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Structural and Electrochemical Properties of Binuclear Complexes Containing 1,10-Phenanthroline-5,6-diolate as a Bridging Ligand

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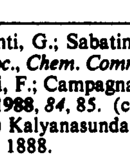
Bis(triphenylphosphine)(1,10-phenanthroline-5,6-diolato)platinum(II), $(PPh_3)_2Pt(O',O\text{-PhD})$, may be prepared by treating 1,10-phenanthroline-5,6-dione with $Pt(PPh_3)_4$. The oxygen-bound diolate form of the PhD ligand can coordinate to an additional metal through the nitrogen donor atoms forming a binuclear complex with the $(PPh_3)_2Pt(O',O\text{-PhD})$ unit serving as a bipyridine-like ligand. Complexes of general form $(PPh_3)_2Pt(O',O\text{-PhD-}N,N')ML_n$ have been prepared with $ML_n = PdCl_2$, $Ru(PPh_3)_2Cl_2$, and Pt(DBCat). The Pt,Pd and Pt,Ru complexes could not be characterized from elemental analytical data due to the presence of nonstoichiometric solvate molecules; crystallographic structure determinations provided information on both complexes. $(PPh_3)_2Pt(O',O\text{-PhD-}N,N')PdCl_2$ crystallizes in the orthorhombic space group *Pbcn* with 2.5 molecules of benzene per complex molecule in a unit cell of dimensions $a = 16.175$ (5) Å, $b = 27.792$ (6) Å, $c = 25.801$ (7) Å, $V = 11599$ (5) Å^3, and $Z = 8$. $(PPh_3)_2Pt(O',O\text{-PhD-}N,N')Ru(PPh_3)_2Cl_2$ crystallizes as a mixed toluene–dichloromethane solvate, in the triclinic space group $P\bar{1}$, with unit cell dimensions of $a = 15.758$ (3) Å, $b = 15.715$ (3) Å, $c = 19.193$ (3) Å, $\alpha = 82.91$ (1)°, $\beta = 80.41$ (1)°, $\gamma = 66.89$ (1)°, $V = 4301$ (1) Å^3, and $Z = 2$. Structural features of both molecules include similar, planar $P_2Pt(PhD)MCl_2$ regions, with additional axial PPh_3 ligands for M = Ru, and C–O lengths for the PhD ligand that are typical of catecholate ligands. The electrochemical properties of the complexes consist of first and second electron oxidations of the PhD bridge for all three species, with an additional Ru^{II}/Ru^{III} couple for $(PPh_3)_2Pt(O',O\text{-PhD-}N,N')Ru(PPh_3)_2Cl_2$ and two additional catecholate oxidations for the DBCat ligand of $(PPh_3)_2Pt(O',O\text{-PhD-}N,N')Pt(DBCat)$. Similarities in bonding between $L_nM(O',O\text{-PhD})$ species and the bipyridine and 1,10-phenanthroline ligands is described. However, the redox activity of the PhD bridge at potentials near the redox potentials of electroactive metal ions presents an important difference between PhD-bridged complexes and the simple nitrogen donor analogues.

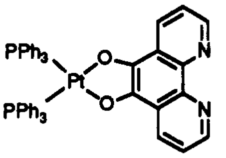
Introduction

Polymetallic complexes consisting of catenated metal ions linked by associated ligands are of interest as species that may show multifunctional activity within a single molecular unit. The polypyridine complexes of ruthenium and osmium have been of specific interest for their photophysical and electrochemical properties.[1] Complexes containing semiquinone and catecholate ligands show rich electrochemical activity.[2] Quinone ligands have also been shown to support intramolecular electron transfer either between metal ions bridged by dihydroxybenzoquinone ligands[3] or between localized metal and quinone electronic levels within the semiquinone/catecholate complex molecule.[4] The incorporation of quinone ligands in polymetallic systems would give additional electrochemical activity at potentials near the redox potentials of the metals and may provide complexes that show unusual photophysical properties.

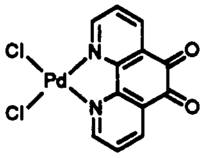
1,10-Phenanthroline-5,6-dione (I, PhD) may serve as a bridging ligand in the construction of multinuclear complexes. The structure and electronic properties of this ligand incorporate features of both the diimine and quinone ligands. Balch described the bifunctional nature of the PhD ligand in a report that appeared in 1975.[5] By use of the ligand as a benzoquinone, $(PPh_3)_2Pt(O',O\text{-PhD})$ (II) was prepared by oxidatively adding PhD to $Pt(PPh_3)_4$. The nitrogen donor site of PhD resembles the bipyridine ligand, and this aspect of its coordination chemistry was demonstrated by the synthesis of $Cl_2Pd(N',N\text{-PhD})$ (III) from $Pd(PhCN)_2Cl_2$. In a later report Abruna described the $M(bpy)_{3-n}(N',N\text{-PhD})_n^{2+}$ (M = Ru, Os; $n = 1$–3) series, $Cu(N',N\text{-PhD})_2^{2+}$, and the $M(N',N\text{-PhD})_3^{2+}$ (M = Fe, Co) complexes.[6]



I



II



III

When coordinated through its oxygen atoms, as in II, the entire complex may be used as a "bipyridine-equivalent" ligand in the synthesis of a binuclear complex. In much the same way, nitrogen bound complexes of the PhD ligand (III) may be used as "benzoquinone equivalents" in reactions with nucleophilic metal complexes that may transfer one or two electrons to the quinone region of the N',N-PhD ligand. In these reations the binuclear products may contain either semiquinone or catecholate bridges.

In this report, we utilize the bifunctional nature of the PhD ligand with the synthesis and characterization of binuclear complexes that use the PhD ligand as a bridging agent.

Experimental Section

Materials. 1,10-Phenanthroline-5,6-dione (PhD),[7] $Pt(PPh_3)_2(O',O\text{-PhD})$,[5] $PdCl_2(N',N\text{-PhD})$,[5] $Ru(PPh_3)_3Cl_2$,[8] and $Pt_2(DBA)_3$[9] were prepared by published procedures. 3,5-Di-*tert*-butylbenzoquinone (H_2DBBQ) was purchased from Aldrich and used as received.

Preparation of Complexes. $\mathbf{(PPh_3)_2Pt(O',O\text{-PhD-}N,N')PdCl_2}$. $Pt(PPh_3)_2(O',O\text{-PhD})$ (0.165 g, 1.77 mmol) and $Pd(PhCN)_2Cl_2$ (0.131 g, 1.77 mmol) were combined under Ar, and 20 mL of degassed dichloromethane was added to the mixture. The $(PPh_3)_2Pt(O',O\text{-PhD-}N,N')PdCl_2$ product was obtained quantitatively as an orange-red solid. Crystals suitable for crystallographic study were obtained as benzene

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(1) (a) Campagna, S.; Denti, G.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *J. Chem. Soc., Chem. Commun.* **1989**, 1500. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Petersen, J. D. *Coord. Chem. Rev.* **1985**, *64*, 261. (d) Kalyanasundaram, K.; Nazeeruddin, Md. K. *Inorg. Chem.* **1990**, *29*, 1888.

(2) (a) Downs, H. H.; Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1736. (b) Bradbury, J. R.; Schultz, F. A. *Inorg. Chem.* **1986**, *25*, 4416.

(3) (a) Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1442. (b) Auburn, P. R.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 2551. (c) Ernst, S.; Hanel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.* **1989**, *111*, 1733.

(4) (a) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951. (b) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.

(5) Girgis, A. Y.; Sohn, Y. S.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2327.

(6) Goss, C. A.; Abruna, H. D. *Inorg. Chem.* **1985**, *24*, 4263.

(7) Dickeson, J. E.; Summers, L. A. *Aust. J. Chem.* **1970**, *23*, 1023.

(8) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

(9) Moseley, K.; Maitlis, P. M. *J. Chem. Soc. D* **1971**, 982.

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Table I. Crystallographic Data for (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)PdCl$_2$·2.5C$_6$H$_6$ (**1**) and (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Ru(PPh$_3$)$_2$Cl$_2$·C$_6$H$_5$CH$_3$·0.5CH$_2$Cl$_2$ (**2**)

	1	**2**
mol wt	1302.4	1760.9
color	red-brown	orange
cryst syst	orthorhombic	triclinic
space group	*Pbcn*	$P\bar{1}$
a, Å	16.175 (5)	15.758 (3)
b, Å	27.792 (6)	15.715 (3)
c, Å	25.801 (7)	19.193 (3)
α, deg	90.00	82.91 (1)
β, deg	90.00	80.41 (1)
γ, deg	90.00	66.89 (1)
vol, Å^3	11 599 (5)	4301 (1)
Z	8	2
D_{calcd}, g cm^{-3}	1.492	1.360
D_{exptl}, g cm^{-3}	1.504	1.358
μ, mm^{-1}	2.93	2.03
T_{max}, T_{min}	0.795, 0.996	0.745, 0.968
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, K	295–297	295–297
R, R_w	0.065, 0.079	0.041, 0.058
GOF	1.23	1.40

solvates by slow evaporation of a CH$_2$Cl$_2$/benzene solution of the complex. UV–vis: 290 nm (21 000 M^{-1} cm^{-1}), 334 (17 600), 323 sh, 430 (4520), 560 (1100).

(PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Pt(DBCat). Pt(PPh$_3$)$_2$(*O*′,*O*-PhD) (0.085 g, 0.91 mmol) and Pt$_2$(DBA)$_3$ (0.050 g, 0.46 mmol) were combined under Ar, and 20 mL of degassed dichloromethane was added to the mixture. 3,5-Di-*tert*-butyl-1,2-benzoquinone (0.020 g, 0.91 mmol) dissolved in 10 mL of degassed CH$_2$Cl$_2$ was added to the solution under Ar. The resulting green solution was evaporated to dryness, and the residue was washed with a 1:10 THF/pentane solution to remove the yellow dibenzylideneacetone. The resulting blue-green precipitate was recrystallized from CH$_2$Cl$_2$ to give 0.102 g of (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Pt(DBCat) in 84% yield. Anal. Calcd for C$_{62}$H$_{56}$N$_2$O$_2$P$_2$Pt$_2$: C, 55.38; H, 4.20; N, 2.08; P, 4.59. Found: C, 55.91; H, 4.79; N, 2.15; P, 4.52. FAB MS: molecular ion at *m*/*e* 1344. ^{1}H NMR (CDCl$_3$): DBCat (*t*-Bu)l 1.56, 1.29 ppm.

(PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Ru(PPh$_3$)$_2$Cl$_2$. Pt(PPh$_3$)$_2$(*O*′,*O*-PhD) (0.140 g, 1.51 mmol) and Ru(PPh$_3$)$_3$Cl$_2$ (0.144 g, 1.51 mmol) were combined under Ar, 20 mL of degassed dichloromethane was added to the mixture, and the solution was heated at reflux for 1 h. The (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Ru(PPh$_3$)$_2$Cl$_2$ product was washed with a 1:1 hexane/toluene solution to remove excess triphenylphosphine and recrystallized from a dichloromethane/toluene solution to give 0.22 g of product in 83% yield. The complex was obtained as red-brown crystals that were found to contain both CH$_2$Cl$_2$ and toluene molecules of crystallization. UV–vis: 288 nm (31 000 M^{-1} cm^{-1}), 340 (11 300), 401 (11 900), 500 (4100).

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Cyclic voltammograms were obtained with a Cypress CYSY-1 computer controlled electroanalysis system in CH$_2$Cl$_2$ solutions. A Ag/Ag$^+$ reference electrode was used, NBu$_4$(ClO$_4$) was used as the supporting electrolyte, and the Fc/Fc$^+$ couple was used as an internal standard. Experiments were typically carried out at a scan rate of 100 mV/s, and ΔE for the Fc/Fc$^+$ couple was approximately 120 mV under these conditions. ^{1}H NMR spectra were recorded on a Varian VXR 300S spectrometer.

Crystallographic Structure Determinations. (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)PdCl$_2$. Crystals obtained by recrystallization from CH$_2$Cl$_2$/benzene solutions were found to be unstable benzene solvates that rapidly lost solvent upon separation from solution. This resulted in erratic elemental analyses on the complex, and the crystal used for crystallographic investigation was coated with an amorphous resin immediately upon isolation. Photographs taken on the red prismatic crystal indicated orthorhombic symmetry. The centered settings of 25 reflections gave the unit cell dimensions listed in Table I. Data were collected by using θ–2θ scans within the angular range 3.0–50.0°. The intensities of four standard reflections monitored during data collection showed only random fluctuations. Systematic absences were consistent with the centrosymmetric space group *Pbcn*. Locations of the Pt and Pd atoms were determined from a Patterson map, and the locations of other atoms of the molecule were determined from phases generated by the metal atoms. Three independent benzene solvate molecules were located, one with approximate atom occupancy factors of 0.5. Final cycles of refinement converged with discrepancy factors of R = 0.064 and R_w = 0.079. Positional parameters for selected atoms are contained in Table II; tables containing full listings of atom positions, thermal parameters, and hydrogen atom locations are available as supplementary material.

Table II. Atomic Coordinates (×10^4) for Selected Atoms of (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)PdCl$_2$

atom	x/a	y/b	z/b
Pt	−28 (1)	2819 (1)	908 (1)
Pd	1585 (1)	826 (1)	2825 (1)
Cl1	2407 (5)	832 (3)	3541 (3)
Cl2	1630 (6)	9 (3)	2782 (4)
P1	180 (4)	3621 (2)	903 (3)
P2	−635 (4)	2734 (3)	136 (3)
O1	517 (10)	2781 (6)	1624 (7)
O2	−72 (11)	2091 (5)	1003 (7)
N1	1474 (12)	1565 (8)	2802 (10)
N2	884 (12)	891 (7)	2192 (8)
C1	1768 (17)	1905 (14)	3129 (11)
C2	1670 (19)	2383 (12)	3030 (13)
C3	1277 (16)	2524 (11)	2595 (11)
C4	1015 (16)	2194 (11)	2238 (10)
C5	622 (15)	2327 (9)	1767 (11)
C6	283 (15)	1963 (9)	1448 (11)
C7	369 (14)	1466 (8)	1581 (9)
C8	−1 (18)	1102 (9)	1280 (9)
C9	119 (19)	644 (9)	1445 (12)
C10	561 (17)	558 (11)	1909 (14)
C11	789 (14)	1346 (8)	2026 (8)
C12	1082 (16)	1693 (10)	2377 (9)

Table III. Atomic Coordinates (×10^4) for Selected Atoms of (PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Ru(PPh$_3$)$_2$Cl$_2$

	x/a	y/b	z/c
Pt	4884 (1)	442 (1)	3022 (1)
Ru	−321 (1)	3164 (1)	2235 (1)
Cl1	−1682 (1)	2750 (1)	2371 (1)
Cl2	−1080 (1)	4691 (1)	1661 (1)
P1	6055 (1)	955 (1)	2801 (1)
P2	5688 (1)	−1057 (1)	3296 (1)
P3	168 (1)	2657 (1)	1060 (1)
P4	−878 (1)	3748 (1)	3368 (1)
O1	3677 (3)	208 (3)	3143 (3)
O2	4034 (3)	1758 (3)	2742 (3)
N1	875 (4)	3386 (4)	2224 (3)
N2	496 (4)	1889 (4)	2661 (3)
C1	1058 (5)	4142 (5)	2009 (4)
C2	1912 (5)	4188 (5)	2047 (5)
C3	2611 (5)	3446 (5)	2284 (4)
C4	2476 (5)	2617 (5)	2506 (4)
C5	3168 (5)	1784 (5)	2737 (4)
C6	2988 (4)	997 (5)	2951 (3)
C7	2082 (5)	1008 (5)	2941 (4)
C8	1842 (5)	230 (5)	3172 (4)
C9	929 (5)	323 (5)	3137 (4)
C10	295 (5)	1159 (5)	2893 (4)
C11	1390 (5)	1827 (5)	2699 (3)
C12	1591 (4)	2619 (4)	2470 (3)

(PPh$_3$)$_2$Pt(*O*′,*O*-PhD-*N*,*N*′)Ru(PPh$_3$)$_2$Cl$_2$. Crystals obtained by recrystallization from a CH$_2$Cl$_2$/toluene solution were found to contain molecules of both solvents in the crystal lattice. The crystal selected for crystallographic study was coated with an amorphous resin to retard decomposition during data collection due to solvent loss. The crystal chosen was an orange parallelepiped. Photographs showed only triclinic symmetry, and the unit cell dimensions obtained from the centered settings of 25 reflections are listed Table I. Data were collected by using θ–2θ scans within the angular range 3.0–45.0°. The intensities of four standard reflections monitored during data collection showed only random fluctuations. Locations of the Pt and Ru atoms were determined from a Patterson map, and the locations of other atoms of the molecule were determined from phases generated by the metal atoms. Toluene and dichloromethane solvate molecules were located in the unit cell; the dichloromethane appeared to have a site occupancy of 0.5 on the basis of the magnitude of the isotropic atomic thermal parameters. Final cycles of refinement converged with discrepancy factors of R = 0.041 and R_w = 0.058. Positional parameters for selected atoms are contained in Table III; tables containing full listings of atom positions, thermal parameters, and hydrogen atom locations are available as supplementary material.

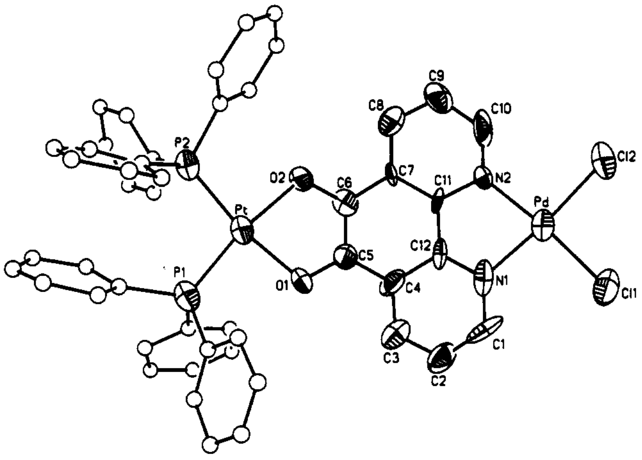
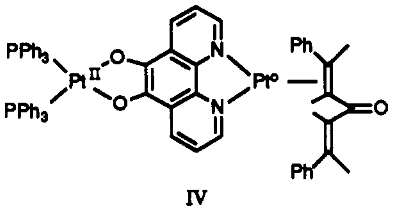


Figure 1. View showing the $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ molecule.

Results

Synthesis. An earlier report described the preparation of $(PPh_3)_2Pt(O',O\text{-}PhD)$ (II) by the addition of the oxidized dione form of PhD (I) to the Pt(0) complex $Pt(PPh_3)_4$.[5] Complex II may serve as a bidentate nitrogen donor ligand, and this aspect of its coordination chemistry has been used in the synthesis of three binuclear complexes. Bipyridine or *o*-phenanthroline would be expected to readily displace the benzonitrile ligands of $Pd(PhCN)_2Cl_2$ to give $Pd(N\text{-}N)Cl_2$ products.[5] Treatment of $Pd(PhCN)_2Cl_2$ with II has been found to give $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ in a related reaction. Similarly, the reaction between II and $Ru(PPh_3)_3Cl_2$ results in displacement of one PPh_3 ligand to give $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$ in a reaction that has precedent in bipyridine chemistry.[10] Characterization of products of both reactions with II was complicated by the presence of solvent molecules of crystallization, which gave erratic analytical results. Both the Pt–Pd and Pt–Ru reaction products were characterized crystallographically to provide unambiguous formulations for the two compounds.

The third synthetic procedure also has precedent in bipyridine chemistry but proceeds through a reactive Pt(0) species. Addition of II to the platinum(0) dibenzylideneacetone complex, $Pt_2(DBA)_3$, results in formation of $(PPh_3)_2Pt^{II}(O',O\text{-}PhD\text{-}N,N')Pt^0(DBA)$ (IV) containing mixed-valence Pt atoms. This complex is related to (bpy)Pt(DBA), formed by treating $Pt_2(DBA)_3$ with bipyridine,[11] and probably has the three-coordinate Pt(0) structure of (bpy)Pd(DBA).[12] Treatment of (bpy)Pt(DBA) with 3,5-di-*tert*-butyl-1,2-benzoquinone (DBBQ) leads to the formation of $(bpy)Pt^{II}(DBCat)$,[11] and in a related reaction, IV and DBBQ give $(PPh_3)_2Pt^{II}(O',O\text{-}PhD\text{-}N,N')Pt^{II}(DBCat)$. Characterization of this complex by chemical analyses, NMR spectroscopy, and mass spectrometry was unambiguous.



IV

Structure Determinations. $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$. Crystals of the complex grown from a dichloromethane/benzene solution form with three molecules of benzene in the asymmetric region of the unit cell. One molecule is located near a crystallographic inversion center that generates a related molecule with the two molecules paired by a weak charge-transfer interaction. The other two solvate molecules have no close contacts, show evidence of disorder and fractional occupancy, and are responsible for the poor quality of crystals formed by this recrystallization procedure. Attempts at growing crystals from other solvent media were unsuccessful. Nevertheless, the features of the $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ complex molecule, shown in Figure 1, are clear from the structure determination, and bond lengths and angles, listed in Table IV, are reasonable values. The coordination environments about both metals are square planar, and the planar PhD bridge results in planarity from the platinum atom to the palladium chloro ligands. Platinum phosphine atoms are twisted slightly from this plane, forming a dihedral angle of 13.5°. Ligand bond lengths to the metals are unexceptional, and the C–O lengths of the phenanthrolinediolate ligand are well within error of the catecholate value of 1.34 Å.[13] An interesting feature of the crystal structure is the intermolecular pairing (Figure 2) that exists between complex molecules related by a crystallographic 2-fold axis. Molecular planes are parallel and separated by 3.29 Å. The adjacent complex molecules are rotated with respect to one another so that the Pt–Pd vectors within the two planes are nearly at right angles. Presumably, this is to allow maximum overlap of donor

Table IV. Selected Bond Lengths and Angles for $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$

	Distances (Å)		
Pd–Cl1	2.275 (9)	Pd–Cl2	2.276 (8)
Pd–N1	2.061 (22)	Pd–N2	1.998 (21)
Pt–P1	2.254 (6)	Pt–P2	2.232 (8)
Pt–O1	2.052 (17)	Pt–O2	2.039 (13)
P1–C111	1.815 (29)	P1–C121	1.838 (28)
P1–C131	1.828 (26)	P2–C211	1.827 (26)
P2–C221	1.834 (27)	P2–C231	1.789 (27)
O1–C5	1.326 (30)	O2–C6	1.333 (32)
N1–C1	1.353 (41)	N1–C12	1.315 (34)
N2–C10	1.287 (38)	N2–C11	1.343 (30)
C1–C2	1.364 (51)	C2–C3	1.349 (43)
C3–C4	1.366 (40)	C4–C5	1.421 (38)
C4–C12	1.443 (40)	C5–C6	1.414 (37)
C6–C7	1.430 (33)	C7–C8	1.407 (33)
C7–C11	1.376 (31)	C8–C9	1.357 (35)
C9–C10	1.416 (46)	C11–C12	1.405 (34)
	Angles (deg)		
Cl1–Pd–Cl2	91.6 (3)	Cl1–Pd–N1	93.9 (7)
Cl2–Pd–N1	174.5 (7)	Cl1–Pd–N2	174.4 (6)
Cl2–Pd–N2	93.9 (6)	N1–Pd–N2	80.6 (9)
P1–Pt–P2	99.6 (3)	P1–Pt–O1	89.6 (5)
P2–Pt–O1	170.8 (5)	P1–Pt–O2	170.7 (5)
P2–Pt–O2	89.2 (5)	O1–Pt–O2	81.6 (7)

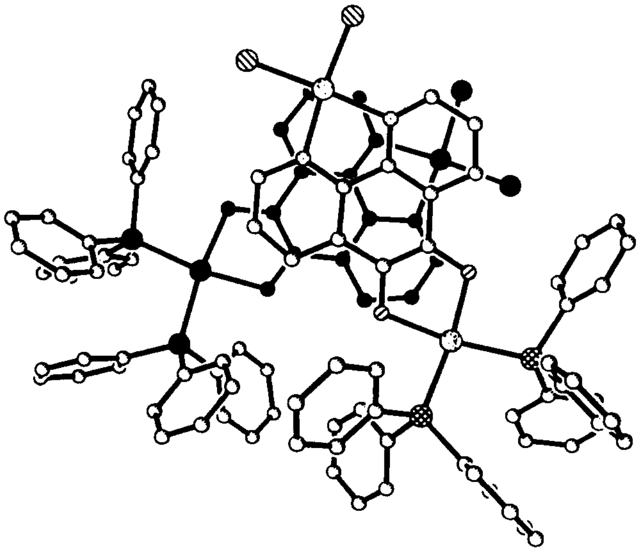


Figure 2. View showing the intermolecular pairing between $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ molecules in the solid state.

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[10] Gilbert, J. D.; Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2198.

[11] Fox, G. A.; Pierpont, C. G. Submitted for publication.

[12] Pierpont, C. G.; Buchanan, R. M.; Downs, H. H. *J. Organomet. Chem.* **1977**, *124*, 103.

[13] Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

Table V. Selected Bond Lengths and Angles for $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$

	Distances (Å)		
Pt–P1	2.248 (2)	Pt–P2	2.237 (2)
Pt–O1	2.046 (5)	Pt–O2	2.038 (4)
Ru–Cl1	2.440 (2)	Ru–Cl2	2.435 (2)
Ru–P3	2.386 (2)	Ru–P4	2.360 (2)
Ru–N1	2.045 (7)	Ru–N2	2.065 (5)
P1–C13	1.821 (8)	P1–C19	1.830 (7)
P1–C25	1.805 (7)	P2–C31	1.819 (7)
P2–C37	1.807 (8)	P2–C43	1.817 (9)
P3–C49	1.827 (9)	P3–C55	1.815 (9)
P3–C61	1.847 (9)	P4–C67	1.828 (12)
P4–C73	1.842 (7)	P4–C79	1.820 (8)
O1–C6	1.348 (7)	O2–C5	1.351 (9)
N1–C1	1.331 (10)	N1–C12	1.385 (7)
N2–C10	1.315 (10)	N2–C11	1.386 (10)
C1–C2	1.389 (13)	C2–C3	1.345 (9)
C3–C4	1.405 (11)	C4–C5	1.413 (8)
C4–C12	1.408 (11)	C5–C6	1.374 (11)
C6–C7	1.424 (11)	C7–C8	1.418 (11)
C7–C11	1.407 (8)	C8–C9	1.400 (12)
C9–C10	1.384 (9)	C11–C12	1.404 (10)
	Angles (deg)		
P1–Pt–P2	99.6 (1)	P1–Pt–O1	169.5 (1)
P2–Pt–O1	90.7 (1)	P1–Pt–O2	86.7 (2)
P2–Pt–O2	173.2 (2)	O1–Pt–O2	82.9 (2)
Cl1–Ru–Cl2	94.8 (1)	Cl1–Ru–P3	92.5 (1)
Cl2–Ru–P3	85.1 (1)	Cl1–Ru–P4	86.6 (1)
Cl2–Ru–P4	91.5 (1)	P3–Ru–P4	176.4 (1)
Cl1–Ru–N1	172.7 (1)	Cl2–Ru–N1	92.0 (1)
P3–Ru–N1	90.8 (2)	P4–Ru–N1	90.5 (2)
Cl1–Ru–N2	92.9 (2)	Cl2–Ru–N2	171.9 (2)
P3–Ru–N2	91.9 (2)	P4–Ru–N2	91.6 (2)
N1–Ru–N2	80.5 (2)		

and acceptor regions of the reduced PhD ligands while minimizing steric contacts between PPh_3 ligands.

$(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$. Structural features of $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$ are shown in Figure 3, and selected bond distances and angles are listed in Table V. Phosphine ligands are bonded in trans coordination sites about the octahedral Ru atom. Intermolecular interactions are not found between adjacent complex molecules as in the previous molecule. Rather, phenyl rings of PPh_3 ligands bonded to Ru stack above and below the bridging PhD ligand. Phenanthrenequinone ligands are known to form stacked lattices, and this structural feature illustrates an intramolecular stacking mechanism possible for quinone complexes containing PPh_3 ligands. Structural features of the PhD ligand show that it is in the reduced diolate form. In particular, C–O bond lengths average to 1.345 (7) Å, typical of catecholate ligands. Solvate molecules in the crystal lattice are disordered and are easily dispaced as in the previous structure. However, this did not affect crystal quality to the extent found in the structure determination on $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$.

Electrochemistry. Electrochemical interest in the three complexes included in this study is related to the redox activity of the PhD ligand in combination with the activity of other metals and ligands in the complex molecule. Results of this characterization are summarized in Table VI. The $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ molecule contains only the bridging PhD ligand as a readily accessible redox center. Cyclic voltammograms of this complex show that the ligand undergoes oxidation in two steps, at potentials of +0.170 and +0.747 V. The irreversible second oxidation corresponds to formation of the benzoquinone form of PhD, and complex dissociation appears to occur from this redox state. The electrochemistry on $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$ shows three oxidation steps at –0.228, +0.199, and +0.682 V. The first two are reversible; the third is irreversible. In this case, the electrochemistry arises from the combined activity of the PhD ligand and the Ru center. A sample of $Ru(PPh_3)_2Cl_2(phen)$ was prepared[10] and characterized electrochemically; the Ru(II)/Ru(III) couple of this complex was observed at –0.026 (140) V. This result, together with the potentials of $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$, leads to the assignment given in Table VI with the couple at –0.228 V as the Ru(II)/Ru(III) oxidation and the remaining two oxidations associated with the PhD bridge.

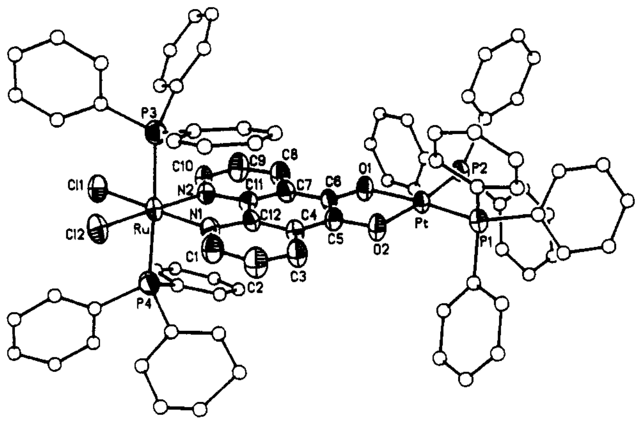

Figure 3. View showing the $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$ complex molecule.

The $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Pt(DBCat)$ complex contains two electroactive quinone ligands. Cyclic voltammograms show two reversible oxidations at –0.260 and +0.250 V and two additional oxidations at +0.624 and +0.795 V that are essentially irreversible. The most negative oxidation lies at a potential that is in the range of values observed for ligand oxidations of M(DBCat) complexes,[2] and it is likely associated with the DBCat ligand of $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Pt(DBCat)$. The second oxidation at 0.250 V is near the first oxidation potentials of the PhD ligands of the previous two complexes and may be assigned as the Cat/SQ oxidation of the PhD bridge. The two irreversible oxidations at more negative potentials correspond to ligand oxidations to the benzoquinone form. The more negative of the two is close to the second oxidation potentials of the PhD bridges of $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ and $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$ and may also be associated with the bridge in this case.

Discussion

Complexes containing an oxygen-bound PhD ligand may serve as nitrogen donor ligands in the synthesis of polymetallic complexes containing reduced PhD bridges between metals. In principle, it is possible that any mononuclear complex containing bipyridine or *o*-phenanthroline ligands may be extended to polynuclear species by using this bridging agent. A broad spectrum of complexes may be prepared by relatively simple synthetic procedures. Charac-

Table VI. Electrochemical Potentials (V, Fc/Fc^+) for Redox Processes of PhD Complexes

complex	PhD Cat/SQ	PhD SQ/BQ	other
PhD	–1.74 (28)	–0.884 (142)	
$Ru(bpy)_2(N',N\text{-}PhD)^{2+}$	–1.261 (98)	–0.504 (62)	
$(PPh_3)_2Pt(O',O\text{-}PhD)$	–0.207 (78)	0.416[a]	
$(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$	0.170 (106)	0.747[a]	
$(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$	0.199 (118)	0.682[a]	–0.228 (104)[b]
$(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Pt(DBCat)$	0.250 (120)	0.624[a]	–0.260 (85),[c] 0.795[a,d]

[a] Irreversible oxidation; potential given as E_a. [b] Ru^{II}/Ru^{III} couple. [c] DBCat/DBSQ couple. [d] DBSQ/DBBQ oxidation.

terization of the complexes included in this report shows structural properties that may be anticipated for PhD-bridged species. Redox properties show that the semiquinone form of the bridging PhD diolate ligand is readily accessible. We have found, in accord with Abruna's results,[6] that the free PhD ligand undergoes reductions to semiquinone and catecholate forms in two steps at −0.884 and −1.74 V (Fc/Fc$^+$). Coordination of PhD through nitrogen atoms in $Ru(bpy)_2(N',N\text{-}PhD)^{2+}$ results in a positive shift in these potentials to −0.504 and −1.261 V. Our electrochemical study on $(PPh_3)_2Pt(O',O\text{-}PhD)$ (Table VI) shows that there is a further positive shift for the ligand coordinated in its diolate form. As a bridging ligand coordinated through both nitrogen and oxygen atoms, these potentials were shifted to the further positive potentials listed in Table VI, reflecting the increased stability of the catecholate form upon coordination. The oxidation potentials of coordinated catecholate ligands are typically found at much more positive potentials than the corresponding potentials of the benzoquinone ligand in free form, often with shifts that are greater than 1.0 V.[2] For PhD, the shift from free ligand to $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Pt(DBCat)$ is nearly 2 V, and the electrochemical activity of the bridge occurs at potentials that are within the range of accessible redox states of metal ions. This is an important difference between the PhD-bridged species and corresponding bipyridine analogues. At the same time, it opens the opportunity for studies on the nature of bimetallic interactions through the bridge as a function of bridge charge and electronic structure.

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Supplementary Material Available: For $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')PdCl_2$ and $(PPh_3)_2Pt(O',O\text{-}PhD\text{-}N,N')Ru(PPh_3)_2Cl_2$, tables giving crystal data and details of the structure determination, atom coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom locations (30 pages); listings of structure factors (54 pages). Ordering information is given on any current masthead page.

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Cluster Synthesis. 33. New Platinum–Osmium Carbonyl Cluster Complexes from $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$: Synthesis and Characterization of $PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6$, $PtOs_5(CO)_{18}(\mu\text{-}H)_4$, and $PtOs_4(CO)_{15}(\mu\text{-}H)_2$

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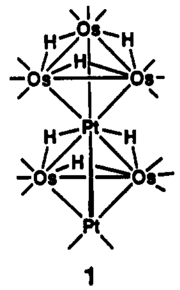
From the reaction of $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ with H_2S at 25 °C the new platinum–osmium carbonyl cluster complex $PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6$ (**2**) was obtained in 83% yield. Compound **2** was characterized by IR, ^1H NMR, ^{13}C NMR, and single-crystal X-ray diffraction analyses. The structure of **2** consists of a $PtOs_3$ tetrahedron fused to a $PtOs_2$ triangle with the platinum atom at the vertex-sharing site. There is a triply bridging sulfido ligand on the $PtOs_2$ triangular grouping. The molecule was shown by variable-temperature ^1H NMR and ^{13}C NMR spectroscopy to undergo a dynamic process that involves an intramolecular rotation of the Os_3 triangular group relative to the Os_2S grouping at the platinum atom. $\Delta G^*_{261} = 12.3$ kcal/mol. The reaction of $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ with $Os(CO)_5$ at 25 °C yielded two new platinum–osmium carbonyl cluster complexes $PtOs_5(CO)_{18}(\mu\text{-}H)_4$ (**3**) and $PtOs_4(CO)_{15}(\mu\text{-}H)_2$ (**4**) in 38% and 25% yields, respectively. Both compounds were characterized crystallographically. The cluster of compound **3** consists of a $PtOs_3$ tetrahedron fused to a $PtOs_2$ triangle by the vertex-sharing platinum atom. The cluster of compound **3** contains a $PtOs_3$ tetrahedron with an edge-bridging $Os(CO)_4$ group. The positions of all of the hydride ligands in **3** and **4** were determined by a combination of ^1H NMR spectroscopy and crystallography. Compound **3** is readily degraded by CO (25 °C/1 atm) to yield the products $PtOs_2(CO)_{10}$, $H_2Os_2(CO)_8$, and $H_2Os(CO)_4$. Crystal data: for **2**, space group $P\bar{1}$, $a = 19.451$ (6) Å, $b = 23.075$ (3) Å, $c = 9.771$ (2) Å, $\alpha = 94.69$ (1)°, $\beta = 100.81$ (2)°, $\gamma = 98.90$ (2)°, $Z = 6$, 5486 reflections, $R = 0.040$; for **3**, space group $P2_1$, $a = 8.875$ (5) Å, $b = 19.47$ (1) Å, $c = 9.370$ (3) Å, $\beta = 116.42$ (3)°, $Z = 2$, 1607 reflections, $R = 0.045$; for **4**, space group $P2_1/c$, $a = 13.337$ (2) Å, $b = 8.809$ (3) Å, $c = 20.141$ (4) Å, $\beta = 90.59$ (2)°, $Z = 4$, 2400 reflections, $R = 0.036$.

Introduction

The importance of heterobimetallic "clusters" containing platinum as catalysts in the petroleum re-forming process[1] has produced a great interest in the chemistry of heteronuclear cluster complexes containing platinum.[2] We have recently discovered a series of new hydrogen-rich platinum–osmium carbonyl cluster complexes that were obtained from the reaction of $Pt_2Os_4(CO)_{18}$ with hydrogen.[3] Their structures consist of vertex-fused polyhedra with platinum atoms at the vertex-sharing positions. The complex $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**1**) is a representative member of this series.



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We have now investigated the reaction of **1** with H_2S and $Os(CO)_5$. The reactions have yielded the new complexes $PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6$ (**2**) and $PtOs_5(CO)_{18}(\mu\text{-}H)_4$ (**3**) plus $PtOs_4(CO)_{15}(\mu\text{-}H)_2$ (**4**), respectively. Details of the preparation, characterization, and reactivity of these compounds toward CO are presented in this report.

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over sodium and deoxygenated by purging with nitrogen prior to use. $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ was prepared by the previously reported procedure.[3] IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-300 FT-NMR spectrometer. Natural-abundance ^{13}C NMR spectra were recorded on a Bruker AM-500 FT-NMR

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(1) (a) Biswas, J.; Bickle, G. M.; Gray, P. G.; Do, D. D.; Barbier, J. *Catal. Rev.—Sci. Eng.* **1988**, *30*, 161. (b) Sinfelt, J. H. *Bimetallic Catalysts. Discoveries, Concepts and Applications*; John Wiley & Sons: New York, 1983.

(2) (a) Farrugia, L. J. *Adv. Organomet. Chem.* **1990**, *31*, 301. (b) Braunstein, P.; Rose, J. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; Vol. 3.

(3) Adams, R. D.; Pompeo, M. P.; Wu, W. *Inorg. Chem.*, in press.

0020-1669/91/1330-2899$02.50/0