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Photoisomerism of (Dimethyl acetylenedicarboxylate)bis(triphenylphosphine)platinum. Structure of (Ethoxycarbonyl)((methoxycarbonyl)acetylido)bis(triphenylphosphine)platinum(II)

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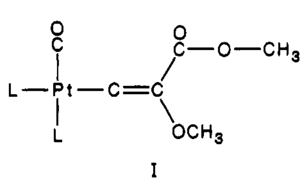
The photolysis of [Pt(PPh$_3$)$_2$(RC$\equiv$CX)] gives the acetylido complex [Pt(Ph$_3$P)$_2$R(C$\equiv$CX)] for R = X = CH$_3$O(CO), but similar photoisomerization does not occur for complexes of acetylenes with R = X = Ph or CH$_2$OH or C(CH$_3$)$_2$OH and R = H and X = CH$_2$OH or CO$_2$H or CH$_2$NH$_2$. The molecular structure of the acetylido complex [Pt(Ph$_3$P)$_2$((CO)OEt)(C$\equiv$C(CO)OCH$_3$)] was determined by X-ray diffraction using 6617 reflections: triclinic, $P\bar{1}$, a = 11.069 (3) Å, b = 13.420 (3) Å, c = 14.242 (3) Å, α = 102.27 (2)°, β = 105.85 (2)°, γ = 104.01 (2)°, Z = 2. The Pt–C bond lengths are 1.991 (8) Å (to (methoxycarbonyl)acetylide) and 2.024 (8) Å (to ethoxycarbonyl), and the Pt–P bond lengths are 2.298 (2) and 2.347 (2) Å.

Introduction

The photoisomerization of organometallic ligands is not as frequently observed as other types of organometallic photoreactions such as ligand dissociation, metal–metal bond cleavage, or oxidation–reduction.[3] We have found that the Pyrex-filtered irradiation of the acetylene complex [Pt(PPh$_3$)$_2$(CH$_3$O(CO)C$\equiv$C(CO)OCH$_3$)] (1) leads to profound changes in the infrared spectra shown in Figure 1 that is indicative of isomerization of the ligands of the compound. The IR bands of 1 with ν(C$\equiv$C) at 1778 cm^{-1} (A) and ν(C=O) at 1697 cm^{-1} (B) decrease in intensity concomitant with growth of product bands at 2124 (C), 1648 (D), and 1678 cm^{-1} (E). Since this type of IR spectral change was observed only for the platinum complex with CH$_3$(CO)C$\equiv$C(CO)CH$_3$ and not for acetylenes without a carbonyl moiety, a compound with CO bonded to platinum was indicated by the 2124 cm^{-1} IR absorption band. Since the 1648 cm^{-1} absorption band is in the region expected for a vinylidene C=C stretch,[4] the 1678 cm^{-1} is expected for a slightly perturbed carbonyl stretch of the methoxycarbonyl substituent, and the proton and ^{31}P NMR data described below were also consistent, structure I with a coordinated vinylidene ligand was indicated. Inasmuch as intermediates with the vinylidene type structure I have been proposed for reactions of platinum acetylene complexes,[5] and monomeric vinylidene compounds of platinum have not yet been reported,[4] it was of importance to conduct a crystallographic study of the compound. The photoproduct was found to have the (alkoxycarbonyl)acetylido type structure II rather than the vinylidene structure I (L = PPh$_3$).



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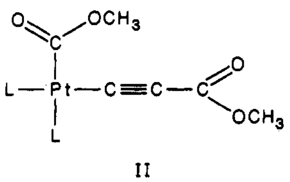

II

Table I. Crystal Data and Data Collection Details

mol formula	C$_{43}$H$_{38}$O$_4$P$_2$Pt
fw	875.77
a, Å	11.069 (3)
b, Å	13.420 (3)
c, Å	14.242 (3)
α, deg	102.269 (18)
β, deg	105.849 (21)
γ, deg	104.010 (22)
ev, Å^3	1885 (2)
λ(Mo Kα), Å	0.7107
space group	$P\bar{1}$
Z	2
d_{calcd} g/cm^3	1.518
μ, cm^{-1}	38.81
scan	θ–2θ
θ scan speed, deg/min	2.51
check reflns	3 every 10 000 s
2θ range, deg	3–50
tota, data collected	14099
total, averaged data	6617
data, $I > 0$	6237
data, $I > 3\sigma$	4933

Experimental Section

The method of Ugo, Cariati, and LaMonica was used to prepare [Pt(PPh$_3$)$_4$].[6] A modification of the Baddley–Venanzi method was used to prepare the platinum acetylene complexes.[7] A suspension of 1 g of [Pt(PPh$_3$)$_4$] in 25 mL of Et$_2$O was treated with 1 mL of dimethyl acetylenedicarboxylate, and the mixture was refluxed for 2 h. The mixture was cooled and the product filtered and washed thoroughly with Et$_2$O to give 0.50 g (72%) of [Pt(PPh$_3$)$_2$CH$_3$O(CO)C$\equiv$C(CO)OCH$_3$] (1). A solution of 0.56 g of 1 in 20 mL of CH$_2$Cl$_2$ was photolyzed for 8 h at 0 °C by placing the sample tube and a Pyrex-jacketed 450-W medium-pressure Hg lamp in a Dewar flask containing a mixture of ice and water. The solvent was removed in vacuo, and recrystallization from benzene–methanol gave 0.41 g (73%) of the colorless product. Anal. Calcd for C$_{42}$H$_{36}$O$_4$P$_2$Pt: C, 58.54; H, 4.21. Found: C, 58.73; H, 4.41. ^{1}H NMR (δ in CDCl$_3$): 7.26 (30, m, PPh$_3$), 2.99 (3, s, CH$_3$), 3.40 (3, s, CH$_3$). IR (Nujol): 2117 (vs) (C$\equiv$C), 1690 (vs) (C=O), 1646 (s) (C=O), 1207 (vs) (C—O), 1094 (vs), 1074 cm^{-1}.

Crystal Structure. Crystals of [Pt(PPh$_3$)$_2$((CO)OEt)C$\equiv$C(CO)OCH$_3$)] grown from dichloromethane/ethanol solution are triclinic, $P\bar{1}$, with a = 11.069 (3) Å, b = 13.420 (3) Å, c = 14.242 (3) Å, α = 102.27 (2)°, β = 105.85 (2)°, γ = 104.01 (2)°, and Z = 2. Intensity data were collected on an Enraf-Nonius diffractometer with graphite monochromator and Mo Kα radiation. The entire Ewald sphere, 14 099 reflections, was collected out to a θ of 25°; equivalent reflections were combined to yield an averaged data set of 6617 reflections and were reduced to F^2. The overall goodness-of-fit upon averaging 6616 reflections was 1.02, and the

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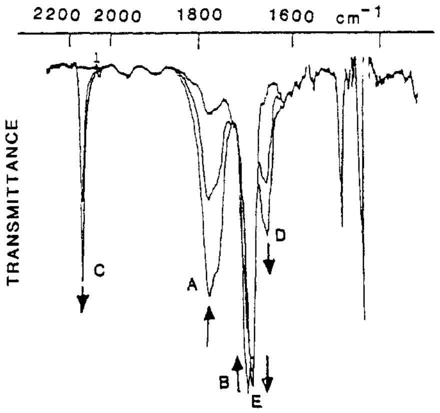

Figure 1. Infrared spectra during the course of photolysis of $[Pt(PPh_3)_2(CH_3O(CO)C{\equiv}C(CO)OCH_3)]$ in dichloromethane.

Table II. Atom Coordinates and U_{eq}'s ($\times 10^4$)

atom	x	y	z	U_{eq}, Å^2
Pt	2595.7 (3)	2537.5 (2)	2216.1 (2)	366 (1)
C	3813 (7)	2665 (6)	1384 (5)	432 (19)
O(1)	4808 (5)	3378 (4)	1567 (4)	650 (16)
O(2)	3454 (5)	1764 (4)	590 (4)	598 (15)
E1	4274 (9)	1734 (8)	−54 (7)	786 (26)
E2	3620 (11)	778 (10)	−912 (8)	1302 (41)
C(1)	3802 (7)	1858 (6)	2958 (5)	468 (19)
C(2)	4567 (7)	1477 (6)	3372 (6)	537 (20)
C(3)	5424 (9)	914 (8)	3793 (7)	695 (26)
O(4)	5500 (8)	86 (6)	3349 (6)	1372 (30)
O(3)	6078 (7)	1349 (5)	4753 (5)	1037 (23)
C(5)	6898 (12)	789 (11)	5245 (10)	1579 (49)
P(1)	1394 (2)	3377 (1)	1259 (1)	401 (5)
11A	−190 (6)	2500 (6)	318 (5)	445 (19)
12A	−569 (7)	1406 (6)	237 (5)	508 (20)
14A	−2563 (8)	1108 (8)	−1103 (7)	818 (35)
15A	−2205 (8)	2182 (8)	−1056 (6)	791 (30)
13A	−1758 (9)	724 (6)	−474 (7)	696 (27)
16A	−1002 (8)	2877 (6)	−347 (6)	643 (24)
11B	2165 (6)	4013 (6)	476 (6)	464 (20)
12B	2216 (7)	3355 (7)	−403 (6)	639 (24)
13B	2858 (8)	3793 (9)	−1014 (6)	745 (26)
14B	3403 (8)	4882 (10)	−760 (8)	817 (31)
15B	3323 (8)	5521 (8)	65 (8)	793 (29)
16B	2727 (7)	5100 (7)	693 (6)	641 (24)
11C	1127 (7)	4490 (5)	2065 (5)	472 (21)
12C	−48 (8)	4711 (7)	1921 (6)	714 (26)
13C	−93 (11)	5603 (9)	2589 (8)	1038 (34)
14C	1003 (13)	6268 (8)	3378 (8)	1097 (39)
15C	2185 (10)	6076 (7)	3531 (7)	916 (35)
16C	2252 (7)	5176 (6)	2888 (6)	625 (25)
P2	1415 (2)	2306 (2)	3337 (1)	402 (5)
21A	696 (7)	905 (5)	3251 (5)	444 (18)
22A	992 (7)	107 (6)	2697 (6)	616 (23)
23A	401 (9)	−959 (7)	2609 (7)	795 (30)
24A	−459 (9)	−1218 (7)	3110 (7)	748 (29)
25A	−767 (10)	−426 (8)	3641 (8)	953 (33)
26A	−229 (9)	622 (7)	3707 (7)	824 (28)
21B	2530 (6)	2933 (6)	4663 (5)	461 (19)
22B	3171 (8)	4025 (7)	5006 (6)	701 (27)
23B	3987 (9)	4541 (8)	5999 (9)	947 (37)
24B	4220 (10)	3970 (13)	6662 (8)	1154 (52)
25B	3660 (12)	2876 (13)	6328 (8)	1350 (54)
26B	2813 (9)	2353 (8)	5334 (7)	912 (32)
21C	−13 (6)	2762 (6)	3306 (5)	498 (20)
22C	−106 (7)	3498 (7)	4087 (6)	783 (29)
23C	−1264 (9)	3729 (8)	3999 (7)	1012 (35)
24C	−2347 (8)	3250 (9)	3160 (8)	922 (34)
25C	−2296 (8)	2486 (9)	2371 (7)	888 (34)
26C	−1159 (7)	2241 (7)	2433 (6)	701 (26)

Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) for $[Pt(PPh_3)_2(C{\equiv}C(CO)OCH_3)(COC_2H_5)]$ with Estimated Standard Deviations in Parentheses[a]

	Bond Distances		
Pt–P(1)	2.298 (2)	C–O(2)	1.356 (9)
Pt–P(2)	2.347 (2)	C(3)–O(3)	1.284 (11)
Pt–C	2.024 (8)	C–O(1)	1.194 (9)
Pt–C(1)	1.991 (8)	O(2)–C(E1)	1.436 (16)
C(1)–C(2)	1.180 (11)	C(3)–O(4)	1.190 (13)
C(2)–C(3)	1.434 (13)	O(3)–C(5)	1.444 (15)
	Bond Angles		
C–Pt–C(1)	84.1 (3)	C–C(2)–C(E1)	117.9 (6)
C–Pt–P(1)	88.7 (2)	O(2)–C(E1)–C(E2)	108.1 (8)
P(1)–Pt–P(2)	99.7 (7)	Pt–C(1)–C(2)	176.3 (7)
C(1)–Pt–P(2)	87.4 (2)	C(1)–C(2)–C(3)	174.3 (9)
P(2)–Pt–C	171.5 (2)	C(2)–C(3)–O(3)	113.5 (9)
P(1)–Pt–C(1)	172.7 (2)	C(2)–C(3)–O(4)	125.8 (10)
Pt–C–O(1)	127.6 (6)	O(3)–C(3)–O(4)	120.5 (10)
Pt–C–C(2)	112.1 (5)	C(3)–O(O)–C(5)	116.7 (9)
O(1)–C(1)–C(2)	120.0 (7)		

[a] Torsion angles: Pt–C–O(2)–C(E1) = 178.1 (5)°; C–O(2)–C(E1)–C(E2) = 172.6 (8)°; C(2)–C(3)–O(3)–C(5) = 176.1 (9)°.

R_{av} for those reflections with only two observations, 5511 reflections, was 0.088. No correction for absorption or extinction was made, and there was no indication of radiation damage; anomalous dispersion corrections were included for the platinum atom. Atom form factors were taken from ref 19. The Patterson map and conventional Fourier maps were used to solve the structure. Full-matrix least squares of F^2 yielded a goodness-of-fit of 1.30, $R_F = 0.060$ for the 6237 data with $I > 0$, and $R_F = 0.042$ for the 4933 data with $I > 3\sigma$. The CRYM system of programs were used on a VAX 11/750. The final cell parameters and the details of the data collection procedure are given in Table I; the atom coordinates of the non-hydrogen atoms are given in Table II. Selected bond distances and angles are presented in Table III.

Results and Discussion

The course of photoisomerization of $[Pt(PPh_3)_2(CH_3O(CO)C{\equiv}C(CO)OCH_3)]$ (**1**) is shown by the IR spectrum presented in Figure 1. The $\nu(C{\equiv}C)$ band at 1778 cm^{-1} (A) of the acetylene complex **1** decays as the strong band at 2124 cm^{-1} (C) assigned to the $\nu(C{\equiv}C)$ of the acetylido complex **2** grows. Acetylido complexes $[Pt(PPh_3)_2(C{\equiv}CR)_2]$ have bands in the 2120–2130 cm^{-1} region.[8] The 1678 (E) and 1648 cm^{-1} (D) bands are the C=O stretching frequencies of the carbonyl moieties attached to the acetylene carbon and the platinum atom.

Proton NMR spectra of the photoisomerization in $CDCl_3$ showed the decay of a singlet methyl resonance of **1** at 3.32 ppm and growth of two singlet resonances at 3.40 and 2.99 ppm. The $^{31}P\{^1H\}$ NMR ($\delta(P_1)$ 16.83 ($J(Pt\text{–}P_1) = 1392$ Hz); $\delta(P_2)$ 11.14 ($J(Pt\text{–}P_2) = 811$ Hz); $J(P_1\text{–}P_2) = 22$ Hz) indicates that the PPh_3 ligands retain the cis geometry in the product.

Recrystallization of the acetylido complex **2** in ethanol gave crystals that have a methoxy moiety of the carbonyl attached to the platinum atom substituted by an ethoxy group. Reversible reactions of platinum(II) carbonyl complexes with alkoxides have been previously reported.[9] An ORTEP plot of the ethoxycarbonyl-(methoxycarbonyl)acetylido complex is presented in Figure 2. The coordination of the platinum atom is distorted from an accurately square-planar geometry in order to relieve the steric interaction of the cis PPh_3 ligands. The P(1)–Pt–P(2) angle is 99.74 (7)°, and the P(1)–Pt–C, P(2)–Pt–C(1), and C(1)–Pt–C angles are slightly compressed to 88.7 (2)°, 87.4 (2)°, and 84.1 (3)°, respectively. Crowding of the ligands does not lead to serious out-of-plane distortions of the platinum, and the donor atoms of the ligands as the four donor atoms of the ligands are planar within ±0.005

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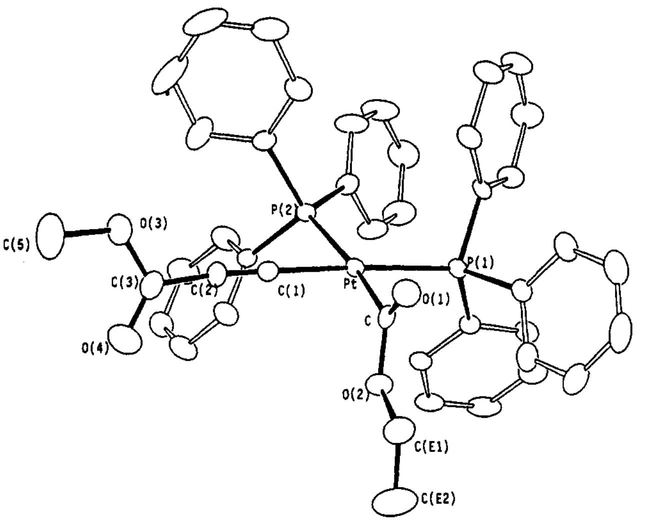
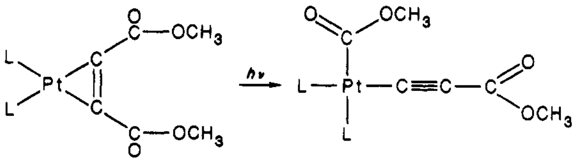


Figure 2. Structure of [Pt(PPh$_3$)$_2$((CO)OEt)(C$\equiv$C)(CO)OCH$_3$].

Å. The platinum atom lies out of this plane by 0.023 Å. Distances and bond angles in the two PPh$_3$ ligands are normal. The Pt–P(1) distance of 2.298 (2) Å compares favorably with the mean Pt–P bond distance of 2.31 Å reported for *cis*-[Pt(PPh$_3$)$_2$(C$\equiv$CPh)$_2$].[10] The slightly elongated Pt–P(2) distance of 2.347 (2) Å may reflect a strong trans influence of the ethoxycarbonyl ligand analogous to the trans influence observed in acyl platinum(II) complexes.[11] The Pt–C(1) distance of 1.991 (8) Å and Pt–C(1)–C(2) angle of 176.3 (7)° are consistent with the bond distances and angles reported[12] for eight platinum(II) acetylide complexes that have Pt–C distances between 1.9 and 2.1 Å and Pt—C$\equiv$C angles between 172 and 178°. The C(1)–C(2) triple bond distance of 1.180 (11) Å which compares favorably with the distance 1.18 (3) Å reported for *trans*-[Pt(PEt$_2$Ph)$_2$Cl(C$\equiv$CPh)][12a] and *trans*-[Pt(PPh$_3$)$_2$(C$\equiv$CMe=CH$_2$)$_2$][12i] and 1.212 Å found in acetylene indicates retention of the C$\equiv$C triple bond.[12a] The platinum atom and the five atoms of the ethoxycarbonyl group are planar, |0.055 Å| maximum displacement; the dihedral angle between this plane and the square-planar platinum plane is 90.5 (3)°. The platinum atom and the six atoms of the (methoxycarbonyl)acetylido ligand are also planar, |0.041 Å| maximum displacement. The latter plane makes a dihedral angle of 119.0 (4)° with the square-planar platinum plane. The double-bonded oxygen atoms in the two ligands are on opposite sides of the square platinum plane.

The photoisomerization of the acetylene complex **1** thus proceeds as shown in reaction 1. This photoisomerization is analogous to the photoisomerization of [Pt(PPh$_3$)$_2$(NCC$\equiv$CCN)] and [Pt(PPh$_3$)$_2$(TCNE)] reported by Baddley, Belluco, and co-workers.[13,14]



(1)

Similar photoisomerization to form acetylido complexes was not found to proceed for the acetylene complexes [Pt(PPh$_3$)$_2$(RC$\equiv$CX)] (R = X = Ph or CH$_2$OH or C(CH$_3$)$_2$; R = H, X = CH$_2$OH or CO$_2$H or CH$_2$NH$_2$). Failure to observe photoisomerization with terminal acetylenes is noteworthy in view of the acidity of the C–H bond of the acetylene and the strength of the Pt–H bond of the anticipated product. The insertion of iridium into a acetylene carbon–hydrogen bond has been previously observed.[15] A reasonable explanation of the observed photoisomerization must thus be linked to the susceptibility of the methoxycarbonyl carbon atom to nucleophilic displacement by the platinum atom in a photoexcited state arising from ligand to metal change transfer. The net reaction would then be a photoinduced oxidative addition of platinum across a carbon–carbon bond. Oxidative addition reactions across activated carbon–carbon bonds of nitriles and strained carbocyclic compounds have been reported.[16] The thermal isomerization of [Pt(PPh$_3$)$_2$(Cl$_2$C=CCl$_2$)] to the chloro σ-vinyl platinum complex σ-vinyl complex, which is an oxidative addition reaction, has also been reported.[17] Finally, it has been demonstrated previously that oxidative reactions as in the example of the reaction of 1,2-naphthoquinone and *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] may be photoinduced.[17]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Additional support was provided by the National Science Foundation (Grant No CHE 8410454). The CAD 4 diffractometer was obtained by a grant from the National Science foundation to the California Institute of Technology (CHE-82-19039).

Registry No. 1, 22853-55-0; 2, 108009-15-0; Pt(PPh$_3$)$_4$, 14221-02-4; Pt(PPh$_3$)$_2$(C$\equiv$(CO)OCH$_3$)(COC$_2$H$_5$), 108009-16-1; Pt(PPh$_3$)$_2$(PhC$\equiv$CPh), 15308-61-9; Pt(PPh$_3$)$_2$(HOCH$_2$C$\equiv$CCH$_2$OH), 31976-84-8; Pt(PPh$_3$)$_2$((CH$_3$)$_3$CC$\equiv$CC(CH$_3$)$_3$), 108009-17-2; Pt(PPh$_3$)$_2$(HC$\equiv$CCH$_2$OH), 52653-42-6; Pt(PPh$_3$)$_2$(HC$\equiv$CCO$_2$H), 31853-68-6; Pt(PPh$_3$)$_2$(HC$\equiv$CCH$_2$NH$_2$), 108009-18-3; CH$_3$O(CO)C$\equiv$C(CO)OCH$_3$, 762-42-5.

Supplementary Material Available: Atom numbering scheme (Figure 3), selected bond lengths and angles (Figure 4), anisotropic Gaussian amplitudes of the non-hydrogen atoms (Table IV), hydrogen atom coordinates (Table V), and a complete list of bond lengths and angles (Table VI) (7 pages); a listing of structure factor amplitudes (Table VII) (26 pages). Ordering information is given on any current masthead page.

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