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σ - π Rearrangements of Organotransition Metals.

XI. Platinum(II) π -Vinyl Alcohol Complexes

J. Hillis, J. Francis, M. Ori, and M. Tsutsui*

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. Received February 20, 1974

Abstract: The stable vinyl alcohol complex, chloro(acetylacetonato)(π -ethenol)platinum(II), has been prepared by two separate approaches: preparation and hydrolysis of the analogous π -vinyl trimethylsilyl ether complex and the reaction of chloro(acetylacetonato)(ethylene)platinum(II) and acetaldehyde in the presence of aqueous base. This complex, the first well-characterized π -enol metal complex, was found to be a moderately strong acid ($pK_a = 3.5$) and nmr indicates that in solution it is in rapid equilibrium with its conjugate base, a σ -bonded β -oxoethyl complex. Evidence for a similar equilibrium in the case of the π -acetylacetonate complex $\text{HPt}(\text{acac})_2\text{Cl}$ suggests that this complex might be best described by a localized enol structure rather than the delocalized structure previously proposed. A chloro(acetylacetonato)(π -2-propenol)platinum(II) complex and attempts to prepare other platinum-(II) enol complexes are also described.

While it is well established that a variety of unstable compounds such as cyclobutadiene,¹ benzyne,² carbene,³ and ketenimine⁴ can be isolated through coordination with transition metals, only recently has an interest in such complexes of vinyl alcohols (enols) appeared in the literature. In the earliest report, Ariyaratne and Green⁵ found that cyclopentadienyldicarbonyl(β -oxoethyl)iron could be protonated to give a complex which they tentatively described as the π -enol complex. This is principally based on the infrared spectrum which revealed the absence of the aldehydic C=O absorption of the β -oxoethyl complex and new intense absorptions in the 2400–2800 cm^{-1} region, assignable to O–H stretching vibrations. However, the unexplained A_2X pattern assigned to the three vinyl protons of the π -bonded ethenol has led some to reject this structure for the protonated derivative.⁶ In a later study, Wakatsuki, Nozakura, and Murahashi,⁷ employing a different synthetic approach, obtained 1,3-bis(π -ethenol)-2,4-dichloro- μ -dichloro-platinum(II) by hydrolysis of the vinyl trimethylsilyl ether complex. The nmr spectrum of the compound could not be obtained due to its poor solubility and again the structural assignment was based on infrared data. This work, however, has been questioned by Thyret⁶ who reported it to be unreproducible. Employing a vinyl trimethylsilyl ether intermediate, he was able to isolate tetracarbonyl(π -ethenol)iron by low

temperature hydrolysis. The complex decomposed above -70° , but the nmr spectrum obtained at -75° revealed the expected ABX pattern for the three vinyl protons in contrast to Ariyaratne and Green's results.

The synthetic approach employed by Wakatsuki suggested the possibility of preparing the π -ethenol analog of chloro(acetylacetonato)(π -ethylene)platinum(II),⁸ hopefully providing a complex of greater solubility than that of Wakatsuki's. This complex has been prepared, and its stability and high solubility have allowed its thorough characterization by nmr,⁹ X-ray diffraction,¹⁰ and exchange studies.¹¹ The rapid equilibrium observed between this π -enol and a σ -bonded β -oxoethyl complex not only explains the A_2X pattern observed for the vinyl protons here and in Ariyaratne and Green's iron complex but also suggests a localized π -enol structure for the π -acetylacetonate complex $\text{HPt}(\text{acac})_2\text{Cl}$ for which a delocalized structure has been postulated.¹²

Results and Discussion

The stable vinyl alcohol complex, chloro(acetylacetonato)(π -ethenol)platinum(II), can be prepared by either of two methods. The procedure first employed⁹ involved the preparation and hydrolysis of the intermediate vinyl trimethylsilyl ether complex. Thus a benzene solution of vinyl trimethylsilyl ether and chloro(acetylacetonato)(ethylene)platinum(II) allowed to stand at room temperature for 60 hr yielded the chloro(acetylacetonato)(π -vinyl trimethylsilyl ether)platinum(II) complex, **1**, as a viscous yellow oil upon

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(2) E. W. Gowling, S. F. A. Kettle, and G. M. Sharples, *Chem. Commun.*, 21 (1968).

(3) E. O. Fisher and A. Massbol, *Chem. Ber.*, **100**, 2445 (1967).

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(6) H. Thyret, *Angew. Chem., Int. Ed. Engl.*, **11**, 520 (1972).

(7) Y. Wakatsuki, S. Nozakura, and S. Murahashi, *Bull. Chem. Soc. Jap.*, **42**, 273 (1969).

(8) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1653 (1970).

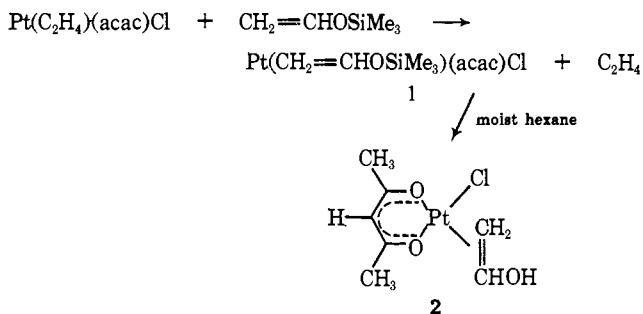
(9) M. Tsutsui, M. Ori, and J. Francis, *J. Amer. Chem. Soc.*, **94**, 1414 (1972).

(10) F. A. Cotton, J. N. Francis, B. A. Frenz, and M. Tsutsui, *J. Amer. Chem. Soc.*, **95**, 2483 (1973).

(11) M. Tsutsui and J. Francis, *Chem. Lett.*, 663 (1973).

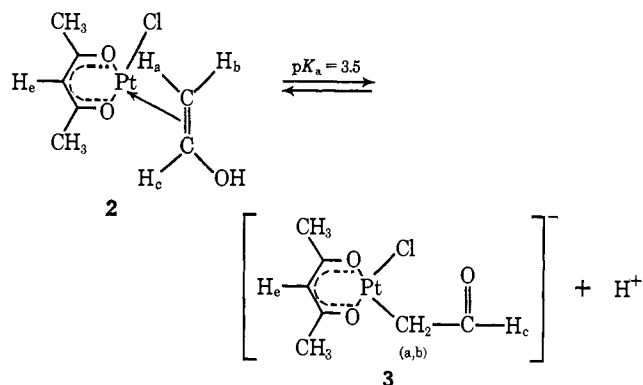
(12) D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc. A*, 72 (1967).

removal of the solvent. When this oil, in hexane solution, was exposed to a stream of moist argon, the π -ethenol complex, **2**, was obtained as a yellow powdery



precipitate. The compound is unaffected by air or water but is somewhat thermally unstable and should be stored in the refrigerator if it is to be kept for a period of weeks or months. It is soluble in acetone, tetrahydrofuran, diglyme, and dioxane and insoluble in hydrocarbons, chlorinated hydrocarbons, carbon disulfide, alcohols, and water.

The complex, **2**, was found to behave as a monobasic acid, $pK_a = 3.5$, and could be titrated with sodium hydroxide in 50% aqueous acetone. By treating **2** with an equivalent amount of potassium hydroxide, the β -oxoethyl complex, **3**, could be isolated from methanol



as the yellow crystalline potassium salt. This complex shows greater thermal stability than **2** and is soluble in water, alcohols, acetone, and tetrahydrofuran.

More recently, a simplified procedure for the preparation of **2** and **3** was found which eliminated the tedious preparation and reaction of vinyl trimethylsilyl ether.^{13,14} Addition of aqueous potassium hydroxide to a THF solution of chloro(acetylacetonato)-(ethylene)platinum(II) and excess acetaldehyde at 0° resulted in noticeable effervescence and a deepening of the yellow color. After 30 min, the solvent was removed and the residue was recrystallized from methanol, yielding crystals of **3** as the potassium salt. Compound **2** was then readily obtained by protonation of the β -oxoethyl complex with HCl.

The infrared spectra of the vinyl alcohol and β -oxoethyl complexes revealed the expected characteristic absorptions. Thus, the spectrum of **2** exhibited two intense OH bands at 3330 and 3220 cm^{-1} and an intense band at 1551 cm^{-1} assigned to the C=C stretching mode and **3** exhibited an intense C=O absorption at

1650 cm^{-1} . While the nmr spectrum of the vinyl trimethylsilyl ether, **1**, showed an ABX pattern for the vinyl protons, **2** in acetone solution exhibited an A_2X pattern (a 1 H triplet at δ 7.23 ppm and a 2 H doublet at δ 3.90 ppm, $J = 5$ Hz). The ^{195}Pt -H coupling constants, however, were found to be very similar for a π complex: $J_{\text{Pt-H}_{ab}} = 76$, $J_{\text{Pt-H}_c} = 71$ Hz. The nmr spectrum of **3** reveals the A_2X pattern, expected in this case, for the protons of the β -oxoethyl group (a 1 H triplet at δ 9.3 ppm and a 2 H doublet at δ 3.3 ppm, $J = 5.5$ Hz). Here the ^{195}Pt -H coupling constant for H_c (20 Hz) is drastically reduced, while that for H_a and H_b protons is much larger (114 Hz).

The A_2X pattern observed for the π -vinyl alcohol complex, **2**, is not surprising if the acidity of the complex is considered. Thus, in polar solvents or in the presence of a basic impurity, **2** would be expected to exist in equilibrium with its conjugate base, **3**. If this were a rapid process, the equivalence of H_a and H_b would be due to scrambling of these protons in the β -oxoethyl complex ion. Evidence for such a rapid equilibrium was found in the nmr spectra of mixtures of **2** and **3**, which exhibit a single spectrum with averaged J and δ values. Table I lists the shift and cou-

Table I. Nmr Data^a for **2**, **3**, and a 1:2 Mixture

| (t) | 2 | 3 | 2-3 (1:2) | % shift |
|-------------------------------------|----------|----------|-----------|---------|
| δH_c , ppm | 7.27 | 9.16 | 8.48 | 64 |
| $J_{\text{H}_{ab}-\text{H}_c}$, Hz | 8 | 5.5 | 6.5 | 60 |
| $J_{\text{Pt}-\text{H}_c}$, Hz | 71 | 20 | 38 | 65 |
| δH_{ab} , ppm | 3.89 | 3.28 | 3.49 | 66 |
| $J_{\text{Pt}-\text{H}_{ab}}$, Hz | 76 | 113 | 99 | 64 |
| δCH_3 , ppm | 1.99 | 1.68 | 1.88 | 61 |
| δCH_3 , ppm | 1.89 | 1.64 | 1.80 | 64 |
| δH_e , ppm | 5.64 | 5.32 | 5.41 | 72 |

^a At 100 MHz in aqueous acetone.

pling parameters observed for a 1:2 mixture of **2** and **3**, respectively. These can be seen to be consistently two-thirds of the way between those of the pure components.

This suggests that if the ionization of **2** could be slowed sufficiently, it should exhibit the expected ABX pattern for the vinyl protons. At -20° in dry acetone, the clean doublet-triplet pattern did change to a rather nondescript multiplet; however, the fine structure could not be resolved due to the poor solubility of the complex at this temperature.

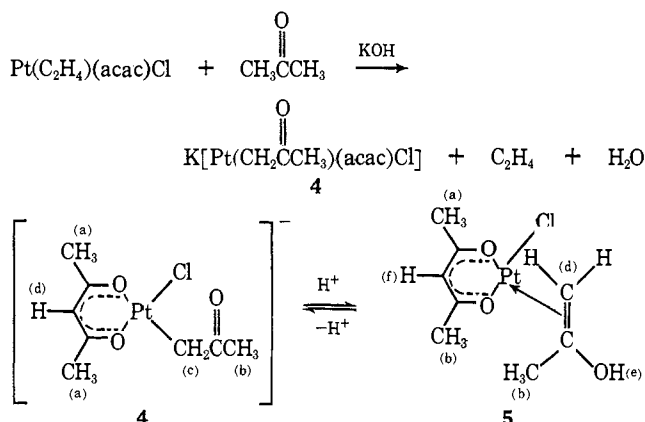
An X-ray crystal structure of **2**¹⁰ has confirmed the olefinic character of the complex. The principal coordination plane of the platinum atom does not bisect the olefin bond, as is usually found in platinum(II) olefin structures. Instead, the plane cuts the olefin bond only 0.09 Å from the β -carbon. Although both carbon atoms are within bonding distance of the platinum atom, the metal-carbon bond lengths differ significantly (2.098 (8) Å to β -carbon and 2.222 (8) Å to α -carbon). Overall the structural features of the complex are best described by a hybrid bonding model intermediate between a conventional π -olefin structure and σ -bonded β -oxoethyl structure. This would seem to correlate well with the ready interconversion of this complex with its conjugate base **3**, which is indicated by the above nmr results.

(13) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

(14) M. Tsutsui and J. Hillis, *J. Amer. Chem. Soc.*, **95**, 7907 (1973).

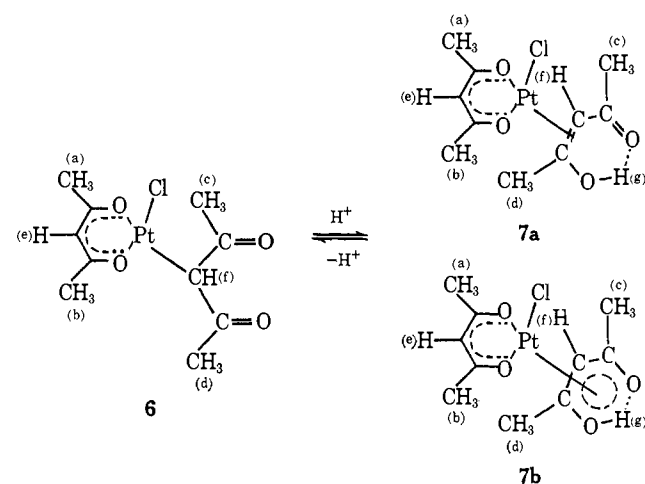
This same rapid equilibrium between the acidic π -enol complex and the β -oxoethyl conjugate base could also account for the A_2X pattern observed by Ariyaratne and Green for the cyclopentadienyldicarbonyl (π -ethenol)iron complex cation.⁵ The authors did not make quantitative measure of the acidity of the complex, but, from their description, it appears to be a stronger acid than **2**, thus lending support to this hypothesis.

An analogous complex, chloro(acetylacetonato)(β -oxopropyl)platinum(II) (**4**), was formed when the ethylene complex was treated with acetone and aqueous alkali. Protonation of **6** with HCl in anhydrous ether converted it to the moisture-sensitive π -enol form, **5**.



Structural assignment of these two compounds was made on the basis of elemental analysis and the strong similarity in the infrared spectra of **3**, **4**, **2**, and **5**.

In a study of the acid derivatives of some carbon bonded acetylacetonate complexes of platinum **6**, Gibson, Lewis, and Oldham¹² favored the delocalized structure **7b** over that of the previously proposed structure **7a**.¹⁵ Their preference for **7b** was based on the nmr equiv-



alence of the methyl protons of the π -bonded ligand. However, rapid, reversible ionization of **7a** to **6** (similar to the **2**-**3** equilibrium we observe) with consequent averaging of the methyl protons would seem to be a better explanation of the nmr spectrum in view of the infrared study of Behnke and Nakamoto¹⁶ which supports a localized olefin structure. While a quantitative

(15) G. Allen, J. Lewis, R. F. Long, and C. Oldham, *Nature (London)*, **202**, 589 (1964).

(16) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **7**, 2030 (1968).

measure to the acid strength of **7** has not been reported, the fact that it can be precipitated from aqueous solutions of **6** using hydrochloric, nitric, or sulfuric acid but not with acetic acid¹² suggests that it is an acid of at least moderate strength, so that ionization in polar solvents is not unlikely. Evidence for a rapid equilibrium in polar solvents was found in the single spectrum obtained for a 1:2 mixture of **6** and **7** in acetone- d_6 , Table II. Here, as in the case of **2** and **3**, averaged J

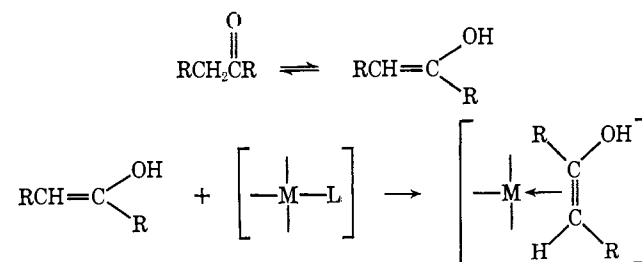
Table II. Nmr Data^a for **6**, **7** and a 1:2 Mixture

| | 6 | 7 | 6-7 (1:2) | |
|----------------------------|-------|-------|-----------|-------------------------------|
| | | | Obsd | Predicted $\frac{2}{3}$ av |
| δ Me (a), ppm | 1.68 | 1.92 | 1.84 | 1.84 |
| (b), ppm | 1.73 | 1.85 | 1.82 | 1.81 |
| (c,d), ppm | 2.10 | 2.50 | 2.38 | 2.37 |
| δ H (e), ppm | 5.37 | 5.57 | 5.52 | 5.47 |
| (f), ppm | 5.42 | 5.90 | 5.75 | 5.75 |
| (g), ppm | | 11.01 | 1.32 | |
| $J_{\text{Pt-Me}}$ (a), Hz | 2.4 | 4.4 | 3.2 | 3.7 |
| (b), Hz | 5.2 | 5.6 | 5.5 | 5.5 |
| (c,d), Hz | 9.8 | 24.0 | 19.0 | 19.0 |
| $J_{\text{Pt-H}}$ (e), Hz | 7.2 | 7.6 | 7.5 | 7.5 |
| (f), Hz | 121.0 | 84.0 | 98.0 | 96.0 |

^a At 60 Hz in acetone- d_6 .

and δ values were found consistently two-thirds of the way between those for the pure components. An effort to limit the rapid equilibrium and render the methyl groups c and d nonequivalent failed. The nmr spectrum of **7** in dry methylene chloride was run at temperatures as low as -80° but the c,d methyl resonance at δ 2.50 remained unsplit. Therefore, whether the equivalence of the methyl groups is due to the rapid equilibrium observed or to the delocalized structure **7b** would seem to await X-ray analysis.

The reaction of acetaldehyde or acetone with chloro(acetylacetonato)(ethylene)platinum(II) in the presence of aqueous base is interesting not only because it provides a more convenient route to the π -ethenol complex, **2**, but also because of its novel character. A number of attempts have been made previously to prepare π -enol complexes from aldehydes or ketones by a direct displacement reaction.



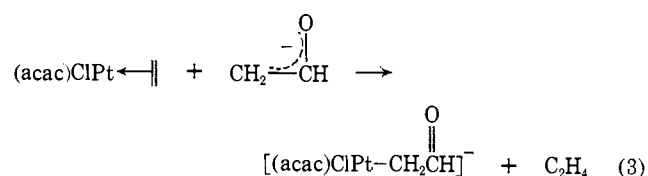
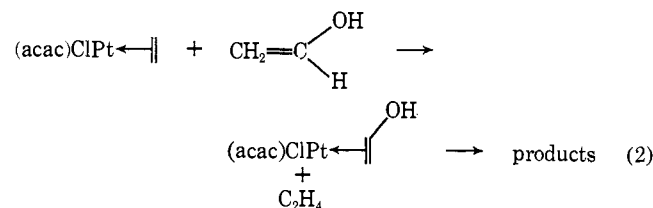
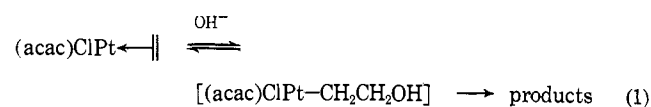
All these attempts (conducted in anhydrous neutral solution), however, were unsuccessful. Thus, Wakatsuki⁷ found no reaction between Zeise's dimer, $[\text{PtCl}_2\text{-C}_2\text{H}_4]_2$, and acetaldehyde (enol content less than $10^{-5}\%$ ¹⁷), phenylacetone (enol content 2.9%¹⁷), or acetylacetonate (enol content 76.4%¹⁷) at room temperature. When the reaction mixtures were allowed to stand for long periods, decomposition of the platinum complex and formation of aldol condensates were

(17) A. Gero, *J. Org. Chem.*, **19**, 469 (1954).

noted. Here similar results were obtained when chloro(acetylacetonato)(ethylene)platinum(II) was allowed to stand in dry acetaldehyde solution. After 4 days in a sealed tube at 25°, the only detectable products were a small amount of metaldehyde and a trace of metallic platinum. Better than 90% of the starting material was recovered.

Evidence for exchange between free acetaldehyde and the coordinated enol of **2** was obtained, however.¹¹ A sample of chloro(acetylacetonato)(π -ethenol)platinum(II), recovered from a dioxane solution of ¹⁴C-labeled acetaldehyde after 45 hr at room temperature, exhibited an activity corresponding to 0.46% exchange. If the exchange proceeds by attack of free enol, the limited amount of exchange observed could be attributed to the small amount of vinyl alcohol in equilibrium with acetaldehyde.

The reaction of chloro(acetylacetonato)(ethylene)platinum(II) with aqueous alkali in acetaldehyde-THF was initially assumed to proceed by one of three possible mechanisms.



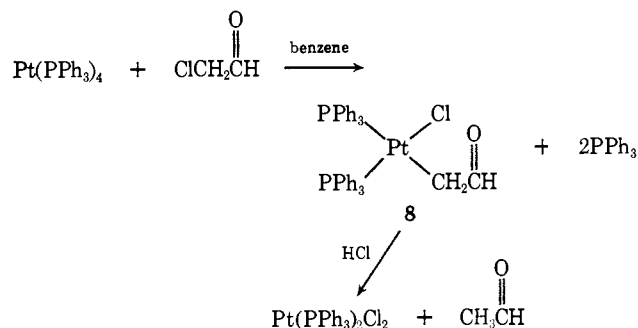
The first involving nucleophilic attack of coordinated ethylene is similar to the mechanism proposed for the PdCl₂ catalyzed oxidation of ethylene to acetaldehyde.¹⁸ However, this was eliminated when it was found that the ethylene complex failed to react if acetaldehyde was eliminated from the reaction mixture and the substitution of acetone for acetaldehyde led to the β -oxopropyl complex, **4**.

The second mechanism involving the initial displacement of ethylene by the enol rather than the enolate ion was considered unlikely because of the failure of acetaldehyde or acetone to react under acidic conditions to give the π -enol complexes **2** and **5**. At room temperature or below, aldol condensation was the only detectable reaction, the bulk of the ethylene complex being recoverable. When approximately 1 equiv of HCl was employed and the temperature raised to 50°, the acetylacetonate ligand was hydrolyzed giving Zeise's dimer, [Pt(C₂H₄)Cl₂]₂. While further work is required to determine the details of the mechanism involved, we feel that the reaction must proceed *via* enolate ion displacement of ethylene (3).

Attempts to obtain other stable π -enol complexes of

(18) R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 99 (1966); J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, and A. Sabel, *Angew. Chem. Int. Ed. Engl.*, **1**, 80 (1962).

platinum(II) employing a ligand system other than the acetylacetonate have failed thus far. The β -oxoethyl complex, **8**, was obtained as a colorless crystalline prod-



uct by the oxidative addition of chloroacetaldehyde to tetrakis(triphenylphosphine)platinum(0).

However, attempts to convert this complex to the analogous π -ethenol complex by protonation failed. When acidified with dry HCl in chloroform solution, acetaldehyde and dichlorobis(triphenylphosphine)platinum(II) were obtained.

Further attempts employing both the vinyl trimethylsilyl ether intermediates and the simplified enolate displacement reaction are currently being made in an effort to clarify the factors affecting the stability of these novel olefinic complexes.

Experimental Section

Synthesis. (π -C₂H₃OH)(acac)PtCl, Preparation via the Vinyl Trimethylsilyl Ether. To a dry benzene solution of chloro(acetylacetonato)(ethylene)platinum(II)⁸ (1.07 g, 3 mmol, in 19 ml), 1 ml (10 mmol) of vinyl trimethylsilyl ether¹³ was added under argon. After 60 hr at room temperature, the solution was centrifuged and decanted to remove a trace of black residue, then evaporated under reduced pressure to yield an oily yellow residue, chloro(acetylacetonato)(vinyl trimethylsilyl ether)platinum(II). This was dissolved in 20 ml of dry *n*-hexane and hydrolyzed by bubbling moist argon through the solution for 30 min at room temperature (the moist argon was obtained by passing argon through distilled, deoxygenated water). The precipitated yellow crystals of the vinyl alcohol complex were washed with *n*-hexane and dried *in vacuo*, yield 0.89 g (79.8% based on the starting ethylene complex), 115–140° dec. *Anal.* Calcd for C₇H₁₁O₃PtCl: C, 22.50; H, 2.97; Pt, 52.20; Cl, 9.49. Found: C, 23.37; H, 3.03; Pt, 52.16; Cl, 8.90. Infrared spectrum (KBr pellet, Beckman IR-8): 3330 m, 3320 m, 3020 w, 2920 w, 2860 w, 1570 s, 1525 s, 1430 w, 1385 s, 1365 s, 1315 s, 1280 m, 1258 s, 1202 w, 1157 w, 1053 w, 1030 m, 1003 m, 968 s, 952 w, 935 m, 853 w, 797 s, 711 w, 647 m cm⁻¹.

K[σ -C₂H₃O](acac)PtCl, Isolation from an Alkaline Solution of the (π -C₂H₃OH) Complex. A 50.12 mg (134 μ mol) sample of the π -ethanol complex in 9 ml of reagent THF was treated with 0.38 ml of 0.663 *N* aqueous KOH (174 μ mol). The solvents were then evaporated under reduced pressure to yield a solid yellow residue of the β -oxoethyl complex. This was recrystallized from 2 ml of methanol by adding an equal volume of 1:1 ether-hexane and cooling at 0° for 1 hr. The yellow crystalline product was filtered off and air dried, yield 42.30 mg (76.2%); 170–175° dec (yellow-black). Infrared spectrum (KBr pellet; Beckman, IR-8): 3100 vw, 3020 w, 2970 w, 2920 w, 2840 and 2820 w, 2750 w, 1650 s, 1570 s, 1545 s, 1520 s, 1470 w, 1420 m, 1385 s, 1360 m, 1275 m, 1205 w, 1168 m, 1081 m, 1069 w, 1029 m, 1018 m, 941 m, 933 w, 782 m, 698 w, 655 vw, 628 m cm⁻¹.

(π -C₂H₃OH)(acac)PtCl, Preparation via the β -Oxoethyl Complex. A THF solution of chloro(acetylacetonato)(ethylene)platinum(II) (31.03 mg, 86.8 μ mol, in 10 ml of solvent) was prepared and cooled to 0°. To this solution 2 ml of freshly distilled acetaldehyde was added, followed by 0.2 ml of 0.66 *N* aqueous KOH (132 μ mol). On addition of the base the pale yellow solution deepened in color and a slight effervescence was noted. After 30 min at 0°C, the solvent was evaporated under reduced pressure, giving an oily, yellow-brown residue. This was dissolved in 2 ml of methanol followed by the addition of an equal volume of 1:1 ether-hexane. After

cooling at -10° , greenish yellow crystals of $K[(\beta\text{-oxoethyl})(\text{acac})\text{PtCl}]$ were filtered off, washed with ether, and dried *in vacuo*, yield 18.17 mg (52.5%, 170–175° dec (yellow to black)). Repeated recrystallization results in a bright yellow product.

This is converted to the desired π -enol complex by dissolution in a minimum amount of water and acidification with 3 *N* HCl nearly quantitatively precipitating $(\pi\text{-C}_2\text{H}_3\text{OH})(\text{acac})\text{PtCl}$.

$(\pi\text{-C}_2\text{H}_3\text{OH})(\text{acac})\text{PtCl}$, Preparation via the β -Oxopropyl Complex. (a) **β -Oxopropyl Complex.** Aqueous potassium hydroxide, 0.5 ml of 0.680 *N* (340 μmol), was added to an acetone solution of chloro(acetylacetonato)(ethylene)platinum(II), 100.7 mg (282 μmol) in 10 ml of acetone. After 30 min at room temperature, the solution was evaporated to dryness under reduced pressure. The resulting yellow crystalline residue, thoroughly dried *in vacuo*, was then dissolved in a minimum amount of warm acetone and recrystallized by slowly adding an equal volume of 1:1 ether–hexane and cooling at 0° , yield of potassium chloro(acetylacetonato)(β -oxopropyl)platinum(II) 105 mg (87.5%), 158–172° dec (yellow to black). *Anal.* Calcd for $K[\text{C}_8\text{H}_{12}\text{O}_3\text{PtCl}]$: C, 22.6; H, 2.84; Pt, 45.8; Cl, 8.33. Found: C, 22.8; H, 2.68; Pt, 46.6; Cl, 9.46. Infrared spectrum (KBr pellet, Beckman IR-8): 3090 w, 3020 w, 2960 m, 2920 m, 2840 w, 1645 s, 1560 s, 1540 s, 1520 s, 1425 s, 1383 s, 1362 s, 1348 s, 1275 m, 1248 s, 1202 m, 1108 m, 1073 m, 1028 m, 1015 m, 1007 m, 960 w, 944 w, 924 w, 778 s, 697 w, 657 w, 646 w, 627 s cm^{-1} . Proton nmr spectrum (Varian T-60, in D_2O vs. external TMS): 2.42 (6 H_a , s), 2.75 (3 H_b , s), 3.94 (2 H_c , s), and 6.16 (1 H_d , S) ppm. Each singlet was accompanied by ^{195}Pt satellites, and the observed ^{195}Pt -H coupling constants were <5, 18, 116 and 8 Hz, respectively.

(b) **π -Propen-2-ol Complex.** To a suspension of 50.03 mg (117 μmol) of the β -oxopropyl complex in 17 ml of dry ether was added 0.35 ml of dry THF (0.40 *M*) in HCl (140 μmol of HCl). The mixture was stirred for 30 min at room temperature. Then the yellow ether solution was decanted from the residue of unprotonated starting material and evaporated under reduced pressure to a volume of 1 ml. To this, 2 ml of hexane was slowly added and the solution was then cooled at -18° , producing a light yellow crystalline precipitate. This was washed twice under argon with dry 1:3 ether–hexane and dried *in vacuo*, yield 18.09 mg (60.7%, based on unrecovered starting material), 81–83° dec (yellow-orange), 165–185° dec (orange-black). *Anal.* Calcd for $\text{C}_8\text{H}_{13}\text{OPtCl}$:

C, 24.8; H, 3.38; Pt, 50.7. Found: C, 24.4; H, 3.54; Pt, 51.5. Infrared spectrum (KBr pellet, Beckman IR-8): 3230 m, 3040 w, 2970 w, 2930 w, 1560 s, 1530 s, 1425 m, 1385 s, 1362 s, 1278 m, 1218 m, 1200 m, 1028 m, 982 w, 953 m, 935 w, 858 w, 828 m, 780 m, 702 w, 671 w, 643 cm^{-1} . Proton nmr spectrum (Varian T-60, in CDCl_3): 1.88 (3 H_a , s), 2.02 (3 H_b , s), 2.03 (3 H_c , s), 3.96 (2 H_d , s), 5.42 (1 H_e , s) ppm. Each singlet was accompanied by ^{195}Pt satellites and the observed ^{195}Pt -H coupling constants were ~ 6 , 44, <5, 78, and 8 Hz, respectively.

$(\pi\text{-C}_2\text{H}_3\text{O})(\text{PPh}_3)_2\text{PtCl}$, Preparation of. A dry benzene solution of $\text{Pt}(\text{Ph}_3)_4$, 0.97 g (0.84 mmol) in 10 ml of solvent, was treated with 2.5 mmol of ClCH_2CHO and 2 ml of dry methylene chloride 1.25 *M* in chloroacetaldehyde. After 30 min at room temperature 10 ml of 1:1 ether–heptane was added to the reaction mixture, and the white crystalline product was filtered off, yield 0.57 g (85%), mp 218–220°. *Anal.* Calcd for $\text{C}_{38}\text{H}_{33}\text{OP}_2\text{PtCl}$: C, 57.18; H, 4.17; P, 7.76; Cl, 4.44. Found: C, 57.07; H, 4.20; P, 7.75; Cl, 4.68. Infrared spectrum (KBr pellet, Beckman IR-8): 3090 m, 2970 w, 2820 w, 2720 w, 1650 s, 1480 m, 1430 s, 1380 w, 1308 w, 1183 w, 1158 w, 1140 m, 1090 s, 1025 w, 998 m, 847 w, 755 m, 742 s, 699 s, 690 s cm^{-1} . Proton nmr spectrum (Varian HA-100, in CDCl_3): The methylene protons (H_a) appeared as a seven-line multiplet at 2.76 ppm with ^{195}Pt satellites, the phenyl protons appeared between 7.0 and 7.6 ppm, and the aldehydic proton (H_b) appeared as a triplet at 9.93 ppm with ^{195}Pt satellites. The observed coupling constants were $J_{\text{P}-\text{H}_a(\text{trans})} = 11.0$, $J_{\text{P}-\text{H}_a(\text{cis})} = 6.2$, $J_{\text{Pt}-\text{H}_a} = 70$, $J_{\text{Pt}-\text{H}_b} = 16$, and $J_{\text{H}_a-\text{H}_b} = 4.7$ Hz.

$(\pi\text{-C}_2\text{H}_3)(\text{PPh}_3)\text{PtCl}$, Attempted Conversion to $(\pi\text{-C}_2\text{H}_3\text{OH})(\text{PPh}_3)_2\text{PtCl}$. A 20-mg sample of the β -oxoethyl complex was dissolved in 0.5 ml of CDCl_3 and the nmr spectrum was observed as 1 equiv of dry HCl gas was added in aliquots at 25° . The signals of the β -oxoethyl group were progressively replaced by the doublet-quartet pattern of acetaldehyde, and a white precipitate of $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ formed.

$K[(\sigma\text{-acac})(\text{acac})\text{PtCl}]$ and $(\pi\text{-acac})(\text{acac})\text{PtCl}$, Preparation of. These complexes were prepared *via* the procedures described by Holloway, Hulley, Johnson, and Lewis.⁸

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Structure of *trans*-Chlorobis(triethylphosphine)-(*p*-fluorophenyldiazene)platinum(II) Perchlorate

Steven D. Ittel and James A. Ibers*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received December 26, 1973

Abstract: The structure of the title compound $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{HNNC}_6\text{H}_4\text{F})\text{Cl}][\text{ClO}_4]$ has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final *R* index (on *F*) of 0.052 based on 4292 observations above background. The material crystallizes in the triclinic space group C_2^1-P1 with two molecules in a cell of dimensions $a = 9.167$ (2) \AA , $b = 16.983$ (3) \AA , $c = 8.947$ (2) \AA , $\alpha = 91.46$ (1)°, $\beta = 96.34$ (1)°, and $\gamma = 77.04$ (1)°. The platinum atom has square-planar coordination. The *cis* diazene moiety lies in a plane roughly perpendicular to the coordination plane and its phenyl group is twisted to relieve steric interaction with the diazene proton. The diazene proton, which was refined, also has a close contact with the perchlorate anion. This compound, formed by protonation of an aryldiazonium complex of platinum, is the first aryldiazene complex to be structurally characterized and is an intermediate in a proposed model system for nitrogen fixation.

Transition metal complexes of aryldiazoniums can exist in three modes of coordination, the predominant canonical forms of which are shown in Figure 1. Several complexes of the singly bent diazenido (type B) have been characterized structurally.^{1–4} (The

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