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LETTER

# Probing the electronic structure of selected diplatinum($\mu$-alkenylidene) complexes

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Recent theoretical calculations and structural data support the conclusion that alkynyl ligands coordinate to transition metal atoms essentially as simple $\sigma$-donor ligands [1–3]. This bonding mode for a phenylacetylide ligand is indicated by the structural data of [Mo(C≡CPh)(dppe)($\eta$-$C_7H_7$)] and its one-electron oxidized derivative, [Mo(C≡CPh)(dppe)($\eta$-$C_7H_7$)][$BF_4$], as reported very recently by Whiteley and coworkers [4]. Oxidation at the molybdenum center results in an expected decrease of the Mo–C(phenylacetylide) bond distance (of 0.07(1) Å). We have determined the molecular structure of the Pt(II) phenylacetylide complex, [*trans*-Pt($PEt_3$)$_2$(C≡CPh)$_2$], to obtain the value of the Pt–C(phenylacetylide) bond distance. This Pt–CCPh distance and the analogous distances in selected diplatinum complexes containing phenylacetylide ligands can be used as probes to the electronic structures of these mono- or diplatinum compounds.

A unique series of diplatinum($\mu$-alkenylidene) complexes that have a $Pt_2L_2$ 'T-frame' skeleton and a general formulation of [$ZL_2Pt$($\mu$-alkenylidene)PtLZ′], where L is $PEt_3$ and Z or Z′ are one-electron ligands, have been synthesized and characterized recently [5, 6]. Three such compounds for which Z is phenylacetylide have been structurally characterized. Elucidation of the electronic environment at the Pt centers of this type of complex is of continuing interest, because these compounds exhibit extensive photochemical reactivity, including stoichiometric or catalytic atom-transfer chemistry [6, 7] and very unusual C–C coupling reactions with alkynes [8]. These compounds also emit luminescence following photoexcitation [6]. Theoretical calculations and $^{195}$Pt NMR data of these complexes reveal an electronic environment around the Pt atoms more similar to that of Pt(0) compounds than to that of Pt(II) compounds [9]. These calculations also predict a net Pt–Pt repulsive interaction in this type of complex. The structural data for those compounds where Z is phenylacetylide and where Z′ are ligands of differing electronegativity reveal a decrease in the Pt–Pt distance with an increase in the electronegativity of Z′. This structural trend results presumably from a reduction of the Pt–Pt repulsive interaction with an increasing drift of electron density away from the Pt atom bearing the phenylacetylide ligand. Such a partial oxidation of this Pt atom should be reflected in a decrease of the corresponding Pt–C(phenylacetylide) distance.

In this letter, we report the structural determination of the complex [*trans*-Pt($PEt_3$)$_2$(C≡CPh)$_2$] and compare the structural data of this compound to that of selected diplatinum($\mu$-alkenylidene) complexes. Variations in the Pt–C(phenylacetylide) distances of these compounds are consistent with (i) the Pt atom of the mononuclear complex being more highly oxidized than is the corresponding Pt atom of the dinuclear complexes, and (ii) a drift of electron density away from the $PtL_2$(C≡CPh) moiety in these dinuclear complexes as the electronegativity of Z′ increases.

## Experimental

The complex, [*trans*-Pt($PEt_3$)$_2$(C≡CPh)$_2$], was prepared by a known procedure [10] and was crystallized from methanol at −20 °C. Appropriate crystal data are: $C_{28}H_{40}P_2Pt$, $M=750.47$, monoclinic, space group $P2_1/c$ (No. 14), $a=9.136(1)$, $b=10.944(3)$, $c=14.746(1)$ Å, $\beta=105.78(1)°$, $Z=2$, $D_{calc}=1.757$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 51.54 cm$^{-1}$. Crystal dimensions: 0.50×0.38×0.25 mm. Intensity data ($+h$, $+k$, $\pm l$; 2645 unique reflections; $2\theta_{max}=50.1°$) were recorded on a Rigaku AFC 6S diffractometer (Mo K$\alpha$ radiation $\lambda=0.71069$ Å; graphite monochromator; $\omega$–$2\theta$ scans) at 23 °C. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied to the data (with relative transmission factors ranging from 0.44 to 1.00). The crystal structure was solved by direct methods and was refined using the TEXSAN software package of the Molecular Structure Corporation. Full-matrix least-squares refinement of atomic parameters (anisotropic C, P and Pt; fixed isotropic H atoms at calculated positions) converged (max. shift of 0.09$\sigma$) at $R=0.036$ ($R_w=0.036$, $GOF=1.22$) over 1395 re-

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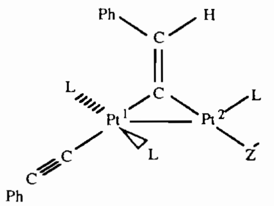
flections with $I > 3.00\sigma(I)$. The largest remaining difference peak was 1.34 $e^-$ Å$^{-3}$.

## Results and discussion

Atomic positional and equivalent isotropic thermal parameters of [*trans*-Pt($PEt_3$)$_2$(C≡CPh)$_2$] (**1**) are given in Table 1. The values of selected interatomic distances and angles are listed in Table 2. A diagram of the molecular structure of **1** showing the atomic numbering scheme is shown in Fig. 1.

The structure of **1** reveals a rigorously planar coordination geometry about the Pt atom (which lies on a crystallographic inversion center). There are no unusual structural features. The Pt(1)–P distances of 2.289(3) Å and the Pt(1)–C(phenylacetylide) distances of 1.98(1) Å are typical values for Pt(II) complexes [11]. More specifically, Pt–C(alkynyl) distances of *trans*-Pt(II)$L_2$(alkynyl)(R) compounds containing a variety of differing ligands *trans* to the alkynyl ligands are usually observed in the range of 1.94(2)–2.00(2) Å [11]. The C(1)–C(2) triple bond distances of **1** are 1.21(1) Å, and the C(1)–C(2)–C(3) angles of 176(1)° indicate nearly linear hybridization at C(2) as expected.

Selected structural data for **1** and the diplatinum($\mu$-alkenylidene) complexes, **2a–c**, are listed below. The Pt–Pt distance decreases on going from **2a** to **2c** as the electronegativity of the ligand Z′ increases. This observation has been rationalized by presuming that increased oxidation of Pt(2) will decrease the Pt(1)–Pt(2) repulsive interaction and, thereby, enhance the donation of electron density from Pt(1) to Pt(2) to give a stronger Pt–Pt bond [6]. According to this bonding model, Pt(1) should also undergo increased partial oxidation on going from **2a** to **2c**.



| **2** (L = $PEt_3$) | Z′ |
|---|---|
| **a** | $PEt_3^+$ |
| **b** | I |
| **c** | Cl |

| Complex | Distance (Å) | |
|---|---|---|
| | Pt(1)–Pt(2) | Pt(1)–CCPh |
| **2a** | 2.750(2) | 2.17(2) |
| **2b** | 2.721(1) | 2.01(1) |
| **2c** | 2.711(1) | 2.05(2) |
| **1** | | 1.98(1) |

TABLE 1. Atomic positional and equivalent isotropic thermal parameters for complex **1**

| Atom | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| Pt(1) | 0 | 0 | 0 | 3.67(2) |
| P(1) | −0.1325(3) | 0.0763(3) | 0.0987(2) | 4.7(1) |
| C(1) | −0.178(1) | 0.042(1) | −0.1067(7) | 4.2(5) |
| C(2) | −0.284(1) | 0.065(1) | −0.1736(7) | 4.3(4) |
| C(3) | −0.406(1) | 0.087(1) | −0.2559(7) | 4.1(5) |
| C(4) | −0.486(1) | 0.196(1) | −0.2689(8) | 5.5(6) |
| C(5) | −0.606(1) | 0.213(2) | −0.348(1) | 7.2(7) |
| C(6) | −0.647(2) | 0.124(2) | −0.416(1) | 8.2(9) |
| C(7) | −0.570(2) | 0.017(2) | −0.404(1) | 8.2(8) |
| C(8) | −0.448(1) | −0.000(2) | −0.3249(7) | 6.1(5) |
| C(10) | −0.028(1) | 0.082(1) | 0.2215(8) | 6.2(6) |
| C(11) | −0.112(2) | 0.123(2) | 0.292(1) | 11(1) |
| C(20) | −0.205(2) | 0.229(1) | 0.069(1) | 7.5(8) |
| C(21) | −0.083(2) | 0.323(1) | 0.069(1) | 10(1) |
| C(30) | −0.302(1) | −0.009(2) | 0.093(1) | 8.5(7) |
| C(31) | −0.273(2) | −0.142(2) | 0.116(1) | 12(1) |

TABLE 2. Values of selected interatomic distances (Å) and angles (°) of complex **1**[a]

| | | | |
|---|---|---|---|
| Distances | | | |
| Pt(1)–P(1) | 2.289(3) | C(3)–C(4) | 1.38(1) |
| Pt(1)–P(1)′ | 2.289(3) | C(3)–C(8) | 1.37(2) |
| Pt(1)–C(1)′ | 1.98(1) | C(4)–C(5) | 1.38(2) |
| Pt(1)–C(1)′ | 1.98(1) | C(5)–C(6) | 1.37(2) |
| P(1)–C(10) | 1.80(1) | C(6)–C(7) | 1.36(2) |
| P(1)–C(20) | 1.81(1) | C(7)–C(8) | 1.38(2) |
| P(1)–C(30) | 1.79(1) | C(10)–C(11) | 1.52(2) |
| C(1)–C(2) | 1.21(1) | C(20)–C(21) | 1.52(2) |
| C(2)–C(3) | 1.43(1) | C(30)–C(31) | 1.50(2) |
| Angles | | | |
| P(1)–Pt(1)–P(1) | 180.00 | C(1)–C(2)–C(3) | 176(1) |
| P(1)–Pt(1)–C(1) | 87.7(3) | C(2)–C(3)–C(4) | 122(1) |
| P(1)–Pt(1)–C(1) | 92.3(3) | C(2)–C(3)–C(8) | 121(1) |
| P(1)–Pt(1)–C(1) | 92.3(3) | C(4)–C(3)–C(8) | 118(1) |
| P(1)–Pt(1)–C(1) | 87.7(3) | C(3)–C(4)–C(5) | 120(1) |
| C(1)–Pt(1)–C(1) | 180.00 | C(4)–C(5)–C(6) | 121(1) |
| Pt(1)–P(1)–C(10) | 115.1(4) | C(5)–C(6)–C(7) | 120(1) |
| Pt(1)–P(1)–C(20) | 113.9(4) | C(6)–C(7)–C(8) | 120(2) |
| Pt(1)–P(1)–C(30) | 112.3(5) | C(3)–C(8)–C(7) | 122(2) |
| C(10)–P(1)–C(20) | 105.7(6) | P(1)–C(10)–C(11) | 118.0(9) |
| C(10)–P(1)–C(30) | 106.4(6) | P(1)–C(20)–C(21) | 114(1) |
| C(20)–P(1)–C(30) | 102.4(8) | P(1)–C(30)–C(31) | 113(1) |
| Pt(1)–C(1)–C(2) | 177.8(9) | | |

[a] The primed atoms are generated by inversion symmetry.

A comparison between the electronic environment of Pt(1) in **1** and in complexes **2a–c** is appropriate only to the extent that the Pt–C(phenylacetylide) distance of a *trans*-Pt($PEt_3$)$_2$(C≡CPh) moiety can act as a probe to changes in the electronic environment at the Pt center of compounds containing

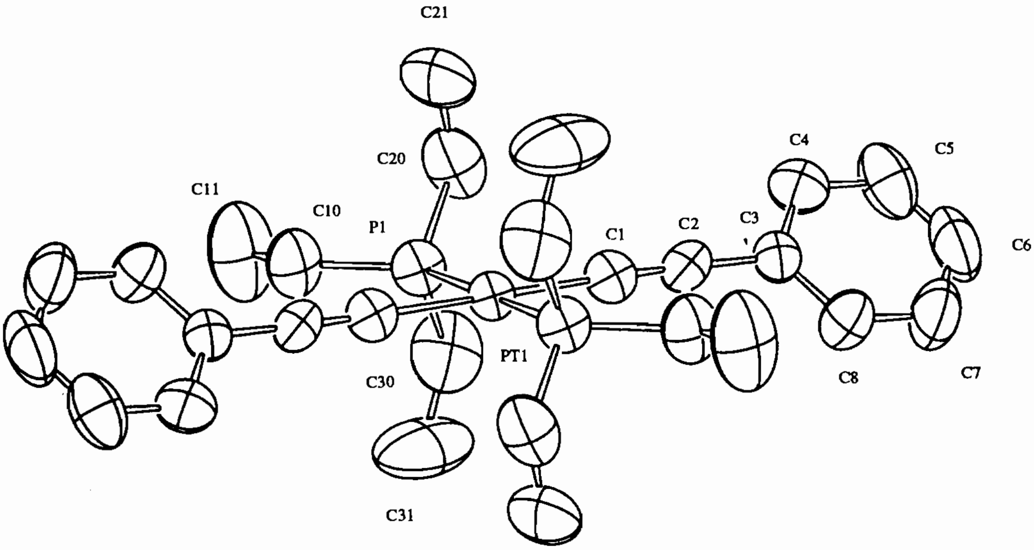


Fig. 1. A diagram of complex **1** showing the atomic numering scheme. Hydrogen atoms are omitted for clarity.

such a fragment. Even within a $\pm 2\sigma$ limit, the Pt–CCPh distance of **2a** is significantly longer than that of **1**. The strong donor strength of the $PEt_3$ ligand presumably weakens the Pt–Pt bonding, favors the retention of electron density around Pt(1) and, therefore, weakens the Pt–C(phenylacetylide) bond. The Pt–CCPh distances of **2b** and **2c** are not significantly different and are only slightly longer than that of complex **1**. The greater electronegativity of I or Cl ligands compared to that of a $PEt_3$ ligand presumably strengthens the Pt–Pt bonding through the partial oxidization of both Pt(1) and Pt(2). This effect results in a decrease in both the Pt–CCPh and the Pt–Pt distances of **2b** and **2c** compared to those distances of **2a**.

Although these structural data do not permit a distinction between different specific bonding models for the Pt–Pt interaction in complexes like **2**, the observed dependence of the Pt–CCPh distance on the electronegativity of the set of ancillary ligands indicates increased oxidation at Pt(1) with an increase in the electronegativity of Z′. $^{195}$Pt NMR data indicate a similar relationship between the partial oxidation of Pt(1) and Pt(2) and the electronegativity of Z′ in these and related compounds [9]. Proper regulation of the electronic environments of both Pt(1) and Pt(2) will be necessary for the systematic control of the photophysical properties of these dinuclear complexes.

## Supplementary material

A comprehensive listing of bond lengths and angles, anisotropic thermal parameters, hydrogen atomic coordinates, and observed and calculated structure factors are available from the authors on request.

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