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Note

Base-promoted synthesis of monometallic and bimetallic platinum complexes containing chelating O,O- or S,S-donor ligands

Ngamjit Praingam, Gordon K. Anderson *, Nigam P. Rath

Department of Chemistry and Biochemistry, University of Missouri-St. Louis, One University Boulevard, St. Louis, MO 63121, USA

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Abstract

Dichloroplatinum complexes $[PtCl_2L_2]$ (L_2 = cod, dppp) react with 1,2-$C_6H_4E_2$ (E = O, S) in the presence of a base to produce mononuclear complexes. The diene was not readily displaced from $[Pt(E_2C_6H_4\text{-}EE)(cod)]$. A second approach to complexes containing dianionic chelating ligands involved $[Pt(acac)_2]$ as precursor. Reaction with dppp and oxalic acid gave $[Pt(C_2O_4)(dppp)]$, whereas the analogous reaction with $Ph_2PC{\equiv}CPPh_2$ produced the bimetallic complex $[Pt(C_2O_4\text{-}OO)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$. Similar reactions with 1,2-$C_6H_4E_2$ (E = O, S) also gave bimetallic products. The structures of $[Pt(C_2O_4)(dppp)]$ and $[Pt(C_2O_4\text{-}OO)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$ have been determined by X-ray crystallography.

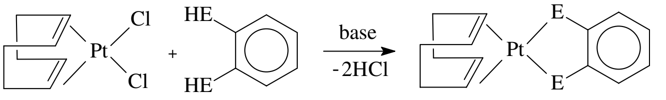
Keywords: Platinum complexes; Oxalate complexes; Bimetallic complexes; Chelate complexes; X-ray crystal structure

1. Introduction

The design of transition metal molecular squares typically has involved the use of square planar complexes with chelating ligands that occupy mutually *cis* positions, thereby forcing the potential bridging groups to also adopt 90° angles with respect to each other [1–4]. Charged molecular squares have been prepared using platinum(II) or palladium(II) centers with chelating diamine or diphosphine ligands and linear linkers such as 4,4′-bipyridine [5–19]. We recognized that neutral molecular squares could be generated either by incorporating neutral chelating ligands and dianionic linkers, or through the use of dianionic chelating groups and neutral bridging moieties. We and others have shown previously that neutral squares may be generated with diphosphineplatinum corner units and butadiynyl edges [20–22]. In this paper we report on two methods aimed at the generation of platinum(II) centers with chelating dianionic ligands (which might subsequently be used to prepare neutral squares), and their initial use to prepare monometallic and bimetallic derivatives.

2. Results and discussion

Treatment of $[PtCl_2(cod)]$ with 1,2-dihydroxybenzene (catechol) or benzene-1,2-dithiol in methanol, in the presence of KOH or Et_3N, results in proton abstraction from the –OH or –SH groups and displacement of the chlorides from platinum to give $[Pt(E_2C_6H_4\text{-}EE)(cod)]$ (E = O, S) (Eq. (1)). The reaction to form the thioplatinum derivative occurs more rapidly, since the softer $C_6H_4S_2^{2-}$ anion is a better ligand towards platinum(II). Similarly, reactions of $[PtCl_2(dppp)]$ generate the corresponding $[Pt(E_2C_6H_4\text{-}EE)(dppp)]$ complexes, the thioplatinum species again being produced more rapidly.



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[*] Corresponding author. Present address: College of Arts and Sciences, East Tennessee State University, Johnson City, TN 37614, USA. Tel.: +1 423 439 5671; fax: +1 423 439 4565.
E-mail address: andersgk@etsu.edu (G.K. Anderson).

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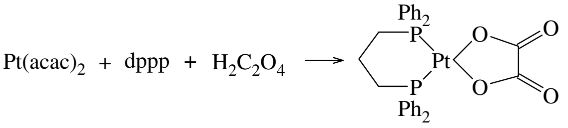
The complexes have been characterized by NMR spectroscopy and mass spectrometry and, for the cyclooctadiene complexes, they have been confirmed by X-ray crystallography. The ^{1}H and ^{13}C NMR spectra of the cod complexes show the expected NMR signals for the diene and the aromatic ligand; those for the dppp complexes are less informative due to the broad signals arising from the diphosphine. The ^{31}P NMR spectra of $[Pt(E_2C_6H_4\text{-}EE)(dppp)]$ (E = O, S) each consist of a single resonance that exhibits coupling to ^{195}Pt; the $^{1}J_{PtP}$ couplings of 3318 and 2665 Hz, respectively, illustrate the greater *trans*-influence of the S-containing ligand [23]. The cyclooctadiene complexes $[Pt(1,2\text{-}E_2C_6H_4\text{-}EE)(cod)]$ (E = O, S) do undergo protonation under FAB conditions and provide satisfactory high-resolution mass spectra, but they ionize more efficiently in the presence of $AgOCOCF_3$. In the case of $[Pt(1,2\text{-}S_2C_6H_4\text{-}SS)(cod)]$, clusters of peaks are found for $M + Ag^+$, $M + AgOCOCF_3 + Ag^+$ and $2M + Ag^+$, in addition to those for $M + H^+$, indicating that extensive chemistry takes place in the gas phase. The molecular structures of $[Pt(1,2\text{-}E_2C_6H_4\text{-}EE)(cod)]$ (E = O, S) have been reported previously [24,25]. To confirm the identities of these complexes here, their structures were determined by X-ray crystallography.

We postulated that displacement of the diene from $[Pt(E_2C_6H_4\text{-}EE)(cod)]$ (E = O, S) by linear bidentate ligands, such as 4,4′-bipyridine or bis(diphenylphosphino)ethyne, might provide a method for the generation of neutral molecular squares with chelating dianionic corner groups. Even reactions with chelating diphosphine ligands, such as dppe or dppp, to generate mononuclear complexes do not proceed cleanly, however, so we decided to consider a second approach.

Our second synthetic strategy was to use $[Pt(acac)_2]$ as the starting material. First, we sought to determine if this method could be used to prepare mononuclear complexes. When an acetone suspension of $[Pt(acac)_2]$ is treated with $1,2\text{-}C_6H_4(EH)_2$ (E = O, S) or oxalic acid in the presence of dppp, acetylacetone is formed along with the chelated platinum complex. This is illustrated for the case of oxalic acid in Eq. (2). The oxalate complex has been characterized by NMR spectroscopy and by X-ray crystallography. Its ^{1}H and ^{13}C NMR spectra are quite 2uninformative, whereas $[Pt(C_2O_4)(dppp)]$ exhibits a single ^{31}P resonance at −10.2 ppm, with $^{1}J_{PtP} = 3451$ Hz [26]. Its solid state structure (Fig. 1) reveals the anticipated planar geometry (the sum of the angles around platinum is 360.0°), the smaller O–Pt–O angle of the chelated oxalate being balanced by the larger bite angle of the dppp ligand. The solid state structures of the analogous oxalate complexes $[Pt(C_2O_4)L_2]$ (L_2 = dppm, dppf) have been reported previously [27,28].



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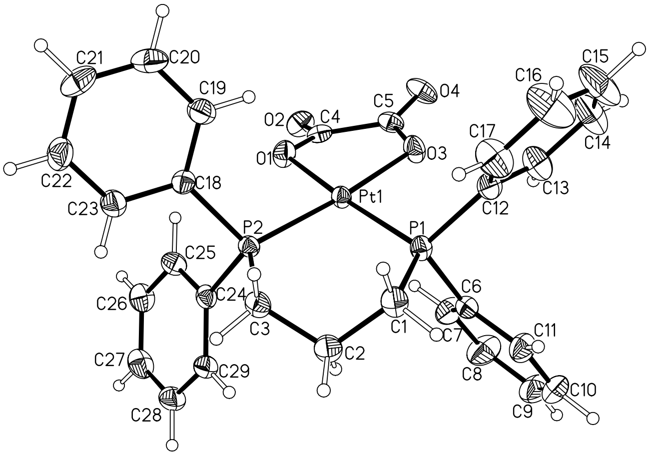
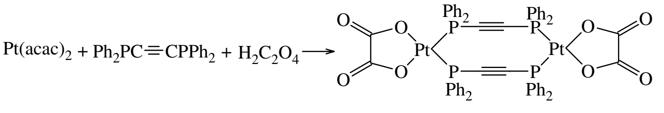


Fig. 1. Molecular structure of $[Pt(C_2O_4\text{-}OO)(dppp)]$. Selected bond distances (Å) and angles (°): Pt–P(1) 2.2245(8), Pt–P(2) 2.2244(8), Pt–O(1) 2.065(2), Pt–O(3) 2.064(2); P(1)–Pt–P(2) 96.45(3), P(1)–Pt–O(1) 170.94(7), P(1)–Pt–O(3) 90.51(7), P(2)–Pt–O(1) 91.27(7), P(2)–Pt–O(3) 172.99(7), O(1)–Pt–O(3) 81.72(9).

Mononuclear complexes are formed, as expected, in the case of dppp. The rigid nature of bis(diphenylphosphino)ethyne, $Ph_2PC{\equiv}CPPh_2$, should preclude chelation, and it appeared possible that it would provide tetrametallic species. Spectroscopic and crystallographic data, however, of the product obtained by the analogous reaction shown in Eq. (3), and those involving $1,2\text{-}C_6H_4(EH)_2$ (E = O, S), indicate that bimetallic species are produced. The oxalate complex formed with $Ph_2PC{\equiv}CPPh_2$ contains a single resonance, with ^{195}Pt satellites, in its ^{31}P NMR spectrum, indicating that it has a symmetrical structure. Its molecular structure (Fig. 2) confirms its dimeric nature, the two platinum-oxalate units being bridged by two diphosphine ligands. Each platinum is again approximately square planar (the sums of the angles at platinum are 360.2° and 360.4°), the smallest angles again being within the platinum-oxalate chelates. The carbon–carbon distances confirm that the triple bond character is maintained, although there is some bending at the carbons (P–C–C angles 171.7–174.2°). The two metal square planes are inclined at an angle of 25.5° to each other, giving a Pt–Pt distance of 6.985 Å.



(3)

The ^{31}P NMR spectra of $[Pt(E_2C_6H_4\text{-}EE)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$ (E = O, S) each exhibit a single resonance with ^{195}Pt satellites, the value of $^{1}J_{PtP}$ being much smaller in $[Pt(S_2C_6H_4\text{-}SS)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$ than in the O-complexed dimers. The high resolution mass spectrum for $[Pt(S_2C_6H_4\text{-}SS)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$ confirms its bimetallic nature, a molecular ion being obtained that corresponds to the $C_{64}H_{48}P_4S_4AgPt_2{}^+$ unit, the Ag^+ deriving from the $AgOCOCF_3$ used in the experiment.

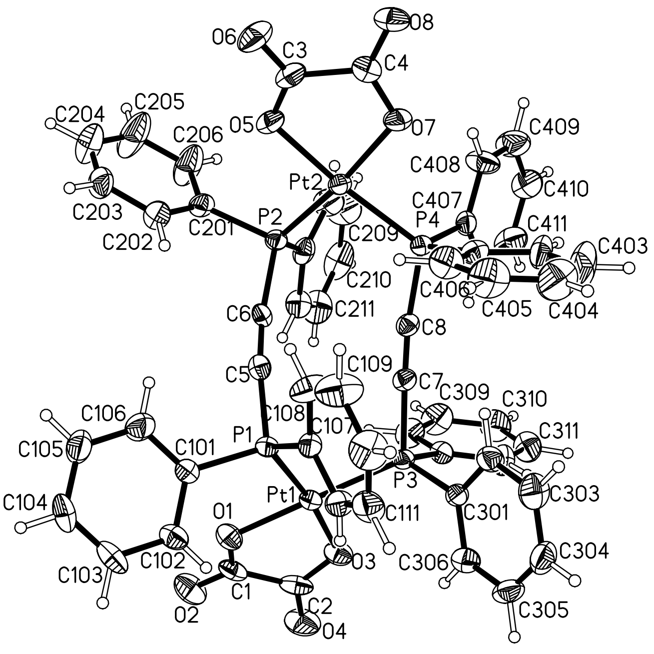


Fig. 2. Molecular structure of $[Pt(C_2O_4\text{-}\mathit{OO})(Ph_2PC{\equiv}CPPh_2)]_2$. Selected bond distances (Å) and angles (°): Pt(1)–P(1) 2.226(2), Pt(1)–P(3) 2.227(2), Pt(1)–O(1) 2.031(6), Pt(1)–O(3) 2.045(6), Pt(2)–P(2) 2.220(2), Pt(2)–P(4) 2.211(2), Pt(2)–O(5) 2.036(5), Pt(2)–O(7) 2.052(6), C(5)–C(6) 1.199(10), C(7)–C(8) 1.195(10); P(1)–Pt(1)–P(3) 94.58(7), P(1)–Pt(1)–O(1) 91.13(17), P(1)–Pt(1)–O(3) 172.37(17), P(3)–Pt(1)–O(1) 173.11(17), P(3)–Pt(1)–O(3) 92.71(17), O(1)–Pt(1)–O(3) 81.8(3), P(2)–Pt(2)–P(4) 94.87(8), P(2)–Pt(2)–O(5) 93.23(18), P(2)–Pt(2)–O(7) 172.34(17), P(4)–Pt(2)–O(5) 171.45(18), P(4)–Pt(2)–O(7) 89.87(16), O(5)–Pt(2)–O(7) 82.4(2), P(1)–C(5)–C(6) 171.9(7), C(5)–C(6)–P(2) 171.7(7), P(3)–C(7)–C(8) 174.2(8), C(7)–C(8)–P(4) 171.7(8).

Although we have not yet been able to use this approach to generate neutral molecular squares with dianionic corners, we have shown that $[Pt(acac)_2]$ is a useful precursor in such endeavors and $Ph_2PC{\equiv}CPPh_2$ has been used as a bridging ligand in a series of bimetallic platinum complexes.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of argon. Dichloromethane was distilled from CaH_2; HPLC grade acetone and methanol were dried over molecular sieves. 1,2-Benzenediol, 1,2-benzenedithiol, and oxalic acid were obtained from ACROS and were used as received. Bis(diphenylphosphino)ethyne was obtained from Strem. $[Pt(acac)_2]$ was obtained from Engelhard, and recrystallized from CH_2Cl_2 prior to use. $[PtCl_2(cod)]$ was prepared by a standard method; $[PtCl_2(dppp)]$ was prepared by displacement of cyclooctadiene from $[PtCl_2(cod)]$.

NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer using $CDCl_3$ as solvent. ^1H and ^{13}C chemical shifts were measured relative to the residual $CHCl_3$ and $CDCl_3$ signals, respectively; ^{31}P shifts were measured relative to external H_3PO_4. High resolution mass spectra were obtained on a JEOL M station under FAB conditions, using $AgOCOCF_3$ in a nitrobenzyl alcohol matrix.

3.2. Preparation of $[Pt(O_2C_6H_4\text{-}OO)(cod)]$

A 1.0 M solution of KOH in methanol (1.0 mL) was added with stirring to a colorless solution of $1,2\text{-}C_6H_4(OH)_2$ (0.030 g, 0.27 mmol) and $[PtCl_2(cod)]$ (0.101 g, 0.27 mmol) in methanol (50 mL). The solution immediately turned yellow, and it was refluxed for 2 h. The solvent was removed *in vacuo*, and the residue was crystallized from CH_2Cl_2 to give the product as yellow crystals (0.073 g, 64%). ^1H NMR: δH 2.32 (m), 2.66 (m), 5.39 ($^1J_{PtH} =$ 66 Hz), 6.61 (m), 6.80 (m). $^{13}C\{^1H\}$ NMR: δC 30.1, 88.6, 115.1, 118.9, 161.8.

3.3. Preparation of $[Pt(S_2C_6H_4\text{-}SS)(cod)]$

This complex was prepared similarly from $[PtCl_2(cod)]$ and $1,2\text{-}C_6H_4(SH)_2$ and obtained as colorless crystals in 72% yield. ^1H NMR: δH 2.54 (m), 3.06 (m), 5.48 ($^1J_{PtH} = 66$ Hz), 6.90 (m), 7.52 (m). $^{13}C\{^1H\}$ NMR: δC 30.5, 92.8, 123.0, 128.0, 146.1. HRMS calc. for $C_{14}H_{16}S_2{}^{109}Ag{}^{194}Pt$ or $C_{14}H_{16}S_2{}^{107}Ag{}^{196}Pt$: 550.9382. Found: 550.9399.

3.4. Preparation of $[Pt(O_2C_6H_4\text{-}OO)(dppp)]$

This complex was prepared from $[PtCl_2(dppp)]$ and $1,2\text{-}C_6H_4(OH)_2$ and obtained as a white solid in 67% yield. ^1H NMR: δH 2.11 (m), 2.52 (m), 7.37–7.79 (m). $^{13}C\{^1H\}$ NMR: δC 24.7, 116.8, 120.2, 128.6, 131.1, 131.5, 133.6. $^{31}P\{^1H\}$ NMR: δP −10.0 ($^1J_{PtP} = 3318$ Hz).

3.5. Preparation of $[Pt(S_2C_6H_4\text{-}SS)(dppp)]$

This complex was prepared analogously from $[PtCl_2(dppp)]$ and $1,2\text{-}C_6H_4(SH)_2$ and isolated as a white solid in 74% yield. ^1H NMR: δH 2.43 (m), 2.58 (m), 6.62 (m), 7.31 (m), 7.64 (m). $^{13}C\{^1H\}$ NMR: δC 122.5, 125.7, 128.3, 128.7, 131.1, 133.8. $^{31}P\{^1H\}$ NMR: δP −5.3 ($^1J_{PtP} =$ 2665 Hz).

3.6. Preparation of $[Pt(C_2O_4\text{-}OO)(dppp)]$

A mixture of $[Pt(acac)_2]$ (0.10 g, 0.26 mmol), oxalic acid (0.023 g, 0.26 mmol) and dppp (0.11 g, 0.26 mmol) was stirred in acetone (50 mL) for 2 h. The solvent was removed and the residue was crystallized from CH_2Cl_2 to give the product as colorless crystals (0.050 g, 84%). $^{31}P\{^1H\}$ NMR: δP −10.2 ($^1J_{PtP} = 3451$ Hz).

3.7. Preparation of $[Pt(C_2O_4\text{-}OO)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$

This complex was prepared from $[Pt(acac)_2]$, oxalic acid and $Ph_2PC{\equiv}CPPh_2$ and obtained as colorless crystals in 86% yield. ^1H NMR: δH 7.30–7.76 (m). $^{13}C\{^1H\}$ NMR:

δC 122.9, 123.9, 129.6 (t), 133.1 (t), 164.6; $^{31}P\{^1H\}$ NMR: δP −14.2 ($^1J_{PtP} = 3760$ Hz). HRMS calc. for $C_{56}H_{41}O_8P_4^{195}Pt_2$: 1355.1046. Found: 1355.1025.

3.8. Preparation of $[Pt(O_2C_6H_4\text{-}OO)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$

This complex was generated from [Pt(acac)$_2$], 1,2-$C_6H_4(OH)_2$ and $Ph_2PC{\equiv}CPPh_2$ and isolated as colorless crystals in 79% yield. ^1H NMR: 5.53 (m), 6.50–7.66 (m). $^{13}C\{^1H\}$ NMR: 115.4, 117.3, 120.2, 128.8, 131.9, 133.3, 144.7. $^{31}P\{^1H\}$ NMR: −13.8 ($^1J_{PtP} = 3867$ Hz).

3.9. Preparation of $[Pt(S_2C_6H_4\text{-}SS)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$

This complex was generated from [Pt(acac)$_2$], 1,2-$C_6H_4(SH)_2$ and $Ph_2PC{\equiv}CPPh_2$ and isolated as colorless crystals in 85% yield. ^1H NMR: 6.79 (m), 7.20–7.81 (m). $^{13}C\{^1H\}$ NMR: 123.6, 130.0, 133.1, 134.9, 160.0. $^{31}P\{^1H\}$ NMR: −4.2 ($^1J_{PtP} = 2815$ Hz). HRMS calc. for $C_{64}H_{48}P_4S_4^{107}Ag^{195}Pt_2$: 1566.9939. Found: 1566.9878.

3.10. X-ray crystallography

Crystals of [Pt(C_2O_4-*OO*)(dppp)] are monoclinic, space group $P2_1/n$, with $a = 10.5049(4)$ Å, $b = 15.3915(5)$ Å, $c = 16.5893(5)$ Å, $\beta = 103.185(2)°$, $V = 2611.55(15)$ Å^3, $Z = 4$, and $\rho_{calcd} = 1.769$ g cm^{-3} for $f_w = 695.53$. A total of 7416 independent reflections were collected at 155(2) K in the θ range 1.83–30.00°, $wR_2 = 0.0538$ and $R_1 = 0.0316$.

Crystals of $[Pt(C_2O_4\text{-}OO)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$ are triclinic, space group $P(\bar{1})$, with $a = 14.6729(3)$ Å, $b = 15.0925(3)$ Å, $c = 15.9589(3)$ Å, $\alpha = 81.8850(10)°$, $\beta = 71.5070(10)°$, $\gamma = 70.4240(10)°$, $V = 3155.48(11)$ Å^3, $Z = 2$, and $\rho_{calcd} = 1.803$ g cm^{-3} for $f_w = 1713.04$. A total of 14488 independent reflections were collected at 160(2) K in the θ range 1.73–27.50°, $wR_2 = 0.1072$ and $R_1 = 0.0639$.

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Appendix A. Supplementary material

Tables of crystal data, atomic coordinates and displacement parameters, and complete lists of bond distances and angles for [Pt(C_2O_4)(dppp)] and $[Pt(C_2O_4\text{-}OO)(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]_2$ are available from CCDC. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.08.060.

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