

Figure 2. Plot of bond distances and angles for 4.

atoms 1, 4, 5, 10, 9, 6 are as follows: 1, -0.04 Å; 2, -0.61 Å; 3, -0.06 Å; 4, 0.03 Å; 5, 0.00 Å; 6, -0.03 Å; 9, 0.03 Å; 10, 0.02 Å; 18, 2.80 Å. Atomic coordinates are given in Tables II and III. The observed and calculated structure factors appear in Table IV.¹⁰

The semiplanar conformation 9 of ring A defined¹¹ by these data places C-2 out of the double bond plane in the α direction and is in that sense related to the half-chair conformation 1. The most severe nonbonded interaction in the structure occurs between the 1α - and 11α -hydrogen substituents whose interatomic distance was found to be 2.18 Å, corresponding to a destabilization energy of 0.4 – 0.5 kcal/mol. Any variation of the semiplanar form toward the half-chair 1 would effect an increase in this interatomic distance and a decrease in repulsion energy.¹² This suggests that preference for a semiplanar form may be intrinsic to β,γ -cyclohexenones and we plan to pursue this question by the study of additional cases.

(10) Tables II–IV (listings of coordinates and structure factors) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(11) While the presence of the iodine atom gives rise to rather large positional standard deviations for the carbon atoms, these deviations could not appreciably alter the conformation of ring A. An analysis of the 17-alcohol 5, now in progress, should lead to more accurate data.

(12) The semiplanar enantiomeric with 9 would place the 1β - and 11α -hydrogen substituents 1.79 Å apart, corresponding to a repulsion interaction of approximately 2.0 kcal/mol.

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Photochemical Isomerization of a Dicyanoacetylene Complex of Platinum and the Structure of Cyano-(cyanoacetylide)bis(triphenylphosphine)platinum(II)^{1,2}

Sir:

We report the first example of the isomerization of an acetylenic complex to the corresponding acetylide

(1) Part X of the series Metal Complexes of Cyanocarbons; ref 2 is part IX.

(2) G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, **27**, 155 (1971).

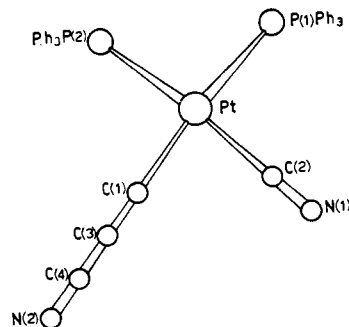
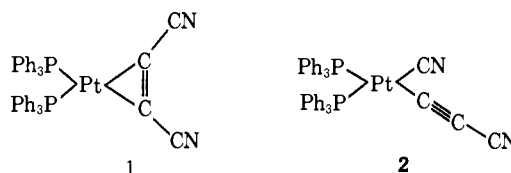


Figure 1. A drawing of the inner coordination sphere about platinum in $\text{Pt}(\text{CN})(-\text{C}\equiv\text{CCN})(\text{PPh}_3)_2$.

complex and describe the structure of the product which contains the novel cyanoacetylide group, $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-$, as a ligand. Thermal isomerizations of olefin complexes of platinum to σ -vinyl complexes have been previously reported,^{3,4} but the analogous reaction in the case of acetylenic complexes had not been directly observed, although it is of interest that a mechanism proposed for the linear and cyclic polymerization of acetylenes catalyzed by $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ includes such a step.⁵

Infrared spectra in the 1600 – 2300-cm^{-1} region of some dicyanoacetylene complexes of noble metals^{2,6} were remeasured recently (3–5 years after the preparation of the compounds) and were found in several instances to be different from the spectra that were originally recorded. For example, the mull spectrum



of orange crystals believed to have structure 1 included bands at 1683 (m) ($\nu_{\text{C}=\text{C}}$), 2177 (m), 2185 (s), and 2196 (m) ($\nu_{\text{C}=\text{N}}$) in the original spectrum, but an aged sample shows not only these bands but also additional bands at 2070 (w), 2140 (w), and 2235 (vs). Refluxing of an aged sample in various solvents causes no significant changes in the spectrum, but irradiation of an acetone solution of aged sample with a sun lamp for 3 hr, followed by removal of solvent, gives a residue of white crystals whose spectrum in the 1600 – 2300-cm^{-1} region contains only the bands at 2070 , 2140 , and 2235 cm^{-1} . We believe these changes are a result of a photochemical reaction wherein 1 undergoes isomerization to 2.

A crystallographic study of an aged sample shows that the title compound crystallizes in the orthorhombic system $Pbca$ with unit cell parameters $a = 21.43$, $b = 21.90$, $c = 14.50$ Å, $M = 795.7$, $U = 6805.1$ Å³, $Z = 8$, $D_c = 1.553$, and $D_m = 1.56\text{ g cm}^{-3}$ (by flotation in *sym*-dichloroethane and *sym*-tetrabromoethane).

(3) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *Chem. Commun.*, 502 (1966).

(4) W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1278 (1968).

(5) L. S. Meriwether, M. F. Leto, E. C. Colthop, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).

(6) G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, **25**, 261 (1970).

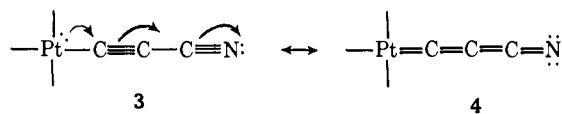
The intensity of 1742 independent nonzero reflections were taken with a Siemens four-circle diffractometer ($\theta \leq 45^\circ$, Cu K α radiation). Absorption corrections were computed with a program based on Busing and Levy's method.⁷ The crystal structure was solved by three-dimensional Patterson-Fourier methods. The trial structure, with anisotropic vibrations and anomalous dispersion (real and imaginary) for platinum and phosphorus atoms, was refined by full-matrix least squares. All hydrogen atoms were assumed to be isotropic, and their parameters were excluded from refinement. During the refinement some anomalies were observed in the thermal parameters and in relatively low electron density distributions at C(4) and N(2) atoms. At the present stage of refinement the *R* index is 0.073. The geometry of the metal coordination is shown in Figure 1, and the most important bond lengths and angles with their estimated standard derivations are listed in Table I.

Table I. Interatomic Distances (Ångströms) and Angles (Degrees)^a

Pt-P(1)	2.32 (1)	P(1)-Pt-P(2)	101.8 (0.3)
Pt-P(2)	2.33 (1)	P(1)-Pt-C(1)	90.5 (1.0)
Pt-C(1)	1.96 (3)	P(2)-Pt-C(2)	84.2 (0.9)
Pt-C(2)	2.02 (3)	C(1)-Pt-C(2)	83.5 (1.3)
C(1)-C(2)	2.65 (4)	Pt-C(1)-C(3)	172.2 (2.9)
C(1)-C(3)	1.24 (5)	Pt-C(2)-N(1)	169.8 (2.8)
C(2)-N(1)	1.17 (4)	C(1)-C(3)-C(4)	173.7 (3.7)
C(3)-C(4)	1.31 (5)	C(3)-C(4)-N(2)	168.5 (4.7)
C(4)-N(2)	1.16 (6)		

^a Estimated standard deviations (in 10^{-2} Å) in parentheses.

The coordination around the platinum atom is strictly planar. Interesting features are the C(1)-C(3) distance of 1.24 Å, which is long for a "triple" bond, and the C(3)-C(4) distance of 1.31 Å, which is short for a "single" bond. These distances are also different from the corresponding distances in uncoordinated molecules of cyanoacetylene⁸ and dicyanoacetylene,⁹ and may indicate extensive electronic delocalization in the coordinated cyanoacetylido moiety, as can be envisaged in the valence-bond method by contributions from canonical form 4.



Explicit in 4 is multiple bonding between platinum and C(1). Since it is reasonable to assume that multiple bonding exists between platinum and C(2), the similar Pt-C(1) and Pt-C(2) distances may imply a comparable π -acceptor capacity for the cyanoacetylido and cyano groups. Consistent with this idea of platinum-carbon multiple bonding are the platinum-phosphorus distances (2.32 and 2.33 Å), which are noticeably longer than Pt-P bonds in such compounds as $\text{Pt}(\text{PPh}_3)_2(\text{CO})_3$ ¹⁰

(7) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(8) A. A. Westenberg and E. B. Wilson, Jr., *J. Amer. Chem. Soc.*, **72**, 199 (1950).

(9) R. B. Hannan and R. L. Collin, *Acta Crystallogr.*, **6**, 350 (1953).

(10) F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Commun.*, 408 (1967).

(mean 2.24 Å), $\text{Pt}(\text{PPh}_3)_2(\text{O}_2)$ ¹¹ (mean 2.27 Å), and $\text{Pt}(\text{PPh}_3)_2(\text{NCCH}=\text{CHCN})$ ¹² (mean 2.28 Å).

Further photochemical studies of noble-metal complexes containing unsaturated organic ligands are being carried out.

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(11) T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *ibid.*, 743 (1969).

(12) C. Panattoni, R. Graziani, G. Bandoli, D. A. Clemente, and U. Belluco, *J. Chem. Soc. B*, 371 (1970).

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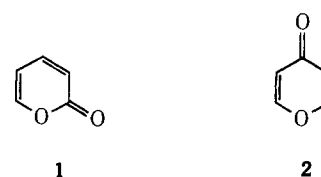
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A Classification of 2- and 4-Pyrone as Nonaromatic on the Basis of Molecular Magnetic Susceptibility Anisotropies

Sir:

We wish to report the determination of the molecular magnetic susceptibility anisotropies of 2-pyrone (1) and 4-pyrone (2). The values obtained reveal a negligible out-of-plane net diamagnetic contribution due to nonlocal effects and suggest that these formally heteroaromatic compounds should be considered nonaromatic, at least by magnetic criteria.



The values of the magnetic susceptibility anisotropies, measured by microwave methods¹ in the gas phase, are: **1**, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 22.1 \pm 1.2$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 27.4 \pm 1.4$; **2**, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 23.9 \pm 1.4$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 21.9 \pm 2.0$.²

The out-of-plane minus the average in-plane molecular magnetic susceptibilities, $\Delta\chi = \chi_{cc} - \frac{1}{2}(\chi_{aa} + \chi_{bb})$, may be separated into local and nonlocal effects;

(1) W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *J. Chem. Phys.*, **50**, 1714 (1969). For the general analysis of an asymmetric top, see W. Hüttner and W. H. Flygare, *ibid.*, **50**, 2863 (1969).

(2) The units are 10^{-6} erg/(G² mol). The *c* axis is the out-of-plane axis and the *a* axis contains the largest electric dipole moment in both molecules. The rotational spectrum of 1 gives rotational constants of $A = 5677.64 \pm 0.02$, $B = 2882.24 \pm 0.01$, and $C = 1912.13 \pm 0.01$ MHz. The rotational constants of 2, provided by J. K. Tyler of the University of Glasgow, are $A = 5859.17 \pm 0.05$, $B = 2715.09 \pm 0.05$, and $C = 1855.55 \pm 0.05$ MHz.