

represent the faster process leading to *m/e* 45 (C₂H₃DO). The slower process *via* an intermediate would lead to *m/e* 57 (C₄H₇D) presumably with the 2-butene structure. Calculations by Boer, Shannon, and McLafferty² indicate that the transition state in the stepwise mechanism is energetically preferable to that in a concerted mechanism. These mechanisms would demand that the transition state for the concerted mechanism be "looser" than that in the stepwise.^{2,3} This would probably mean that the transition state in the concerted mechanism does not need to be exactly planar. The weakly bonding and extended β bond in the concerted transition state might result in the internal rotations of the reactant being less constrained than they would be in the stepwise transition state. This could give the concerted transition state a higher entropy.^{2,4}

The kinetic results leave little doubt that there are two distinct processes in hexanal involving γ -hydrogen transfer and β cleavage. It does not seem useful to refer to two mechanistically distinct reactions by the same name. We would suggest that it is time to give a more precise and therefore more meaningful definition to the term "McLafferty rearrangement."

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(25) Address correspondence to this author at the Department of Chemistry, University College, University of London, London WC1H 0AJ, England.

P. J. Derrick,*²⁵ A. M. Falick, A. L. Burlingame
Space Sciences Laboratory, University of California
Berkeley, California 94720

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Platinum(0) Complexes of Heterocyclic Acetylenes. Synthesis of a Stable Metallacycle: Bis(triphenylphosphine)[di(2-pyridyl)acetylene]- platinumdichlorocobalt(II)¹

Sir:

Since the initial report of Pt(Ar₃P)₂(diphenylacetylene) complexes,² a wide variety of substituted acetylene transition metal complexes have been described.³ In view of the substantial attention devoted specifically to acetylene platinum complexes, we sought to extend this work by exploring the unique coordinating properties of several 2-pyridylacetylenes.

We wish to report the preparation of several new complexes of the type Pt(Ar₃P)₂(2-Pyr-C₂Ar) and an

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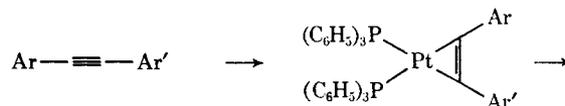
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especially novel heterodinuclear complex, Pt(Ar₃P)₂[(2-Pyr)₂C₂]CoCl₂ (**9**), which exploited the dual functionality of the 2-pyridylacetylene: (1) platinum-acetylene coordination, and (2) N complexation. Formation of this metallacycle (**9**) capitalized on the 2-pyridyl groups in the imposed Z orientation, which was caused by deviation (*ca.* 40°)⁴ from linearity of the acetylene bond in the initial Pt acetylene complex.

Treatment of di(2-pyridyl)acetylene (**3**)⁵ with tetrakis(triphenylphosphine)platinum(0)⁶ in anhydrous benzene at 26° (Scheme I) afforded the yellow crystalline

Scheme I



1, Ar = Ar' = C₆H₅

2, Ar = C₆H₅; Ar' = 2-Pyr

3, Ar = Ar' = 2-Pyr

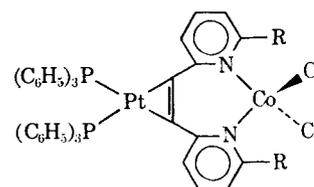
4, Ar = Ar' = 2-(6-CH₃-Pyr)

5, Ar = Ar' = C₆H₅

6, Ar = C₆H₅; Ar' = 2-Pyr

7, Ar = Ar' = 2-Pyr

8, Ar = Ar' = 2-(6-CH₃-Pyr)



9, R = H

10, R = CH₃

platinacyclopropene (**7**):^{7,8} mp 192–193° (ethanol, sealed tube), ν_{\max} (KBr) 1728 (>C=C<), 1583 (Pyr) cm⁻¹; nmr (CDCl₃) δ 8.5 (d, 6-Pyr-H, 2 H), and 7–8 (m, Arom and Pyr-H, 36 H). Reaction of **2**⁹ and **4**⁴ under identical conditions gave the crystalline complexes **6**⁷ (mp 170–175°; ν_{\max} (KBr) 1747 (>C=C<), 1580 (Pyr) cm⁻¹; nmr (CDCl₃) δ 8.45 (d, 6-Pyr-H, 1 H) and a complex aromatic region) and **8**⁷ (mp 189–195° (sealed tube); ν_{\max} (KBr) 1747 (>C=C<), 1580 (Pyr) cm⁻¹; nmr (CDCl₃) δ 2.16 (s, 6-Pyr-CH₃), respectively. From a survey of the infrared data (Table I) for com-

Table I. Selected Infrared Data for Substituted Platinacyclopropenes

Ligand	ν_{\max} , cm ⁻¹	Platina-cyclopropene	ν_{\max}
1	2222 ^a	5	1768, 1740 ^b
2	2227	6	1747
3	2220 ^a	7	1764
4	2215 ^a	8	1754

^a Raman data. ^b E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(4) Initial estimate was derived from the X-ray data of **5** as determined by J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, **7**, 9 (1967).

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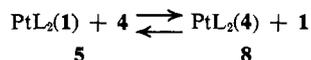
(7) Satisfactory elemental analyses are available for all new compounds being reported.

(8) "a"—Nomenclature, *i.e.*, platinacyclopropene, of these metallacycles is in accord with the IUPAC definitive rules, specifically Section C-0.6-Replacement Nomenclature. See "IUPAC Nomenclature of Organic Compounds," Butterworths, London, 1965, p 49; *Pure Appl. Chem.*, **11**, No. 1–2 (1965).

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plexes 5-8, the observed $\Delta\nu_{C\equiv C}$ (ca. 450 cm^{-1}) was demonstrated to be consistent with the assigned platinumacyclopentene structures, in that these large $\Delta\nu_{C\equiv C}$ values signify strong acetylene to metal bonding and increased deviation of the acetylene bond from linearity. X-Ray crystallographic studies are planned to elucidate the exact degree of deviation.

Both dissociative¹⁰ and associative¹¹ mechanisms have been proposed for the exchange reaction between two different acetylenes. The reaction of 5 with di[2-



(6-methylpyridyl)acetylene (4) was studied in benzene at 37° by measuring the population of the 6-methyl moiety of the complexed and free ligand (δ 2.16 and 2.56, respectively). At equilibrium, the ratio of complexed to free 4 was 4.5. The initial rate of disappearance of 4 and formation of 8 was found to correspond to a first-order rate constant of $15 \times 10^{-4} \text{ sec}^{-1}$. If Cook's interpretation is indeed correct, that is (1) the initial displacement reaction rate is dependent only on the nature of the coordinated acetylene and (2) that the equilibrium constant is essentially the quotient of the rate constants for the forward and reverse reactions, then the calculated first-order rate constant for the dissociation of 8 is 3.2×10^{-4} at 37°.

In a typical preparation of the metallabicyclic 9, a solution of anhydrous cobalt(II) chloride in absolute ethanol was added to a stirred benzene solution of 7 under nitrogen. After 2 hr, the mixture was filtered, solvent was removed *in vacuo*, and the residue was recrystallized from benzene-cyclohexane giving the crystalline green metallabicyclic 9:⁷ mp 270-280° dec (sealed tube); ν_{max} (KBr 1730 ($>C=C<$), 1597 (Pyr), 1120, 874, 770 cm^{-1} ; uv-visible (EtOH) 610 $\text{m}\mu$ (ϵ 246), 577 (182), 392 sh (3020). In the crystalline state, 9 was stable indefinitely; however, in solution, 9 slowly decomposed as shown by constant decrease of the extinction coefficient in the visible spectrum (610 $\text{m}\mu$). Similarly when complex 8 was treated with cobalt(II) chloride, the resultant green metallabicyclic 10 rapidly decomposed during attempted purification.¹² These results indicated that, in both 9 and especially 10, the cobalt was weakly bonded and underwent apparent dissociation in solution.

From the preliminary X-ray data,¹⁴ the Pt-Co bond distance (ca. 4.4 Å), along with the dimensions of the unit cell,¹⁵ indicated that the metallabicyclic 9 was flat, or nearly so. Planarity of the pyridyl rings with the platinumacyclopentene moiety was also reflected by the $\nu_{\text{max}(C-C)}$ stretching frequency (1730 cm^{-1}).

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(12) On warming an ethanolic solution of 10, a color change from green to pale yellow is observed which can be reversed upon cooling. Recently a similar thermochromic change was reported for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{P}]_2(\text{C}_2\text{H}_4)$.¹³

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(15) Preliminary crystal data:¹⁴ $\text{PtCoCl}_2\text{P}_2\text{N}_2\text{C}_{18}\text{H}_{38}$; monoclinic; space group $P2_1/c$; $a = 9.392$ (1), $b = 22.591$ (3), $c = 23.729$ (3) Å; $\beta = 101.41^\circ$; $V = 4935 \text{ \AA}^3$; $Z = 4$.

Preliminary studies¹⁶ using beef heart mitochondria to evaluate the effects of the metallacycles on the electron transport chain indicated that 9 showed strong inhibition of succinate-coenzyme Q reductase (complex II of the electron transport chain) at $10^{-6} M$. Compound 7 showed little, if any, inhibition in these systems at $10^{-6} M$.

New synthetic routes to, as well as biochemical and crystallographic studies of, metallabicycles and metallatricycles are in progress.

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George R. Newkome,* G. L. McClure

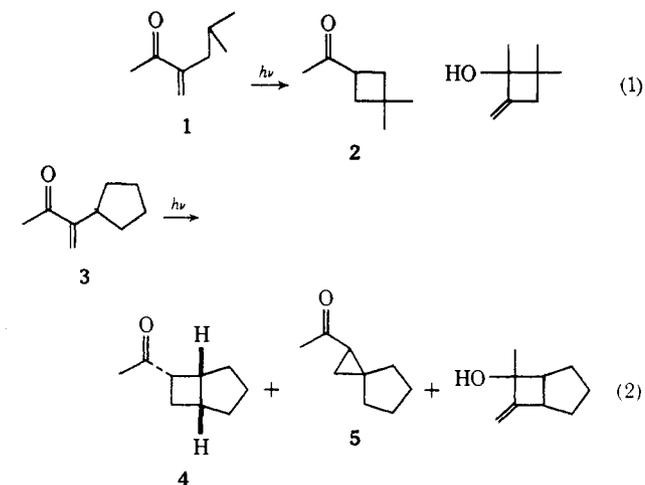
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

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Singlet Biradical Intermediates in the Photochemistry of α -Methylene Ketones

Sir:

We recently described¹ photochemical isomerization of a variety of α -methylene ketones to form primarily cyclobutyl ketones, accompanied in some cases by the related cyclopropyl compounds and methylenecyclobutanols. Typical examples are shown in eq 1 and 2.



We now present evidence that these ketones arise through carbonyl abstraction of γ (for cyclobutanes) or β (for cyclopropanes) hydrogen, closure to enol, and subsequent ketonization, as illustrated in eq 3 and 4. In addition we report quenching and sensitization experiments which suggest that these reactions occur from an excited singlet state.

Specifically labeled ketones 1-D, 2-D, and 3-D were

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