The Chemistry of Low-Valent Complexes. II.[1] Cyclic Azo Derivatives of Platinum

C. D. Cook and G. S. Jauhal

Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Canada. *Received September 20, 1967*

Abstract: Attempts have been made to stabilize benzyne by coordination to zerovalent platinum complexes. Thermal decomposition in solution of benzyne precursors in the presence of platinum(0) complexes is not a feasible route to a benzyne derivative of platinum, since coordination of the precursors to the metal atom interferes. The resulting five- and six-membered heterocycles containing platinum show interesting properties, however, including an example of S- and O-bonded linkage isomerism. Infrared spectroscopy has enabled structural assignments to be made, and the electronic spectra of some of the complexes suggest that considerable aromatic character is possessed by the six-membered heterocyclic systems.

Following Vaska[2] and Collman,[3] a number of workers have initiated investigations of the so-called "unsaturated" phosphine-stabilized group VIII metal complexes. Examples of this type of complex are the square-planar derivatives of iridium(I) and rhodium(I) and the less fully investigated d^{10} derivatives of zerovalent nickel,[4] palladium,[5] and platinum.[6] The former group of complexes maintain their stoichiometry in solution and add a variety of covalent molecules to yield in general six-coordinated d^6 derivatives. It has been known for several years that d^{10} complexes of the type $Pt(PPh_3)_4$ behave similarly in adding oxidatively covalent molecules. It was recognized, however, from cryoscopic[7,8] measurements and nmr spectroscopy[9] that such reactions were somewhat complicated, inasmuch as the tetrakis(phosphine) complexes were extensively dissociated in solution, apparently to the dicoordinated complex, $Pt(PPh_3)_2$. In order to extend the chemistry of these low-valent platinum derivatives, specifically into the area of adduct formation, it was therefore essential to isolate the dicoordinated complex in order to permit studies of its behavior in solution in the absence of tertiary phosphine ligand(s). Our interests were essentially twofold: firstly, to investigate the range of adduct formation and to attempt to correlate the behavior of such complexes in solution with that of a metal surface (this similarity having been commented upon[10] several years earlier by Pearson), and, secondly, to attempt to stabilize short-lived organic intermediates, *e.g.*, benzyne, by coordination to the metal atom.

Our inability to isolate bis(triphenylphosphine)-platinum(0) by conventional techniques (recently accomplished[11] in Milan) prompted us to investigate a report[12] by Japanese workers of an isolable complex described as the oxygen adduct of tetrakis(triphenylphosphine)platinum(0) and formulated as $(PPh_3)_3PtO_2$.

Passage of oxygen through a benzene solution of tetrakis(triphenylphosphine)platinum(0) resulted in the rapid precipitation of the adduct $(PPh_3)_2PtO_2$, containing one molecule of benzene of crystallization. When freshly prepared, the adduct is soluble in ethanol, an important feature for the synthetic work and a characteristic not normally possessed by triphenylphosphine derivatives of platinum. The complex in alcohol solution can be reduced with sodium borohydride in the presence of ethylene to yield the stable derivative, $(PPh_3)_2Pt(C_2H_4)$. This complex has been shown to be isomorphous with the nickel[13a] analog, $(PPh_3)_2Ni(C_2H_4)$, the structure of which is known.[13b]

The reduction of the oxygen adduct constituted a useful route to the *in situ* generation of the bis(triphenylphosphine) complex, and this route was complemented by utilization of the ethylene adduct $(PPh_3)_2Pt(C_2H_4)$. Although stable in the solid state, the ethylene adduct in benzene solution loses ethylene readily when treated with a wide range of reagents, and this technique allowed a variety of reactions (presumably of the dicoordinated complex) to be investigated, which would otherwise have been precluded by the $NaBH_4$–ethanol medium.

We have dealt briefly with some aspects of adduct formation[14] and the subsequent oxidation[15] under mild conditions which the majority of the adducts undergo. We are currently investigating in detail the factors influencing the stability and general chemistry of complexes of this type and will publish a full report shortly.

The second phase of our investigation concerned the stabilization of benzyne by coordination to the bis(triphenylphosphine)platinum complex. To our knowledge only one previous attempt to stabilize benzyne is recorded in the literature. Winkler and Wittig[16] studied the reaction between *o*-dilithiobenzene and dichlorobis(triphenylphosphine)platinum(II) and, al-

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[1] Part I: C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).

[2] L. Vaska, *Science*, **140**, 809 (1963).

[3] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965).

[4] P. Heimbach, *Angew. Chem. Intern. Ed. Engl.*, **3**, 648 (1964).

[5] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

[6] L. Malatesta and C. Cariello, *ibid.*, 2323 (1958).

[7] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

[8] L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963).

[9] C. D. Cook, Ph. D. Thesis, University of Toronto, 1962.

[10] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963); see also *Chem. Britain*, **3**, 103 (1967).

[11] R. Ugo, F. Cariati, and G. LaMonica, *Chem. Commun.*, 868 (1966).

[12] K. Sonogashira and N. Hagihara, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **22**, 165 (1965); S. Takahushi, K. Sonogashira, and N. Hagihara, *J. Chem. Soc. Japan*, **87**, 610 (1966).

[13] (a) G. Wilke and G. Hermann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 549 (1965); (b) C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967).

[14] C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, **3**, 31 (1967).

[15] C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **89**, 3066 (1967).

[16] H. J. S. Winkler and G. Wittig, *J. Org. Chem.*, **28**, 1733 (1963).

Table I. Infrared Spectral Data[a]

Complex	ν_{NN}, cm^{-1}	$\nu_{CO(asym)}$, cm^{-1}	$\nu_{CO(sym)}$, cm^{-1}	$\nu_{SO(asym)}$, cm^{-1}	$\nu_{SO(sym)}$, cm^{-1}
3	1517	1630	1314	. . .	. . .
4	. . .	1646, 1620	1305, 1298	. . .	. . .
5	1446	. . .	. . .	1285	1159, 1136
6	1527	. . .	. . .	1203	1042, 1014
7	. . .	. . .	. . .	1178	1045
8	. . .	. . .	. . .	1274	1164, 1151
9	1444	. . .	. . .	. . .	. . .

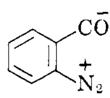
[a] See ref 21.

though observing lithium chloride elimination, found no evidence for the formation of benzyne derivatives.

Chatt, *et al.*,[17] reported that olefinic derivatives of platinum(0) of the type $(PPh_3)_2Pt(olefin)$ reacted readily with acetylenes to yield the considerably more stable acetylenic complexes $(PPh_3)_2Pt(acetylene)$. We have confirmed this observation and have utilized in particular the ethylene adduct, $(PPh_3)_2Pt(C_2H_4)$, in attempts to capture the pseudo-acetylene, benzyne, by complexation. We decided on the simple procedure of thermal decomposition of zwitterionic phenyldiazonium derivatives[18] in the presence of a benzene or toluene solution of $(PPh_3)_2Pt(C_2H_4)$.

Results

Although a number of procedures have been developed for the generation of benzyne under mild aprotic conditions, only two[19,20] proved to be useful in this study, namely, the thermal decomposition of benzenediazonium-1,2-carboxylate (**1**), and of benzo-1,2,3-thiadiazole 1,1-dioxide (**2**).



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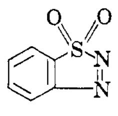
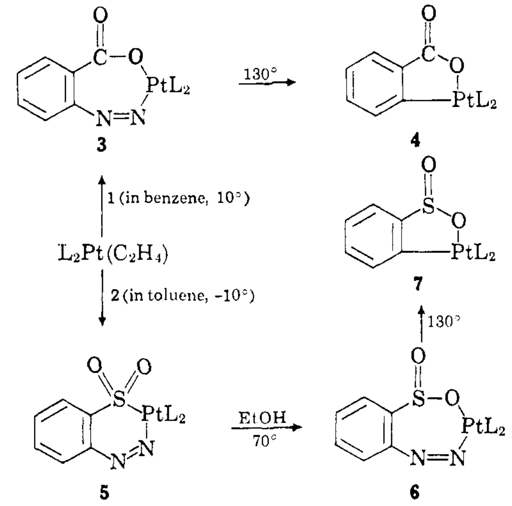


2

Reaction of these benzyne precursors with benzene solutions of $(PPh_3)_2Pt(C_2H_4)$ followed essentially similar paths, and a summary of our interpretation of the data is given in Scheme I. The relevant spectral data concerning complexes 3–7 are contained in Tables I[21] and II.

Scheme I



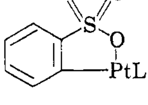
L = triphenylphosphine

The ease with which aryl sufinates undergo oxidation to sulfonates, coupled with the recently demonstrated efficacy[15,23] of ligand oxidation in the presence of Pt(0) complexes, suggested that adventitious ligand oxidation might be a complicating feature of our system. To this end we synthesized complex **8** for comparative purposes.

Table II. Visible and Near-Ultraviolet Spectral Data

Complex	Color	λ, mμ	ε	λ, mμ	ε
3	Red-brown	491	290	388	5,870
5	Yellow	570	90	404	11,650
6	Mauve	567	330	390	7,600
9	Green	557	230	409	8,690

Reaction between $(PPh_3)_2Pt(C_2H_4)$ and benzenediazonium-2-sulfonate results in concurrent ethylene and nitrogen loss and formation of complex **8** slowly but in high yield.



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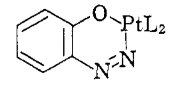

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L = triphenylphosphine

Complex **9** was prepared (by reaction of $(PPh_3)_2Pt(C_2H_4)$ with diazonium-2-phenolate) in order to strengthen our discussions concerning the electronic

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(17) J. Chatt, B. L. Shaw, and A. A. Williams, *J. Chem. Soc.*, 3269 (1962).

(18) M. C. Baird and G. Wilkinson, *J. Chem. Soc., Sect. A.*, 865 (1967). These authors report that a related reaction between $(PPh_3)_3Pt$ and *p*-$FC_6H_4N_2BF_4$ results in general decomposition of the reactants.

(19) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(20) G. Wittig and R. W. Hoffman, *Chem. Ber.*, **95**, 2718 (1962).

(21) A referee made the useful comment that the spectral region below 600 cm^{-1} would yield valuable supporting evidence for the proposed structures if Pt–O, Pt–S, Pt–C, and Pt–N stretching frequencies could be located and assigned. Unfortunately, much of this region is obscured by the presence of two strong, broad absorptions at 410–450 and 490–535 cm^{-1}. The latter band pattern is found in triphenylphosphine at 480–510 cm^{-1} and somewhat higher in seemingly all-platinum(II) complexes thereof. The 410–450-cm^{-1} band has been assigned[7] to the Pt–P stretching vibration. In addition, we are somewhat wary of attempting band assignments based on "known" group frequencies since, as stressed by Nakamoto,[22] coupling between various vibrational modes in a resonating system could, and frequently does, lead to major changes in the anticipated positions of the bands in question.

(22) K. Nakamoto, "Infrared Spectra of Inorganic Complexes," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 201–205.

(23) J. J. Levison and S. D. Robinson, *Chem. Commun.*, 198 (1967); C. J. Nyman, C. E. Wymore, and G. Wilkinson, *ibid.*, 407 (1967); G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Intern. Ed. Engl.*, **6**, 92 (1967).

spectra and thermal stabilities of six-membered heterocycles containing platinum (*vide infra*). Pertinent spectral characteristics of complexes **8** and **9** are contained in Tables I and II.

Further to the main purpose of the investigation, attempts were made to achieve concurrent N_2 and SO_2 elimination from complex **5** by ultraviolet irradiation in benzene solution. In all attempts considerable decomposition of the complex was observed, and the only material isolated (in small yield) was the sulfato complex $(PPh_3)_2PtSO_4$.

Discussion

In assigning structures **3**–**9** we have relied heavily upon infrared spectroscopy. The band assignments contained in Table I are consistent with the structures as shown and are in good agreement with published data on related systems. A medium-strong band found in the 1450–1530-cm^{-1} region in the spectra of complexes **3**, **5**, **6**, and **9** may be assigned to the N=N stretching vibration.[24] The band disappears on mild heating (complexes **3** and **6** only), and its position is in reasonable agreement with that[25] found (1555 cm^{-1}) for the N=N absorption in the heterocycle, 3,5-bis(*p*-methoxyphenyl)-1-pyrazoline.

The infrared spectra of the carboxylato derivatives (complexes **3** and **4**) are characterized by two strong bands at approximately 1630 and 1300 cm^{-1}, strongly resembling in position and intensity bands found in the spectra of a wide variety of chelated amino acid metal complexes.[22] These two bands clearly arise from the antisymmetric and symmetric OCO stretching vibrations.

Support for the proposed transformation of complex **3** to **4** comes from mass spectral identification of nitrogen evolved on heating complex **3**, the disappearance of the 1517-cm^{-1} band (N=N stretch), and the essential similarity of the absorptions attributable to the OCO stretching modes.

The thermally stable complex **5** can be differentiated from its O-bonded isomer (complex **6**) by the position of the OSO antisymmetric stretch (1285 cm^{-1}), found at 1274 cm^{-1} in the sulfito[26] and 1279 cm^{-1} in the sulfato complexes[15] of platinum(II). Sulfinate–sulfone rearrangements[27] have been studied previously, but to our knowledge linkage isomerism[28] involving S- to O-bonded rearrangement has not been reported. Chiswell and Venanzi[29] have recently prepared a series of benzenesulfinate complexes of palladium and found in all cases the ligand to be sulfur bonded. However, these workers did observe ready displacement of coordinated sulfinate by chloride ion, a fact apparently at variance with predictions based on "hard" and "soft" criteria.[10] It was suggested that electronic effects induced by the other, specifically nitrogen chelate, ligands result in a hardening of the metal ion. In our case a similar rationalization might be invoked since Parshall[30] has recently shown by nmr spectroscopy that electrons are transferred effectively from the platinum to the ring of a coordinated phenylazo group in the complex *p*-$FC_6H_4N_2PtCl(PEt_3)_2$. The "hardening" of the metal atom consequential upon this electron transfer could conceivably be the controlling factor in the observed isomerization reaction in our system.

The thermal conversion of complex **6** to complex **7** involves nitrogen loss, disappearance of the 1526-cm^{-1} band, and no profound frequency shifts for the antisymmetric and symmetric stretching modes. The structural proposals would therefore appear to be reasonable.[31]

Oxidation of the various sulfinate complexes to sulfito derivatives did not occur: complex **7** is similar to the sulfito derivative (complex **8**) in both composition and physical properties, but the two complexes are clearly distinguishable on the basis of their ir spectra and powder photographs.

Complexes **5** and **9** showed a similar, unusually high, thermal stability relative to complexes **3** and **6** which lose nitrogen easily on heating. For example, heating complexes **5** and **9** at 130° for 24 hr caused no changes in the spectra of the complexes or in the analytical (nitrogen) data. The evident stability of the six-membered heterocycles in complexes **5** and **9** prompted a study of the electronic spectra of these and related complexes. The results (for the visible–near-ultraviolet region) are given in Table II.

The azo linkages are evidenced by weak absorptions in the range 491–570 mμ, similar in position and intensity to those reported by Parshall.[30] Intense bands, resulting from electronic transitions associated with the phenyl rings, are encountered at higher energy in the spectra, the first of these occurring at approximately 50 mμ to longer wavelength than the analogous bands in noncyclic azo complexes. Furthermore, the band in complex **5** shows an appreciable (14 mμ) shift to longer wavelength when compared with the same band in complex **6**, as well as exhibiting greatly enhanced intensity in the former case. These data suggest electron delocalization in the six-membered heterocyclic systems containing the platinum atom. This conclusion is further supported by the relative positions, in the infrared spectra, of the bands resulting from the N=N stretching vibrations in six- and seven-membered heterocycles. In complex **5** (Table I) the frequency of the N=N band is some 80 cm^{-1} lower than in complex **6**, again indicating effective delocalization in the former case. Complexes **9** and **3** show a similar (70 cm^{-1}) difference in the position of the N=N band. The aromaticity of five-membered cyclic systems incorporating the platinum atom has been invoked[32] to explain atypical kinetic data, and a similar conclusion regarding the six-membered analogs under discussion is indicated by our findings.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer. Mulled samples of the complex using Nujol or

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(24) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3272 (1965), report a band at 1580 cm^{-1} which occurs in azobenzene–platinum complexes and which possibly results from N–N stretching vibrations; see also J. P. Kleiman and M. Dubeck, *ibid.*, **85**, 1544 (1963).

(25) C. G. Overberger, N. Weinshenker, and J. P. Anselme, *ibid.*, **86**, 5364 (1964).

(26) G. Newman and D. B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).

(27) S. Braverman and H. Mechoulam, *Israel J. Chem.*, **4**, 17p (1966).

(28) F. Basolo, J. L. Burmeister, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 1700 (1963).

(29) B. Chiswell and L. M. Venanzi, *J. Chem. Soc., Sect. A*, 1246 (1966).

(30) G. W. Parshall, *J. Am. Chem. Soc.*, **87**, 2133 (1965).

(31) G. B. Deacon, *Australian J. Chem.*, **20**, 1367 (1967).

(32) P. Haake and P. A. Cronin, *Inorg. Chem.*, **2**, 879 (1963).

Fluorolube S-30 (Hooker Chemical Co.) were employed throughout. Visible–uv spectra were recorded on a Bausch and Lomb 505 spectrophotometer. Microanalyses were performed by Hoffman Laboratories Inc., Wheatridge, Colo., and A. B. Gygli Microanalysis Laboratory, Toronto. The complexes (**3–9**) were essentially nonconductors of electricity in organic solvents (Industrial Instruments conductivity bridge, RC 18).

Bis(triphenylphosphine)(oxygen)platinum. Tetrakis(triphenylphosphine)platinum (25 g), prepared from 16 g of dichlorobis(triphenylphosphine)platinum(II) by the method of Malatesta and Cariello,[6] was dissolved in the minimum volume of benzene. A rapid stream of oxygen was passed through the solution, and after 20 min the precipitated product, containing benzene of crystallization, was filtered and washed with benzene and hexane, yield 12.0 g, mp 130–132° dec.

Anal. Calcd for $C_{36}H_{30}P_2PtO_2 \cdot C_6H_6$: C, 60.79; H, 4.34. Found: C, 60.38; H, 4.38.

Bis(triphenylphosphine)(ethylene)platinum. The oxygen adduct (12 g) was dissolved in 200 ml of ethanol and the solution saturated with ethylene. Dropwise addition of 80 ml of a 0.1 *M* solution of sodium borohydride in ethanol over a period of 20 min accompanied further passage of ethylene through the solution. The off-white crystalline ethylene adduct precipitated and was filtered, washed with water, alcohol, and hexane, and dried in the air, yield 10.4 g, mp 122–125°.

Anal. Calcd for $C_{38}H_{34}P_2Pt$: C, 61.04; H, 4.55. Found: C, 61.30; H, 4.81.

The nmr spectrum of the ethylene adduct (in deuteriochloroform, TMS as internal standard) showed the expected triplet (peak ratio 1:4:1) centered at τ 7.85 ($J_{\mathrm{Pt-H}}$ = 62 cps; the proton–P^{31} coupling was not resolved).

Complex 3. To a benzene solution of bis(triphenylphosphine)-(ethylene)platinum was added with stirring 1 equiv of benzenediazonium-2-carboxylate. A red-brown precipitate formed immediately and after 15 min was filtered, washed (water and ether), and recrystallized from boiling acetone, mp 262–266° (decolorizing at 110–120°).

Anal. Calcd for $C_{43}H_{34}N_2O_2P_2Pt$: C, 59.52; H, 3.92; N, 3.20. Found: C, 59.46; H, 4.22; N, 3.03.

Complex 4. Heating complex **3** at 130° for 1 hr resulted in loss of nitrogen and formation of a white crystalline complex, mp 262–266°.

Anal. Calcd for $C_{43}H_{34}O_2P_2Pt$: C, 61.50; H, 4.50; N, 0.0. Found: C, 61.53; H, 4.17; N, 0.0.

Complex 5. To a toluene solution of $(PPh_3)_2Pt(C_2H_4)$ cooled to −10° was added, with stirring a toluene solution of 1 equiv of benzo-1,2,3-thiadiazole 1,1-dioxide, also cooled to −10°. A yellow precipitate formed rapidly, and after 10 min was filtered and washed with toluene, ether, and hexane. The complex was recrystallized from acetone, mp 175–179°.

Anal. Calcd for $C_{42}H_{34}N_2O_2P_2SPt$: C, 56.82; H, 3.83; N, 3.16. Found: C, 56.27; H, 3.89; N, 3.12.

Complex 6. A solution of complex **5** in hot (70°) ethanol darkened rapidly (yellow to deep blue) and on cooling precipitated complex **6** as beautiful mauve crystals, mp 220–223° (with loss of color at 120–130°).

Anal. Calcd for $C_{42}H_{34}N_2O_2P_2SPt$: C, 56.82; H, 3.83; N, 3.16. Found: C, 56.97; H, 3.90; N, 3.04.

Complex 7. Heating complex **6** at 130° for 1 hr resulted in loss of nitrogen and formation of the white crystalline complex **7**, mp 227–229°. The complex can be recrystallized from methylene chloride–hexane.

Anal. Calcd for $C_{42}H_{34}O_2P_2S$: C, 58.67; H, 3.98; N, 0.0. Found: C, 58.22; H, 3.97; N, 0.0.

Complex 8. Prepared in a similar manner to complex **5**, the mixture of $(PPh_3)_2Pt(C_2H_4)$ and benzene diazonium-2-sulfonate[33] in benzene was stirred overnight under nitrogen and the white crystalline product isolated by filtration, mp 255–260°.

Anal. Calcd for $C_{42}H_{34}O_3P_2SPt$: C, 57.67; H, 3.91; N, 0.0. Found: C, 58.04; H, 3.73; N, 0.0.

Complex 9. A solution of diazonium-2-phenolate[34] at 0° in amyl alcohol was added to a benzene solution containing 1 equiv (based on a 90% yield in the diazotization reaction) of $(PPh_3)_2$-$Pt(C_2H_4)$. The deep green crystalline complex separated rapidly, and after 15 min the mixture was filtered, mp 175–180°.

Anal. Calcd for $C_{42}H_{34}N_2OP_2Pt$: C, 60.07; H, 4.52; N, 3.34. Found: C, 60.62; H, 4.54; N, 3.36.

Acknowledgment. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

(33) D. Gerilowski, *Chem. Ber.*, **29**, 1075 (1896).

(34) J. D. C. Anderson, R. J. W. LeFevre, and I. R. Wilson, *J. Chem. Soc.*, 2082 (1949).