

Figure 3. Optimized (STO-3G) geometries for midpoints of orbitally concerted pathways (C_1 is assumed to migrate from C_3 to C_4).

transition state and diradical intermediate **2** makes this potential minimum an interesting target for experimental detection.

Why does the reaction shun orbital concert? The optimized geometries¹⁰ shown in Figure 3 provide some insight. The most extraordinary geometry is that of **4**, in which the migrating bond bends *away* from the nearest, suprafacial face of the allylic group. Conservation of favorable in-phase overlap between the C_1 orbital and the C_3C_4 allylic system is sacrificed in favor of restored conjugation involving C_3 , C_2 , and C_4 , and no profit is to be gained from orbital concert. Another striking structure is **6**. C_1 moves up out of plane, while C_3 and C_4 pyramidalize so as to create large lobes downwards and away. Thus the unfavorable (Woodward–Hoffmann forbidden³) interaction between C_1 and the allylic nonbonding orbital is minimized, while adjacent interactions⁴ between C_1 and the allylic bonding orbital (largely on C_2) are maximized. The high energies of **6** and **7** (agreeing with the experimental exclusion of stereochemical retention^{12b}) may be attributed to their resemblance to the planar diradical **3**. Structures **3** and **1** have extremely high energies¹³—the former due to the large ionic character of its wave function,^{5c} the latter because both the double bond and the ring bond have been lost without compensation.

It must be commented that our assignment of a favored diradical pathway is not entirely in keeping with all the experimental evidence, namely, that at least 10% of the reaction passes through an achiral array. Whether this is due to differences between parent methylenecyclopropane—on which the calculations were performed—and the substituted forms which have undergone experimental scrutiny or to fundamental limitations in the theoretical model is not clear to us at this time.

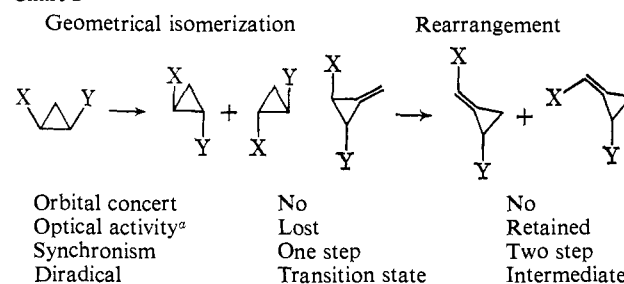
We wish to compare and contrast the geometrical isomerization of cyclopropane¹ and the degenerate methylenecyclopropane rearrangement. Both reactions follow orbitally nonconcerted pathways and yet maintain stereochemical integrity.¹⁴ Here for a *trans* 1,2-

(13) See also A. S. Kende and R. Greenhouse, quoted in ref 2a, p 507.

(14) (a) For the most recent experimental proof on cyclopropane see: W. v. E. Doering and K. Sachdev, *J. Amer. Chem. Soc.*, in press; (b) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968); (c) W. L. Carter

disubstituted reactant, optical activity is preserved,^{2a, 12} only two of the four possible products being obtained. Also, one reaction occurs in a single step, as a time-unified event, the other as a two-step process. Finally both reactions proceed *via* a diradical. In the first it is a *transition state*^{1, 14a} and lies right at the col of the potential surface. Here the diradical **2** is an *intermediate*, lying in a secondary minimum. These results are summarized below (Chart I). The comparison throws light

Chart I



^a Optical activity is retained if X rotates faster than Y.

on the notion of concert^{15, 16} and increases our knowledge of diradicals. It appears that quantum mechanics will yield a diradical transition state⁸ when there is no source of secondary stabilization and an intermediate in those cases where one of the odd electrons finds such a source.¹⁷ Whereas the thermochemical viewpoint consistently leads to diradicals as secondary intermediates,¹⁸ quantum mechanical calculations offer a varied picture of diradicals on potential energy surfaces.¹⁹

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and R. G. Bergman, *ibid.*, **90**, 7344 (1968); R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969); (d) N. E. Howe, E. W. Yankee, and D. I. Cram, *ibid.*, **95**, 4230 (1973). (e) The competitive optical isomerization is orbitally concerted; R. Hoffmann, *ibid.*, **90**, 1485 (1968).

(15) For a stimulating discussion see J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Fortsch.*, **15**, 281 (1970).

(16) J. P. Lowe, *J. Chem. Educ.*, submitted; A. H. Andrist, *J. Org. Chem.*, **38**, 1772 (1973).

(17) See second footnote, p 110 of ref 8, where the possibility was raised that delocalization could stabilize a diradical.

(18) (a) R. G. Bergman in "Free Radicals," Vol. 1, J. Kochi, Ed., Wiley, New York, N. Y., 1973, p 191; (b) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95**, 2849 (1973).

(19) Preliminary results from this laboratory suggest that in other thermal reactions of hydrocarbons, diradicals may be resting points on the side of a hill leading to the transition state.

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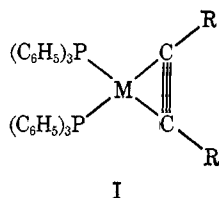
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Synthesis and Structure of π -Phosphinoacetylene Complexes of Zerovalent Palladium and Platinum

Sir:

Acetylene π -complexes of the type $[(C_6H_5)_3P]_2ML$ (I) where M = Ni, Pd, or Pt and L is an acetylene ligand, have played a leading role in the development of models



to describe metal-acetylene interactions.^{1,2} Complexes of type I are also important as possible intermediates in the catalytic oligomerization of acetylenes³ and in synthetic⁴ and mechanistic^{5,6} studies of addition and elimination reactions. The order of stability of acetylene complexes for the zerovalent metals is apparently $\text{Pt} > \text{Ni} > \text{Pd}$.⁶ However, the Ni complexes of type I are too unstable for analysis and only four Pd derivatives have been characterized.⁷ Therefore, chemical and structural studies of Pd(0)-acetylene complexes are virtually nonexistent. We now wish to report the synthesis and structure of the novel, air-stable, phosphinoacetylene π -complexes $[\text{M}(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2]$ (**1**) and $[\text{Ph}_3\text{PM}(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2]$ (**2**) where M is Pd or Pt and also a crystal structure study of **2** with M = Pd. These complexes are the first reported phosphinoacetylene π -complexes of Pd(0) and Pt(0). Previous synthetic attempts have produced only the phosphine coordinated complexes $\text{M}(\text{Ph}_2\text{PC}\equiv\text{CCH}_3)_4$, M = Pd or Pt,⁸ or $\text{Pt}(\text{Ph}_2\text{PC}\equiv\text{CPPH}_2)_2$.⁹

The complexes, **1**, are prepared easily in high yields by the reduction of the *cis*- $\text{MCl}_2(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2$ ¹⁰ derivatives with NaBH_4 in dry THF (M = Pd, 0°, 30 min and M = Pt, 25°, 48 hr). This novel synthetic route to Pd(0)-acetylene complexes¹¹ has not been previously successfully applied to these compounds. Infrared and Raman spectra of **1**, M = Pd, confirmed the absence of $\nu(\text{Pd}-\text{Cl})$ bands and were consistent with the presence of both coordinated ($\nu(\text{C}\equiv\text{C})$ ir, 1819 (s) cm^{-1} ; Raman, 1827 (s) cm^{-1}) and "free" ($\nu(\text{C}\equiv\text{C})$ ir, 2203 (m) cm^{-1} ; Raman, 2207 (vs) cm^{-1}) acetylenic bonds. The higher frequency bands are characteristic of the $\nu(\text{C}\equiv\text{C})$ (ir, 2200 cm^{-1}) in the uncomplexed phosphinoacetylene.¹² The $\Delta\nu$ of 381 cm^{-1} for the lower

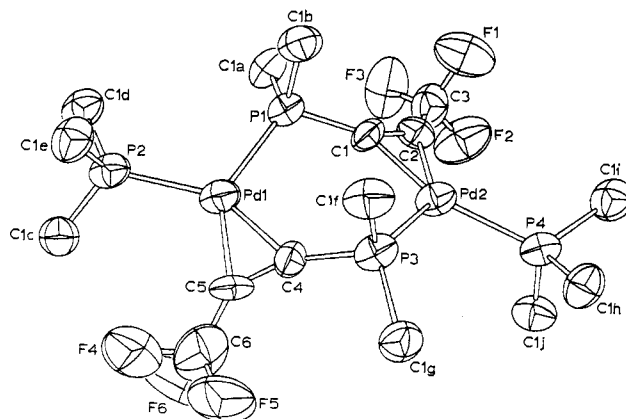


Figure 1. An ORTEP drawing of di- μ -diphenylphosphinoacetylenebis(triphenylphosphine)dipalladium(0) showing the thermal ellipsoids and atomic numbering. The atoms C1a to C1j are the first atoms of the ten phenyl rings which have been omitted from the diagram for clarity.

band (2200–1819 cm^{-1}) is similar to the shift of 475 cm^{-1} for $\nu(\text{C}\equiv\text{C})$ observed in the $(\text{Ph}_3\text{P})_2\text{Pd}(\text{C}_4\text{F}_6)$ complex.⁷ The ^{19}F nmr spectrum of **1**, M = Pd, consisted of a doublet at 45.2 ppm ($J_{\text{P-F}} = 5.7$ Hz) due to a CF_3 group bonded to a coordinated acetylene coupled to a trans phosphorus nucleus. A singlet at 45.1 ppm (with respect to CFCl_3) was assigned to the CF_3 group of the "free" acetylene. For **1**, M = Pt, the spectral features (ir, Raman, and ^{19}F nmr) are similar to and consistent with values found for the Pd derivative.

The complexes, **2**, were isolated from the reaction of $\text{M}(\text{PPh}_3)_4$ with $\text{Ph}_2\text{PC}\equiv\text{CCF}_3$ in a 1:1 mole ratio in dry benzene. Purification was by repeated fractional crystallizations from CH_2Cl_2 - $\text{C}_2\text{H}_5\text{OH}$ for M = Pd and by chromatography on silica gel for M = Pt. For **2**, M = Pd, the absence of $\nu(\text{C}\equiv\text{C})$ near 2200 cm^{-1} but the presence of a strong band at 1812 cm^{-1} (a shift of 388 cm^{-1}) indicated that the acetylene triple bond was coordinated. A larger shift of $\nu(\text{C}\equiv\text{C})$ of 466 cm^{-1} was found for the Pt derivative, in agreement with an expected increase in the metal-acetylene bond strength compared to the Pd complex. The ^{19}F nmr spectra of **2** in CDCl_3 (a multiplet at 45.4 ppm for M = Pd and a 1:4:1 triplet of multiplets at 49.9 ppm for M = Pt) are deceptively simple examples of $\text{X}_3\text{AA}'\text{X}_3'$ spin systems which are not susceptible to a first-order analysis. The data for **1** and **2** are consistent with a dimeric structure involving bridging phosphinoacetylene groups and a terminal phosphine ligand. A crystal structure study of **2**, M = Pd, was undertaken to obtain the first structural data on a Pd(0) complex involving a coordinated acetylene.

The pale yellow crystals of **2**, M = Pd, are monoclinic, space group $P2_1/c$, with unit cell dimensions of $a = 17.547$ (4), $b = 13.088$ (4), and $c = 28.152$ (7) Å, with $\beta = 102.14$ (2)°. There are four molecules of $\text{Pd}_2[(\text{C}_6\text{H}_5)_3\text{P}]_2[(\text{C}_6\text{H}_5)_2\text{PC}\equiv\text{CCF}_3]_2$ per unit cell; no molecular symmetry is required. The intensity data were measured on a Syntex $\text{P}\bar{1}$ diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation and a θ - 2θ scan technique. The structure was solved by the heavy-atom method and refined by least-squares techniques. The usual residual R is 0.091 for the 5465 reflections used in the analysis.

A view of the molecule is given in Figure 1 which also gives the atomic numbering. Each palladium atom of

(1) For recent reviews on this subject see (a) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. I, Academic Press, New York, N. Y., 1971, pp 123-130; (b) F. R. Hartley, "The Chemistry of Palladium and Platinum," Applied Science, London, 1973; (c) J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, **6**, 27 (1971).

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(3) For summaries see (a) C. Hoogzand and W. Hubel, "Organic Synthesis via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, p 343; (b) F. A. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968); and ref 1a, Vol. II.

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(5) K. S. Wheelock, J. H. Nelson, J. D. Kelly, H. B. Jonassen, and L. C. Cusachs, *J. Chem. Soc., Dalton Trans.*, 1457 (1973).

(6) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Inorg. Chem.*, **11**, 422 (1972), and references therein.

(7) (a) E. O. Greaves and P. M. Maitlis, *J. Organometal. Chem.*, **6**, 104 (1966); (b) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(8) K. S. Wheelock, J. H. Nelson, and H. B. Jonassen, *Inorg. Chim. Acta*, **4**, 399 (1970).

(9) R. B. King and P. N. Kapoor, *Inorg. Chem.*, **11**, 1524 (1972).

(10) R. T. Simpson and A. J. Carty, *J. Coord. Chem.*, **2**, 207 (1973).

(11) Satisfactory elemental analyses for C, H, F, and P have been obtained for all the complexes described. The molecular weights determined in CHCl_3 are consistent with the dimeric formulation.

(12) A. J. Carty, N. K. Hota, T. W. Ng, T. J. O'Connor, and H. A. Patel, *Can. J. Chem.*, **49**, 2706 (1971).

the dimeric molecule is coordinated to a triphenylphosphine ligand, a π -bonded alkyne group of one bridging phosphinoacetylene molecule, and the phosphorus atom of the second bridging group. The structure of **1** therefore is similar except that the triphenylphosphine group is replaced by another molecule of the phosphinoacetylene. The geometry about the palladium atom is approximately planar. The dihedral angle between the plane defined by P(1)–Pd(1)–P(2) and C(4)–Pd(1)–C(5) is 14.4° and between the planes P(3)–Pd(2)–P(4) and C(1)–Pd(2)–C(2) is only 5.7° . These values are similar to the values of 8.3° in $(C_7H_{10})Pt(PPh_3)_2$,¹³ 14° in $(PhC\equiv CPh)Pt(PPh_3)_2$,¹⁴ and 8° in $(NCC\equiv CN)Pt(PPh_3)_2$,¹⁵ the only zerovalent nickel triad acetylene complexes reported to date. The angles in Ni(0) and Pt(0) olefin complexes range from 1.3 to 12.3° ¹³ while the only reported angles for a Pd(0)–olefin complex range from 16 to 21° .¹⁶ In general, the trigonal derivatives of zerovalent Ni, Pd, and Pt have the coordinated acetylene or olefin in the molecular plane while, in the +2 state, the olefin is normal to the molecular plane. However, since all the +2 complexes are four-coordinate, this may be simply a steric effect.

The strength of the metal–acetylene interaction is reflected by the C(1)–C(2) and C(4)–C(5) distances of 1.291 (20) and 1.281 (20) Å, respectively, both of which represent a marked increase from the “free” C \equiv C distance of 1.20 Å.¹⁷ Similarly, the P–C–C skeleton shows deviations from linearity in the P(1)–C(1)–C(2) angle of $150(1)^\circ$, P(3)–C(4)–C(5) angle of $156(1)^\circ$, the C(1)–C(2)–C(3) angle of $138(1)^\circ$, and C(4)–C(5)–C(6) angle of $138(2)^\circ$. Although there are few Pd(0) complexes for comparison, the Pd–C distances which range from 1.989 (14) to 2.039 (14) Å are significantly shorter than in the Pd(0)–olefin complex^{16,18} which range from 2.19 to 2.28 Å. The Pd(1)–P(1) and Pd(2)–P(3) distances of 2.301 (4) and 2.296 (4) Å are shorter than Pd(1)–P(2) and Pd(2)–P(4) distances of 2.313 (5) and 2.321 (4) Å, respectively. The difference in the Pd–P bond lengths could reflect a steric effect related to the CF₃ groups or an electronic effect related to the difference between a triarylphosphine and a diphenylphosphinoacetylene. Unfortunately, in the absence of additional structural data, an explanation of this difference would be speculation.

In conclusion, we note that the present structural studies suggest that Pd(0)–acetylene interactions are similar to those in the Pt(0) complexes and hence the lack of Pd(0) complexes does not necessarily reflect a weak interaction. Also, the facile synthesis and air stability of complexes **1** make these attractive derivatives for studies of the reactivities of coordinated acetylenes.

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(15) L. J. Guggenberger, *Inorg. Chem.*, **12**, 499 (1973), has summarized the structural data available on Ni(0) and Pt(0) compounds.

(16) M. C. Mazza and C. G. Pierpont, *Inorg. Chem.*, **12**, 2955 (1973).

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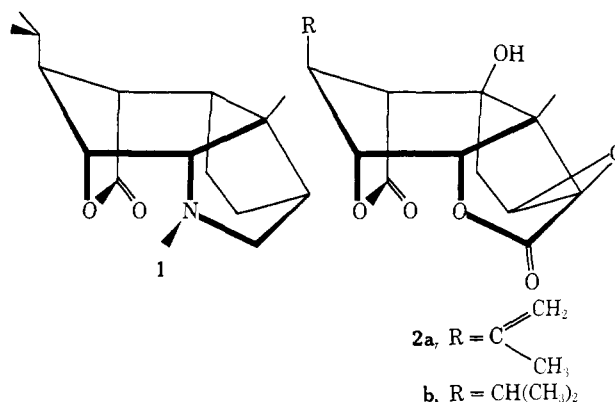
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A Simple Total Synthesis of (\pm)-Dendrobine

Sir:

Dendrobine (**1**), a physiologically active constituent of the Chinese tonic “Chin Shih Hu,” is representative of a group of nitrogenous sesquiterpene lactones related to the powerful convulsant picrotoxinin (**2a**).¹ We now report a stereospecific construction of the tricyclic framework of the Dendrobium alkaloids which leads to a simple total synthesis² of dendrobine and which has given a tricyclic lactone of interest as a possible precursor to dihydropicrotoxinin (**2b**) itself.



Saponification and ferric chloride oxidation of the known triacetate **3**³ gives 100% of the quinone **4**, which with butadiene in ethanol (110° , 24 hr) yields 95% of the Diels–Alder adduct **5** (mp 84.5 – 86° ; λ_{\max} 293, ϵ 6050).⁴ Its methyl ether **6**⁵ (λ_{\max} 278, ϵ 8400) was selectively hydroxylated at the isolated double bond (catalyst OsO₄, Ba(ClO₃)₂, aqueous dioxane)⁶ to give 43% of a crystalline diol, mp 164 – 166° , and 36% of an oily diol, both represented by structure **7**.

Cleavage of crystalline **7** with periodic acid in tetrahydrofuran,⁷ followed by aldol cyclization at 50° with pyrrolidine acetate in benzene, gave 65% of a 1:1 mix-

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(4) All new compounds gave satisfactory analytical, spectroscopic, and mass spectrometric data. Nmr, ir, and uv spectra refer to CDCl₃, CHCl₃, and CH₃OH solvents, respectively.

(5) Methylation was quantitatively achieved by methyl iodide and potassium carbonate in acetone at 25° .

(6) Cf. L. Pláha, J. Weichert, J. Zváček, S. Smolik, and B. Kakác, *Collect. Czech. Chem., Commun.*, **25**, 237 (1960); I. Ernest, *ibid.*, **29**, 266 (1964).

(7) Use of oily diol **7** gave the same aldehydes in slightly lower yields.