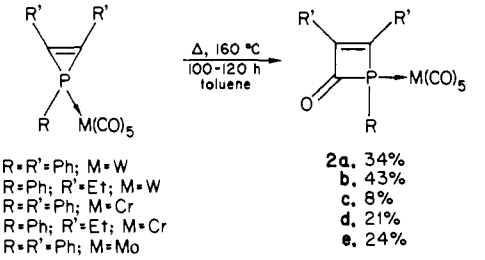
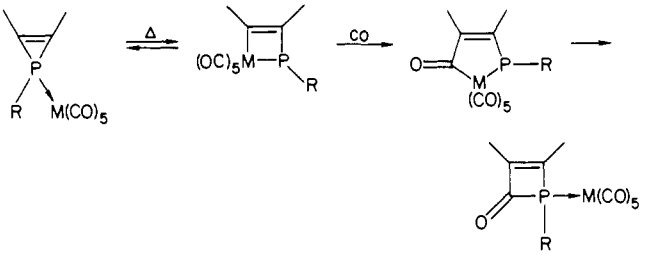
As far as we know, no clear-cut example of CO insertion in a carbon–phosphorus σ bond has ever been reported in the literature although the reverse reaction, i.e., the decarbonylation of acylphosphines by Wilkinson catalyst, has been described some time ago by Lindner.[2] While studying the chemistry of phosphirenes,[3-5] we have discovered such a carbonylation reaction through which the three-membered ring is converted into the still poorly characterized four-membered unsaturated 1,2-dihydrophosphete ring.[6] Of course, the exceptional strain of the phosphirene cycle probably weakens the intracyclic P–C σ bonds and facilitates the process. This ring enlargement has been observed during the thermolysis of phosphirene–chromium, –molybdenum, and –tungsten pentacarbonyl complexes:



1a, R=R'=Ph; M=W
b, R=Ph; R'=Et; M=W
c, R=R'=Ph; M=Cr
d, R=Ph; R'=Et; M=Cr
e, R=R'=Ph; M=Mo

2a, 34%
b, 43%
c, 8%
d, 21%
e, 24%

The reaction is performed in a sealed glass tube under autogenous pressure of carbon monoxide. The products **2a–e**[10] are sufficiently stable toward hydrolysis and can be purified by chromatography on silica gel columns. They are the complexed phosphorus analogues of the long sought and very labile azetinones.[11] We can only speculate about the precise mechanism of their formation. One possibility involves an equilibrium between phosphirene complexes and 1-phospha-2-metallacyclobutenes at high temperature:

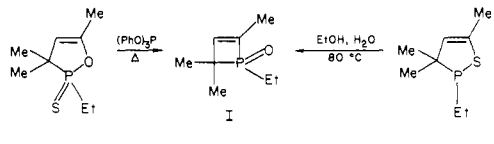


If this mechanism is the correct one, then it may be possible to insert various other small molecules (alkenes, alkynes, SO_2, etc...) into the complexed phosphirene ring.

From a spectroscopic point of view, the most noteworthy change occurring during the carbonylation of phosphirene complexes is a dramatic deshielding of the phosphorus atom close to +247 ppm in all cases. On the ^{13}C NMR spectra, the P–CO resonance of **2** appears close to +190 ppm, suggesting a mixed amide–ketone character for the ring carbonyl of these compounds.

Of course the greatest interest of this new carbonylation reaction lies in its potential application to the synthesis of the still unknown

(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.
(2) Lindner, E.; Thasitis, A. *Chem. Ber.* **1974**, *107*, 2418.
(3) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.
(4) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 45.
(5) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.*, in press.
(6) Recently, Russian workers[7] have reported the following reactions:



I

The four-membered ring was characterized by NMR spectroscopy but no X-ray crystal structure analysis was performed. These reactions appear somewhat surprising. On our side, we have tried to convert similarly a tervalent 1,2-oxaphospholane into a phosphetane oxide without any success even above 200 °C.[8] Moreover, the reported $^1J(Me_2C\text{–}P)$ coupling constant for I (18.3 Hz) is abnormally low for a one-bond P(O)–C coupling in a four-membered ring.[9]

(7) Nurtdinov, S. Kh.; Ismagilova, N. M.; Fakhrutdinova, R. A.; Zykova, J. V. *Zh. Obshch. Khim.* **1983**, *53*, 1045; *Chem. Abstr.* **1983**, *99*, 122548z.
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(10) **2a**: orange solid, mp 137 °C (chromatographed with hexane–toluene 80:20, R_f ~0.4); ^{31}P NMR (C_6D_6) δ +86.9, $^1J(^{31}P\text{–}^{183}W)$ = 231.9 Hz; ^{13}C NMR ($CDCl_3$) δ 151.7 (d, $^1J(C\text{–}P)$ = 51.3 Hz, *P*CPh), 169.5 (d, $^2J(C\text{–}P)$ = 36.6 Hz, *C*OCPh), 190.72 (d, $^1J(C\text{–}P)$ = 34.2 Hz, PCO), 195.08 (d, $^2J(C\text{–}P)$ = 7.3 Hz, WCO cis), 198.17 (d, $^2J(C\text{–}P)$ = 24.4 Hz, WCO trans); IR (decalin) ν(CO) 2074 w, 1955 shoulder, 1948 vs cm^{-1}; (KBr) ν(P–CO) 1710 cm^{-1}; mass spectrum (EI, ^{184}W), *m/e* 638 (M, 18%), 470 (M – 6CO, 100%), (CI, CH_4^+), *m/e* 639 (M + 1, 100%). **2b**: yellow oil (chromatographed with hexane–toluene 70:30, R_f ~0.5); ^{31}P NMR (toluene) δ +85.8, $^1J(^{31}P\text{–}^{183}W)$ = 227 Hz; ^1H NMR (C_6D_6) δ 0.76 (t, CH_3), 0.86 (t, CH_3), 1.83 (q, $^4J(H\text{–}P)$ ~ 0 Hz, CH_2CCO), 2.22 (dq, $^3J(H\text{–}P)$ ~ 10 Hz, CH_2CP), ^{13}C NMR (C_6D_6) δ 12.48 (s, CH_3), 12.72 (s, CH_3), 19.75 (d, $^2J(C\text{–}P)$ = 14.6 Hz, CH_2), 23.54 (d, $^3J(C\text{–}P)$ = 11 Hz, CH_2), 163.21 (d, $^1J(C\text{–}P)$ = 48.8 Hz, *P*CEt), 181.30 (d, $^2J(C\text{–}P)$ = 33 Hz, *C*OCEt), 191.42 (d, $^1J(C\text{–}P)$ = 30.5 Hz, PCO), 196.26 (d, $^2J(C\text{–}P)$ = 6.1 Hz, WCO cis), 199.53 (d, $^2J(C\text{–}P)$ = 23.2 Hz, WCO trans); IR (decalin) ν(CO) 2072 w, 1988 w, 1955 s, 1943 vs, 1910 w cm^{-1}, (KBr) ν(P–CO) 1723 cm^{-1}; mass spectrum (EI, 70 eV, ^{184}W) *m/e* 542 (M, 32%), 374 (M – 6CO, 89%), 372 (100%). **2c**: orange solid, mp 115 °C (chromatographed with hexane–ether 98:2, R_f ~0.5); ^{31}P NMR (C_6D_6) δ +133.3; IR (decalin) ν(CO) 2067 w, 1959 shoulder, 1953 vs cm^{-1}, (KBr) ν (P–CO) 1710 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 506 (M, 8.5%), 366 (M – 5CO, 100%), 338 (M – 6CO, 30%). **2d**: yellow oil (chromatographed with hexane–toluene 75:25, R_f ~0.4); ^{31}P NMR (CH_2Cl_2) δ +131.8; ^1H NMR (C_6D_6) δ 0.78 (t, CH_3), 0.85 (t, CH_3), 1.77 (q, $^4J(H\text{–}P)$ ~ 0 Hz, CH_2CCO), 2.28 (dq, $^3J(H\text{–}P)$ ~ 10 Hz, CH_2CP); IR (decalin) ν(CO) 2065 w, 1990 w, 1960 s, 1946 vs cm^{-1}; (KBr) ν(P–CO) 1730 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 410 (M, 18%), 270 (M – 5CO, 100%). **2e**: orange solid, mp 131 °C (chromatographed with hexane–toluene 80:20, R_f ~0.4), ^{31}P NMR (C_6D_6) δ +109.5; IR (decalin) ν(CO) 2072 w, 1960 shoulder, 1955 vs cm^{-1}; (KBr) ν(P–CO) 1725 cm^{-1}; mass spectrum (EI, 70 eV), *m/e* 552 (M, 2%), 412 (M – 5CO, 6%), 384 (M – 6CO, 19%), 178 (C_2Ph_2, 100%). The starting compound **1e** has not been described before. It is prepared according to the usual procedure[3] from the corresponding 7-phosphanorbornadiene P–$Mo(CO)_5$ complex described in ref 13 (compound 7). Compound 7 is heated with an excess of tolan at 120 °C for 5 h in xylene. Compound **1e** thus obtained is purified by chromatography with hexane–toluene (90:10): yield 29%; mp 105 °C; ^{31}P NMR (hexane) δ –137.8.
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