Platinacyclobutane Complexes from Nucleophilic Attack at a Coordinated Allyl Group and Catalytic Formation of Cyclopropanes in the Presence of Platinum Complexes

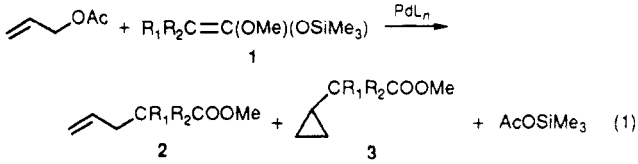
Carla Carfagna,[†] Roberta Galarini,[†] Alfredo Musco,*[,†] and Roberto Santi*[,‡]

Istituto di Scienze Chimiche, Università degli Studi di Urbino, 61029 Urbino, Italy, and Istituto G. Donegani, Via Fauser 4, 28100 Novara, Italy

Received August 6, 1991

Summary: Silylketene acetals react with allylplatinum complexes to yield platina(II)cyclobutanes **4** through nucleophilic attack at the central carbon atom of the allyl group. Cyclopropane **9** has been prepared catalytically from allyl acetate and $(CH_3)_2C{=}C(OMe)(OSiMe_3)$.

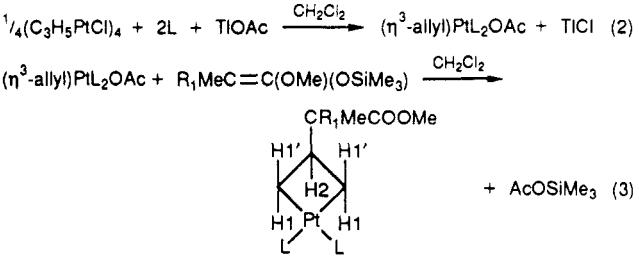
The reaction of carbon nucleophiles with (η^3-allyl)palladium complexes has been investigated by several authors in either stoichiometric or catalytic reactions.[1] We have recently found[2] that allyl acetate and silylketene acetals (**1**) react catalytically in the presence of Pd(0) phosphine complexes to yield mixtures of allyl alkylation products (**2**) and cyclopropane derivatives (**3**) (eq 1).



(1)

While the formation of **2** follows the usual regiochemistry of nucleophilic attack at the terminal carbon of the coordinated allyl group, the formation of **3** is unexpected, although not unprecedented, in stoichiometric reactions.[3] Despite our efforts, the regioselectivity of the above reaction did not exceed 50%. We now report that (η^3-allyl)platinum complexes react with **1** with remarkable regioselectivity in either stoichiometric or catalytic reactions.

Platina(II)cyclobutane complexes **4** may be isolated by following the procedure reported in eqs 2 and 3. The

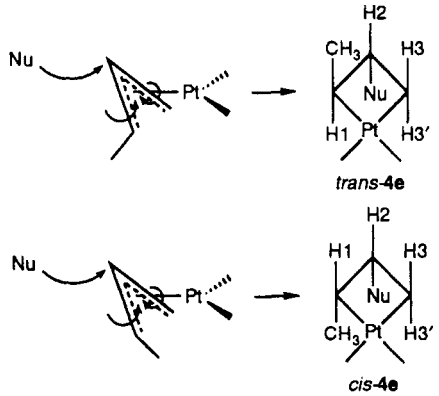


(2)

(3)

allylplatinum complex was suspended in CH_2Cl_2, and stoichiometric amounts of L were added. The resulting solution was reacted with TlOAc at room temperature for 1 h; **1** was then added and the mixture stirred for a further 4–5 h. Following filtration of TlCl, the reaction solvent was evaporated and the residue washed with methanol. Complexes **4** were isolated (40–80% yields) as white, thermally stable, crystalline materials and characterized by NMR spectroscopy and elemental analysis.[4] Allyl

Scheme I



[†] Università degli Studi di Urbino.

[‡] Istituto G. Donegani.

(1) Trost, B. M.; Verhover, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 799.

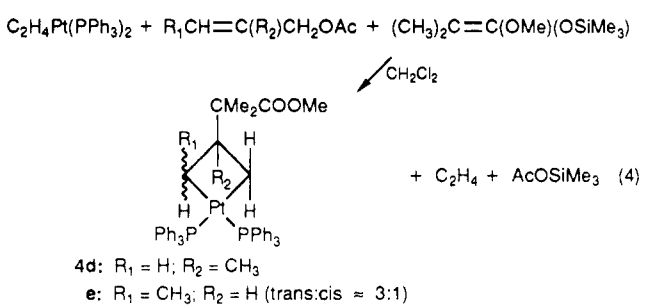
(2) (a) Carfagna, C.; Mariani, L.; Musco, M.; Sallese, G.; Santi, R. *J. Org. Chem.* **1991**, *56*, 3924. (b) Carfagna, C.; Galarini, R.; Musco, A.; Santi, R. Submitted for publication in *J. Mol. Catal.*

(3) (a) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; MacKenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (b) Hegedus, L. S.; Darlington, W. H.; Russel, C. E. *J. Org. Chem.* **1980**, *45*, 5193. (c) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. (d) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (e) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6420. (f) Benyunes, S. A.; Brandt, L.; Green, M.; Parkins, A. W. *Organometallics* **1991**, *10*, 57. (g) Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7057.

(4) Platina(II)cyclobutane complexes **4** have all peculiar upfield resonances in the ^1H and ^{13}C NMR spectra assignable to the methylene group bonded to platinum. Relevant NMR data in $CDCl_3$ and elemental analyses are reported. **4a**: ^1H NMR δ 0.10 (bq, 2 H, H1', J_{H-Pt} = 84 Hz), 0.44 (bq, 2 H, H1, J_{H-Pt} = 80 Hz), 0.89 (s, 6 H, $-CMe_2-$), 3.02 (m, 1 H, H2), 3.47 (s, 3 H, -OMe), 7.10–7.40 (m, 30 H, Ph_3P); ^{13}C NMR δ -7.3 (d, C1, J_{C-Pt} = 413, J_{C-P} = 80 Hz), 19.7 ($-CMe_2-$), 50.7 (-OMe), 50.7 ($-CMe_2-$), 50.8 (s, C2, J_{C-Pt} = 128 Hz), 127.4–134.9 (Ph_3P), 179.3 (C=O); ^{31}P NMR δ 25.9 (s, J_{P-Pt} = 1902 Hz). Anal. Calcd for $C_{44}H_{44}O_2P_2Pt$: C, 61.32; H, 5.11. Found: C, 61.70; H, 5.17. **4b**: ^1H NMR δ -0.01 (bq, 2 H, H1', J_{H-Pt} = 78 Hz), 0.66 (bq, 2 H, H1, J_{H-Pt} = 70 Hz), 1.00 (s, 6 H, $-CMe_2-$), 1.1–2.2 (m, 66 H, Cy_3P), 2.84 (m, 1 H, H2), 3.62 (s, 3 H, -OMe); ^{13}C NMR δ -10.2 (d, C1, J_{C-Pt} = 430, J_{C-P} = 82 Hz), 19.8 ($-CMe_2-$), 25.5–36.7 (Cy_3P), 50.7 (-OMe), 51.2 (s, C2, J_{C-Pt} = 128 Hz), 179.5 (C=O); ^{31}P NMR δ 23.0 (s, J_{P-Pt} = 1882 Hz). Anal. Calcd for $C_{44}H_{80}O_2P_2Pt$: C, 58.84; H, 8.92. Found: C, 58.94; H, 8.83. **4c**: -0.20 and -0.04 (bq, 2 H, H1', J_{H-Pt} = 81 Hz), 0.74 (bt, 2 H, H1, J_{H-Pt} = 78 Hz), 0.89 (d, 3 H, $-CHMe-$, J_{H-H} = 6.8 Hz), 1.70 and 2.60 (bm, 8 H, $Ph_2P(CH_2)_4PPh_2$), 2.06 (m, 1 H, $-CHMe-$), 3.04 (m, 1 H, H2), 3.52 (s, 3 H, -OMe), 7.30–7.70 (m, 20 H, Ph_2P-); ^{13}C NMR δ -8.7 and -7.1 (d, C1 and C3, J_{C-Pt} = 398, J_{C-P} = 83), 12.1 ($-CHMe-$), 23.1 and 27.7 ($Ph_2P(CH_2)_4PPh_2$), 47.4 (s, C2, J_{C-Pt} = 139 Hz), 50.7 (-OMe), 54.6 ($-CHMe-$), 127.7–133.4 (m, Ph_2P-), 177.7 (C=O); ^{31}P NMR δ 15.9 (J_{P-Pt} = 1861 Hz), 16.0 (J_{P-Pt} = 1842 Hz). Anal. Calcd for $C_{35}H_{40}O_2P_2Pt$: C, 56.07; H, 5.34. Found: C, 55.94; H, 5.29. **4d**: ^1H NMR δ 0.11 and 0.56 (bt, 4 H, $-CH_2-$, J_{H-Pt} = 83 Hz), 0.94 (s, 6 H, $-CMe_2-$), 1.01 (bs, 3 H, $-CMe(CMe_2COOMe)-$), 3.47 (s, 3 H, -OMe), 7.10–7.40 (m, 30 H, Ph_3P); ^{13}C NMR δ 1.5 (d, Pt–CH_2-, J_{C-Pt} = 415, J_{C-P} = 79 Hz), 19.6 ($-CMe_2-$), 29.5 ($-CMe(CMe_2COOMe)-$), 50.3 (s, C2, J_{C-Pt} = 116 Hz), 50.4 (-OMe), 52.3 ($-CMe_2-$), 127.3–129.2 (Ph_3P), 178.9 (C=O); ^{31}P NMR δ 26.5 (J_{P-Pt} = 1895 Hz). Anal. Calcd for $C_{45}H_{46}O_2P_2Pt$: C, 61.70; H, 5.25. Found: C, 61.42; H, 5.17. *trans*-**4e**: ^1H NMR 0.00 (m, 1 H, H3', J_{H-Pt} = 90 Hz), 0.34 (m, 1 H, H3, J_{H-Pt} = 80 Hz), 0.60 (m, 1 H, H1), 0.75 (q, 3 H, J_{H-H} = 7.0 Hz, $-CHMe-$), 0.95 and 1.02 (s, 6 H, $-CMe_2-$), 3.06 (m, 1 H, H2), 3.48 (s, 3 H, -OMe), 7.00–7.50 (m, 30 H, Ph_3P); ^{13}C NMR δ -10.3 (d, C3, J_{C-Pt} = 420, J_{C-P} = 76 Hz), -2.8 (d, C1, J_{C-Pt} = 459, J_{C-P} = 85 Hz), 20.5 and 21.1 ($-CMe_2-$), 24.1 ($-CHMe-$, J_{C-Pt} = 34 Hz), 49.0 ($-CMe_2-$), 50.9 (-OMe), 60.0 (s, C2, J_{C-Pt} = 128 Hz), 126.0–136.0 (Ph_3P), 179.8 (C=O); ^{31}P NMR δ 24.3 (J_{P-Pt} = 1610 Hz), 25.8 (J_{P-Pt} = 1985 Hz). *cis*-**4e**: ^1H NMR δ 0.8 (q, 3 H, $-CHMe-$), 0.98 and 1.03 (s, 6 H, $-CMe_2-$), 3.51 (s, 3 H, -OMe), 7.0–7.5 (m, 30 H, Ph_3P); ^{13}C NMR δ -6.8 (d, C3, J_{C-P} = 76 Hz), 9.9 (d, C1, J_{C-P} = 80 Hz), 16.7 ($-CHMe-$, J_{C-Pt} = 38 Hz), 21.5 and 23.3 ($-CMe_2-$), 50.7 (-OMe), 53.7 (s, C2, J_{C-Pt} = 130 Hz), 126–136 (Ph_3P), 179.8 (C=O); ^{31}P NMR δ 21.7 and 28.4; missing resonances were not detected. Anal. Calcd for $C_{45}H_{46}O_2P_2Pt$: C, 61.70; H, 5.25. Found: C, 61.56; H, 51.12.

0276-7333/91/2310-3956$02.50/0

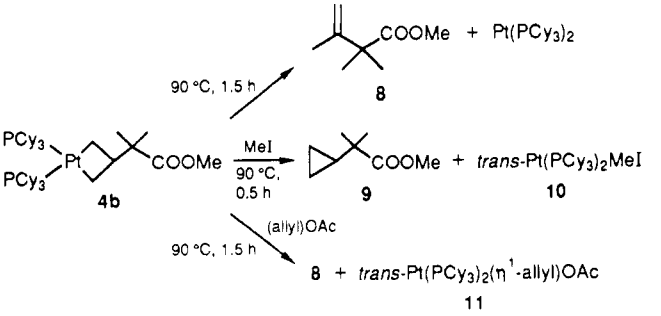
acetates and $C_2H_4Pt(PPh_3)_2$ are also convenient starting materials for preparation of **4d,e** (eq 4). Formation of



compounds **4d,e** indicates that alkyl substitution of the allylic group does not hamper nucleophilic attack of the silyl enolate on the central carbon. Conversely in the Pd case (eq 1) alkyl substitution of the allyl electrophile inhibits formation of cyclopropanes. Isolation of **4c** indicates that branching of the silyl enolate is not a prerequisite for the attack of the carbon nucleophile.[3b] Spectroscopic characterization of (η^3-allyl)PtL_2OAc (eq. 2), although limited to the PCy_3 derivative, clearly indicates that the allyl group is η^3-bonded to Pt. It is noteworthy that (η^3-allyl)$Pt(PCy_3)_2OAc$ (**5**) and [(η^3-allyl)$Pt(PCy_3)_2$]$^+BF_4^-$ (**6**) have different chemical shifts in $CDCl_3$ at room temperature.[5] Therefore, whether **5** is better represented as a contact ion pair or a covalent pentacoordinate complex remains to be elucidated. The role played by the acetate group is to activate the Si–O bond of the silyl enolate.[6] Silyl enolate **1** ($R_1 = R_2 = CH_3$) consistently does not react in methylene chloride with [(η^3-crotyl)$Pt(PPh_3)_2$]$^+BF_4^-$ (**7**; syn:anti = 3:1),[7] but in the presence of $[Bu^n_4N]^+F^-$ it does react to produce **4e** in low yields (20%). Reaction of **7** (0.024 mmol, 2 mL of CH_2Cl_2) with the lithium enolate of methyl 2-methylpropanoate (0.024 mmol, 2 mL of THF) at −50 °C for 19 h produced **4e** (28%), further indicating that complexes **4** are formed through attack of the nucleophile on the central carbon atom of a cationic η^3-allyl complex. In all the above reactions as well as for the acetate route of eq 4, **4e** was isolated as a 3:1 mixture of trans and cis isomers, i.e. in the same syn:anti isomeric ratio of **7**. Thus, assuming an external attack of the nucleophile[2] on C-2, *trans*-**4e** and *cis*-**4e** are respectively formed from the syn and anti η^3-crotyl complex through a disrotatory motion around the allylic C–C bonds (Scheme I).

At this point we may conclude that (i) the reaction of allylplatinum complexes with **1** proceeds regioselectively through nucleophilic attack of the enolate on the central carbon atom of the coordinated group, (ii) the same reaction is not regioselective for allylpalladium complexes, and (iii) reductive elimination of cyclopropane from palladacyclobutane is a fast process, as no Pd analogue of **4** was isolated. We thought that a platinum-based catalytic cycle could be envisaged if reductive elimination of cyclopropane from **4** is feasible at moderate temperature. Thus, oxidative addition of allyl acetate to the resulting Pt(0) complex and subsequent reaction with silylketene acetals sustain the catalytic cycle. Whitesides has previously found that bis(trialkylphosphine)-3,3-dimethylplatinacyclobutanes thermally decompose to cyclopropane and PtL_2.[8] Aware of this result, we decided to investigate the thermal behavior of **4b**.[9] A solution of **4b** (0.040–0.016 mmol) in dimethoxyethane (DME, 2 mL)–benzene-d_6 (0.2 mL) heated at 90 °C for 1 h yielded PtL_2 and olefin **8**[10] (Scheme II). Thus, β-hydrogen elimination followed by olefin reductive elimination is a lower energy path than C–C bond formation. Heating a mixture of **4b** (0.032 mmol) and methyl iodide (0.32 mmol) in DME (2 mL) and benzene-d_6 (0.2 mL) at 90 °C for 0.5 h quantitatively produced **9**[2b] and *trans*-$Pt(PCy_3)_2(CH_3)I$ (**10**).[11] This result is consistent with an oxidative addition of CH_3I to produce a platina(IV)cyclobutane intermediate, which as expected[12] reductively eliminates cyclopropane through C–C bond formation. Conversely, reaction of **4b** with allyl acetate under the same reaction conditions as above for methyl iodide produced **8** and *trans*-Pt(η^1-allyl)$(PCy_3)_2OAc$ (**11**).[13] Surprisingly, a mixture of **4b** (0.011 mmol), allyl acetate (0.22 mmol), and **1** ($R_1 = R_2 = Me$; 0.44 mmol) in DME (2 mL)–benzene-d_6 (0.2 mL) heated at 110 °C for 24 h yielded cyclopropane **9** in moderate yields (20%, based on allyl acetate), minute quantities of the allylated product **2**, and unchanged **4b**, suggesting that cyclopropane can be produced catalytically. Although the mechanism remains to be elucidated, it may be proposed that the silyl enolate assists the formation of a Pt(IV) species which, as in the methyl iodide case, reductively eliminates **9**, making a catalytic cycle possible. Finally, we found that preparation of **4b** directly in the reaction medium affords **9** in even better yields at shorter reaction times. A typical catalytic run is as follows: $((allyl)PtCl)_4$ (0.013 mmol) and

Scheme II[a]



[a] Solvent: DME.

(5) **5** was prepared in $CDCl_3$ (eq 2) and submitted to NMR investigation. Allyl resonances: ^1H NMR δ 4.7 (m, 1 H, central proton), 4.45 (dd, 2 H, H-*syn*, J_{H-H} = 7.3, J_{H-P} = 5 Hz), 3.14 (dd, 2 H, H-*anti*, J_{H-H} = 13.3, J_{H-P} = 8, J_{H-Pt} = 30 Hz), 2.07 (s, 3 H, OAc); ^{13}C NMR δ 105.6 (C2), 67.4 (d, C1–C3, J_{C-P} = 28, J_{C-Pt} = 48 Hz); ^{31}P NMR δ 38.6 (J_{P-Pt} = 4343 Hz). **6**: ^1H NMR ($CDCl_3$) δ 5.00 (m, 1 H, central proton), 4.42 (bd, 2 H, H-*syn*), 2.52 (dd, 2 H, H-*anti*, J_{H-H} = 12.4, J_{H-P} = 8, J_{H-Pt} = 40 Hz) (See also: Attig, T. G.; Clark, H. C. *J. Organomet. Chem.* **1975**, *94*, C49); ^{13}C NMR ($CDCl_3$) δ 114.3 (C2), 62.8 (d, C1–C3, J_{C-P} = 28, J_{C-Pt} = 70 Hz); ^{31}P NMR ($CDCl_3$) δ 28.2 (J_{P-Pt} = 3786 Hz).

(6) Carfagna, C.; Musco, A.; Sallese, G.; Santi, R.; Fiorani, T. *J. Org. Chem.* **1991**, *56*, 261.

(7) Brown, J. M.; Macintyre, J. E. *J. Chem. Soc., Perkin Trans. 2* **1985**, 961.

(8) DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601.

(9) The thermal behavior of **4b** has been followed by ^{31}P NMR spectroscopy in sealed tubes followed by GLC analysis of the formed volatile products.

(10) **8** was characterized by thermal decomposition of **4b** in benzene-d_6: ^1H NMR δ 4.88 and 4.81 (bb, 2 H, $=CH_2$), 3.29 (s, 3 H, OMe), 1.66 (m, 3 H, =CMe–), 1.29 (s, 6 H, $-CMe_2-$); MS *m/z* (relative intensity) 142 (M^+, 1), 127 (100), 83 (92), 67 (24), 55 (72), 41 (35).

(11) **10**: ^1H NMR ($CDCl_3$) δ 2.9–2.6 and 2.1–1.2 (bb, 66 H, PCy_3), 0.49 (t, 3 H, Me, J_{H-P} = 5.5, J_{H-Pt} = 80 Hz); ^{31}P NMR (DME/benzene-d_6) δ 17.1 (J_{P-Pt} = 2773 Hz). Anal. Calcd for $C_{37}H_{69}IP_2Pt$: C, 49.49; H, 7.69. Found: C, 49.48; H, 7.91.

(12) (a) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115. (b) Hoover, J. H.; Stryker, J. M. *Organometallics* **1989**, *8*, 2973.

(13) **11** was characterized by comparison with an authentic sample prepared by reaction of $Pt(PCy_3)_2$ and allyl acetate: ^1H NMR (toluene-d_8) δ 6.43 (m, 1 H, =CH–), 5.22 (bd, 1 H, $=CH_2$, J_{H-H} = 16.9 Hz), 4.97 (bd, 1 H, $=CH_2$, J_{H-H} = 9.9 Hz), 2.17 (2 H, $-CH_2-$), 2.11 (s, 3 H, OAc), 2.5–1.1 (bb, 66 H, PCy_3); ^{31}P NMR (toluene/benzene-d_6) δ 19.7 (J_{P-Pt} = 3037 Hz).

PCy_3 (0.10 mmol) were dissolved in toluene (13 mL). To the resulting solution was added TlOAc (0.12 mmol), followed by allyl acetate (1.02 mmol) and **1** ($R_1 = R_2 = CH_3$; 2.0 mmol). The reaction mixture was heated with stirring at 110 °C for 14 h to yield **9** in 86% yield.

Extension of the catalytic reaction to other allylic electrophiles is under way and will be reported later.

Acknowledgment. A.M. thanks the CNR and MURST for financial support.

Synthesis of a 2,3-Dihydro-1,2-diphosphete Ring by Electrocyclization of a 3,4-Diphosphahexatriene Unit

Ngoc Hoa Tran Huy, Louis Ricard, and François Mathey*

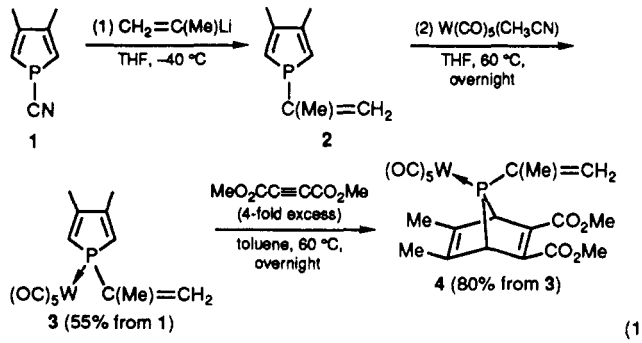
Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS UM 13, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received September 23, 1991

Summary: A 7-(2-propenyl)-7-phosphanorbornadiene P-$W(CO)_5$ complex has been synthesized and shown to be an efficient precursor of the transient (2-propenylphosphinidene)tungsten pentacarbonyl terminal complex. In the absence of trapping reagent, the propenylphosphinidene complex dimerizes to give a 3,4-diphosphahexatriene unit, which undergoes a spontaneous four-π-electron cyclization leading to a 2,3-dihydro-1,2-diphosphete ring. This heterocycle has been characterized by the X-ray crystal structure analysis of a [2 + 4] cycloadduct between its P=C double bond and 2,3-dimethylbutadiene.

Unsaturated four-membered rings are probably the least known carbon-phosphorus monocycles. 1,2-Dihydrophosphetes have been discovered only recently and have been the subject of several investigations.[1] 1,2-Dihydro-1,2-diphosphetes have been known since 1964[2] but only investigated in some depth during the last decade by our group.[3] Finally, the first example of the 2,3-dihydro-1,2-diphosphete ring has been briefly mentioned by Becker et al.,[4] but no characterization has been provided. In this work, we wish to describe the synthesis of this last ring via the unexpected four-π-electron cyclization of a 3,4-diphosphahexatriene unit.

Our work started as a classical investigation of the properties of the transient terminal vinylphosphinidene complexes.[5] Our hope was to observe a cyclization somewhat similar to the conversion of vinylcarbenes into cyclopropenes.[6] Accordingly, we first synthesized the appropriate 7-phosphanorbornadiene precursor **4**[7] from the readily available 1-cyano-3,4-dimethylphosphole[8] (eq 1).



(1)

Complex **4** proved to be a convenient precursor for the transient (2-propenylphosphinidene)tungsten pentacarbonyl complex **5** in the presence of catalytic amounts of copper(I) chloride at 60 °C. Contrary to our expectation, complex **5** shows no tendency to cyclize. Instead, in the absence of trapping reagent, it undergoes a classical dimerization to give the *trans*-diphosphene complex **6** as do the other terminal phosphinidene complexes.[9] Unex-

(1) Selected references: (a) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001. (b) Neilson, R. H.; Boyd, B. A.; Dubois, D. A.; Hani, R.; Scheide, G. M.; Shore, J. T.; Wettermark, U. G. *Phosphorus Sulfur* **1987**, *30*, 463. (c) Boyd, B. A.; Thoma, R. J.; Neilson, R. H. *Tetrahedron Lett.* **1987**, *28*, 6121. (d) Marinetti, A.; Mathey, F. *Organometallics* **1988**, *7*, 633. (e) Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791. (f) Dötz, K. H.; Tiriliomis, A.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 788. (g) Doxsee, K. M.; Shen, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 9129. (h) Tran Huy, N. H.; Mathey, F. *Tetrahedron Lett.* **1988**, *29*, 3077. (i) Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Myers, J. B., Jr.; Soni, H. K. *Organometallics* **1989**, *8*, 1007. (j) Tumas, W.; Suriano, J. A.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 75. (k) Marinetti, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1990**, 153. (l) Marinetti, A.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 788. (m) Doxsee, K. M.; Shen, G. S.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1649. (n) Dema, A. C.; Li, X.; Lukehart, C. M.; Owen, M. D. *Organometallics* **1991**, *10*, 1197.

(2) Mahler, W. *J. Am. Chem. Soc.* **1964**, *86*, 2306. See also: Ecker, A.; Schmidt, U. *Chem. Ber.* **1973**, *106*, 1453. Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, *21*, 1923. Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergsträsser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207.

(3) (a) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3. (b) Charrier, C.; Mathey, F.; Robert, F.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1707. (c) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623. (d) Ricard, L.; Maigrot, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 548. (e) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 950. (f) Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 1363. (g) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 534.

(4) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildenbrand, U.; Westerhausen, M. *Phosphorus Sulfur* **1987**, *30*, 349.

(5) Three recent reviews have been devoted to the chemistry of terminal phosphinidene complexes: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81. Mathey, F. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; pp 33-47.

(6) Leading references: Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1961**, *83*, 2015. Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796. Stechl, H. H. *Chem. Ber.* **1964**, *97*, 2681.

(7) Both **3** and **4** were purified by chromatography on silica gel (70-230 mesh) with hexane-dichloromethane (4/1 and 1/1) as the eluent. ^{31}P NMR: **3**, δ +13.8, $^1J(^{31}P-^{183}W)$ = 210 Hz (CH_2Cl_2); **4**, δ +213.5, $^1J(^{31}P-^{183}W)$ = 234 Hz ($CDCl_3$).

(8) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.

(9) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

0276-7333/91/2310-3958$02.50/0