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## Communications

### Structure, Synthesis, and Characterization of Chiral Secondary Diphosphine Platinum(II) Mono- and Dimeric Complexes: Molecular Structure of $[Pt_2Cl_4(SMe_2)_2\{(R^*,R^*)\text{-}\mu\text{-}H^tBuPCH_2P^tBuH\}]$

The use of diphosphine ligands in the stabilization of both dinuclear and higher nuclearity metal centers has been an area of intensive investigation.[1] Of primary interest have been the factors influencing whether chelating or bridging coordination modes are adopted by the specific diphosphines.[2] Such investigations have also extended beyond tertiary diphosphine systems into secondary diphosphine systems.[2a,3,4] Disecondary diphosphines of the type $HRPCH_2PRH$ (R = $^iPr$, $^tBu$) have been only reported as occupying bridging coordination modes.[2a,3b] Such observations had previously been reported for tertiary diphosphines, $R_2PCH_2PR_2$ (R = Me, Et) possessing less bulky substituents at the phosphorus atoms.[2,3] Therefore, this behavior in disecondary diphosphines was attributed to the reduction of steric crowding at the phosphorus atoms.[2a,3b]

The formation of bridging bis(diphosphine) dinuclear systems, by substitution of dimethyl sulfide ligands within platinum(II) complexes, has been rationalized by utilizing mechanisms involving complexes containing diphosphine and dimethyl sulfide, i.e. $[Pt_2Cl_4(SMe_2)_2(\mu\text{-}R_2PCH_2PR_2)]$.[2b] To date, no such complexes have been reported. We are therefore prompted to report the isolation and characterization of $[Pt_2Cl_4(SMe_2)_2\{(R^*,R^*)\text{-}\mu\text{-}H^tBuPCH_2P^tBuH\}]$, a complex possessing extensive intramolecular hydrogen bonding.

Reaction of $[PtCl_2(SMe_2)_2]$, in greater than a 2-fold excess, with a 1:1 mixture of mono- and disecondary diphosphines, $H^tBuPCH_2P^tBuH$ and $H^tBuPCH_2P^tBu_2$, has led to the isolation of the two new complexes $[PtCl_2(H^tBuPCH_2P^tBu_2)]$ (**1**) and $[Pt_2Cl_4(SMe_2)_2\{(R^*,R^*)\text{-}\mu\text{-}H^tBuPCH_2P^tBuH\}]$ (**2**) with no evidence of mixed-ligand products.[5] Complex **1** is readily characterized by $^1H$ and $^{31}P$ NMR data.[5] The high-field shift of the observed $^{31}P$ NMR resonances relative to those of the free ligand confirmed the presence of a chelating diphosphine ($\delta$(complex) − $\delta$(free ligand): $\Delta P^a$, −43; $\Delta P^b$, −45).[6] The $^1H$ NMR spectrum reveals the presence of only one PH functionality within the coordinated diphosphine ligand: $\delta$ 4.08; $^1J(P^bH)$ = 397 Hz, $^3J(HH)$ = 6.8 Hz, $^3J(HH)$ = 6.8 Hz. The methylene protons of the diphosphine ligand appear as two nonequivalent resonances, $\delta$ 3.66 and 2.67, due to the asymmetry introduced into the complex by the PH functional group. These observations are consistent with a mononuclear chelate structure for complex $[PtCl_2(H^tBuPCH_2P^tBu_2)]$ (**1**).

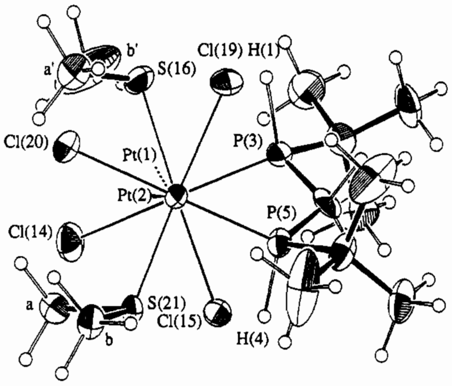

**Figure 1.** Molecular structure of $[Pt_2Cl_4(SMe_2)_2\{(R^*,R^*)\text{-}\mu\text{-}H^tBuPCH_2P^tBuH\}]$ viewed along the metal–metal vector. Selected bond distances (Å) and angles (deg) are as follows: Pt(1)Cl(14), 2.373 (3); Pt(1)Cl(15), 2.323 (3); Pt(1)S(16), 2.262 (3); Pt(1)P(3), 2.221 (3); Pt(2)Cl(19), 2.314 (3); Pt(2)Cl(20), 2.358 (3); Pt(2)S(21), 2.273 (4); Pt(2)P(5), 2.215 (3); P(3)H(1), 1.4 (1); P(5)H(4), 1.54 (9); Cl(14)Pt(1)Cl(15), 90.4 (1); Cl(14)Pt(1)S(16), 91.7 (1); Cl(14)Pt(1)P(3), 178.5 (1); Cl(15)Pt(1)S(16), 177.2 (1); Cl(15)Pt(1)P(3), 89.42 (1); S(16)Pt(1)P(3), 88.4 (1); Cl(19)Pt(2)Cl(20), 90.0 (1); Cl(19)Pt(2)S(21), 176.3 (1); Cl(19)Pt(2)P(5), 89.6 (1); Cl(20)Pt(2)S(21), 92.8 (1); Cl(20)Pt(2)P(5), 175.4 (1); S(21)Pt(2)P(5), 87.8 (1). The nonbonding distance Pt(1)Pt(2) is 3.747 Å.

An X-ray diffraction study was carried out to determine the structure of complex **2**. The results are summarized in Figure

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(5) Selected spectroscopic data for **1**. $^1H$ NMR ($CDCl_3$): $\delta$ 4.08, $^3J(HH)$ = 6.8 Hz, $^3J(HH)$ = 6.8 Hz, $^1J(P^bH)$ = 397 Hz, ddd, *H*P; $\delta$ 3.66, $^2J(HH)$ = 16.1 Hz, $^3J(HH)$ = 6.8 Hz, $^2J(PH)$ = 11.2 Hz, $^2J(PH)$ = 7.8 Hz, m, $CH^aH^bP_2$; $\delta$ 2.67, $^2J(HH)$ = 16.1 Hz, $^3J(HH)$ = 6.8 Hz, $^2J(PH)$ = 12.2 Hz, $^2J(PH)$ = 9.8 Hz, m, $CH^aH^bP_2$; $\delta$ 1.49, $^3J(P^aH)$ = 16.5 Hz, d, $CMe_3$; $\delta$ 1.47, $^3J(P^aH)$ = 16.0 Hz, d, $CMe_3$; $\delta$ 1.39, $^3J(P^bH)$ = 19.3 Hz, d, $CMe_3$. $^{31}P$ NMR ($CD_2Cl_2$): $\delta$ −16.2, $^2J(P^aP^b) \approx 60$ Hz, $^1J(PtP^a) \approx 2950$ Hz, m, $P^a$; $\delta$ −64.6, $^2J(P^bP^a) \approx 60$ Hz, $^1J(PtP^b) \approx 3010$ Hz. Selected spectroscopic data for **2**. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 5.01, $^3J(HH)$ = 7.0 Hz, $^1J(PH)$ = 414 Hz, $^2J(PtH) \approx 36$ Hz, dt, *H*P; $\delta$ 2.75, $^3J(HH)$ = 7.0 Hz, $^2J(PH)$ = 12.6 Hz, tt, $CH_2P_2$; $\delta$ 2.94, $^3J(PtH)$ = 54 Hz, s, 2 $SMe$; $\delta$ 2.64, $^3J(PtH)$ = 54 Hz, s, 2 $SMe$; $\delta$ 1.36, $^3J(PH)$ = 17 Hz, $^4J(PtH) \approx 26$ Hz, d, 2 $CMe_3$. $^{31}P$ NMR ($CDCl_3$): $\delta$ 9.7, $^1J(PtP)$ = 3545 Hz, $^3J(PtP)$ = 72.4 Hz, s, $P_2CH_2$.

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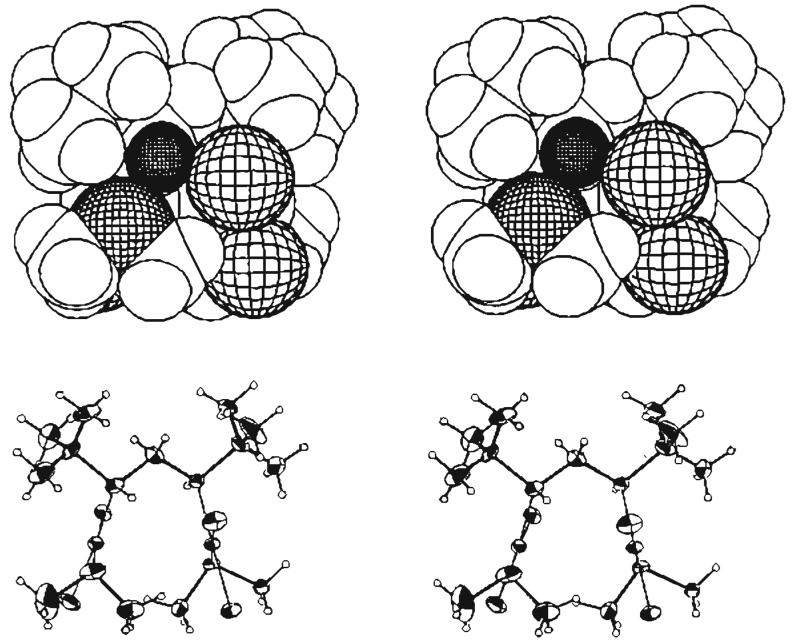
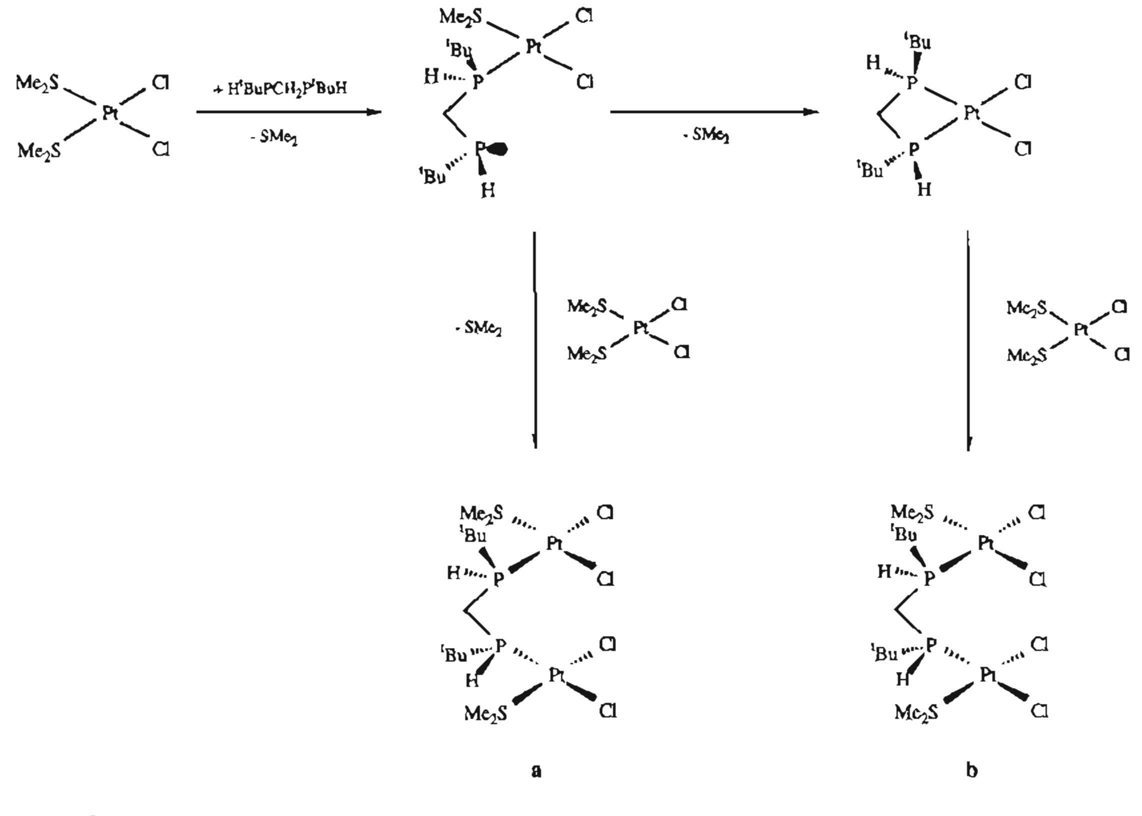


**Figure 2.** ORTEP stereoview and space-filling stereoview of the molecular structure of $[Pt_2Cl_4(SMe_2)_2\{(R^*,R^*)\text{-}\mu\text{-}H^tBuPCH_2P^tBuH\}]$. Cross-hatched atoms from left to right are S(21), H(4), Cl(15), and Cl(14). Selected intramolecular close hydrogen contacts (Å) and angles (deg) are as follows: H(1)S(16), 2.66; H(4)S(21), 2.77; H(1)Cl(19), 2.86; H(4)Cl(15), 2.76; P(3)H(1)S(16), 95; P(5)H(4)S(21), 88; P(3)H(1)Cl(19), 105; P(5)H(4)Cl(15), 111.

**Scheme I**



1 and its caption.[7] Complex **2** consists of two square-planar platinum(II) centers bridged by the diphosphine ligand, $H^tBuPCH_2P^tBuH$. Each center possesses two chloride ligands in a cis orientation. The two square planes of each platinum(II) center are essentially parallel, facing each other in a staggered conformation. One dimethyl sulfide ligand is coordinated to each platinum atom trans to a chloride ligand and cis to a phosphorus atom of the bridging diphosphine. The occupancy of equatorial sites by bulky *tert*-butyl groups and axial sites by protons on the diphosphine minimizes the steric interactions within this complex. The dimethyl sulfide ligands are oriented such that the lone pair of electrons on each sulfur is directed toward a proton of the diphosphine ligand. This orientation clearly minimizes any steric interactions with the methyl groups of the dimethyl sulfide ligands. The hydrogen–sulfur and hydrogen–chlorine separations are all

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(7) Crystal data for **2**: $C_{13}H_{34}Cl_4P_2Pt_2S_2$, $M_r = 848.47$, monoclinic, $P2_1/a$ (a nonstandard setting of $P2_1/c$), $a = 23.43$ (1) Å, $b = 11.203$ (3) Å, $c = 9.734$ (3) Å, $\beta = 99.33$ (2)°, $V = 2521$ (2) Å$^3$, $T = 118$ K, $Z = 4$, $D_c = 2.235$ g cm$^{-3}$, $\lambda$(Mo K$\alpha$) = 0.71069 Å. Of the 3305 unique intensities measured, 2856 with $F_o > 2.33\sigma(F_o)$ yielded $R(F) = 0.0396$ and $R_w(F) = 0.0373$.

suggestive of a hydrogen-bonding interaction (Figure 2).[8] It is apparent that a hydrogen-bonding interaction, above and below the planes defined by the phosphorus and platinum atoms, would contribute to the overall stabilization of this conformation.

Complex **2** was further characterized by its $^1$H and $^{31}$P{$^1$H} NMR spectra.[5] The $^{31}$P{$^1$H} spectrum shows a singlet resonance at $\delta$ 9.7. The low-field shift of this resonance, relative to that of its free ligand, confirms the presence of a bridging diphosphine ligand.[6] The presence of inner platinum satellites, due to a three-bond platinum-phosphorus coupling constant, $^3J$(PtP) = 72.4 Hz, supports the assignment of a dinuclear structure to the complex. The $^1$H NMR spectrum also supports this assignment, with an observed PH proton resonance at $\delta$ 5.01 and a resonance appearing as a triplet of triplets, $\delta$ 2.75, due to the protons of the methylene group bridging the two phosphorus atoms. The methyl protons of the sulfide ligands generate two nonequivalent resonances, $\delta$ 2.64 and 2.94, due to the proximal methyl groups a and a′, those directed toward each other, and the distal methyl groups b and b′, those directed away from each other (Figure 1). These data suggest that the solution structure at room temperature is static with regard to the sulfide ligands and identical with the solid-state structure.

The formation of complex **2** may involve reaction of one phosphorus of the diphosphine ligand with a platinum(II) center displacing one dimethyl sulfide ligand (Scheme I). This would be followed by reaction of the "dangling" end of the diphosphine with a second platinum(II) center and loss of a dimethyl sulfide ligand. An alternative mechanism would involve coordination of the "dangling" end of the diphosphine ligand to the original platinum(II) center, forming a mononuclear chelate. This mononuclear species could react with another platinum(II) center and undergo a ligand-exchange process[9] to generate the observed product. The former mechanism (path a in Scheme I) is favored over mononuclear chelate formation (path b in Scheme I) since such chelate complexes are without precedent within disecondary diphosphine, $HRPCH_2PRH$, platinum systems.

Complex **2**, a mixed bis(dimethyl sulfide) diphosphine dimer, represents a useful model for many of the intermediates invoked to rationalize dimer formation within related bis(diphosphine)-platinum(II) dimeric systems.[2a] This complex is also a likely intermediate in the formation of the complex $[Pt_2Cl_4(\mu\text{-}H^tBuPCH_2P^tBuH)_2]$.[2b] The premise that reduced steric bulk around the phosphorus center enhances preference for occupancy of bridging coordination modes over chelating coordination modes is illustrated by the structure of complex **2**. Intramolecular hydrogen bonding in the disecondary diphosphine complex possibly plays a contributive role in the generation of this mode of diphosphine coordination.

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**Supplementary Material Available:** Details of the data collection and listings of final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (12 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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## Large Intensity Enhancement of the Spin-Forbidden $^4A_{2g} \rightarrow {}^2E_g$ Transition in Chromium(III)-Semiquinone Complexes

The interaction of transition-metal ions with organic radicals that are directly bound to them can result in many new experimental properties that are currently being actively investigated. For instance strong ferromagnetic couplings have been observed,[1] of which perhaps the most striking example is that of $[Ni(CTH)(DTBSQ)]PF_6$ (CTH = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; DTBSQ = 3,5-di-*tert*-butylsemiquinone), which has a ground quartet state, as a result of the interaction between nickel(II) ($S = 1$) and the semiquinone ($S = {}^1/_2$), and no evidence, even at room temperature, of populated doublet levels.[2] In a quantitative way this corresponds to the isotropic coupling constant $J \geq 400$ cm$^{-1}$ (throughout the paper we use the spin Hamiltonian in the form $H = JS_1S_2$), which is determined by the fact that the magnetic orbitals of the metal ion and of the radical are orthogonal to each other and are in close contact. Such high values of ferromagnetic couplings are quite unusual for pairs of metal ions,[3] and this example shows well how extremely enhanced effects can be observed when the metal ion interacts directly with a radical.

Another field where dramatic effects can be anticipated due to the coupling of metal and radical orbitals is that of optical transitions. In fact it is well-known that formally spin-forbidden transitions of single ions can acquire high intensities in pairs due to exchange effects.[4] The phenomenon has been studied with many different metal ions,[5] and particularly interesting results have been observed for chromium(III) pairs,[6,7] which are characterized by large enhancements of the $^4A_{2g} \leftrightarrow {}^2E_g$ transitions.

We have now found that in the octahedral complexes $Cr(CTH)(DTBSQ)^{2+}$ and $Cr(CTH)(TCSQ)^+$ (TCSQ = 3,4,5,6-tetrachlorosemiquinone) a large intensity enhancement of the $^4A_{2g} \rightarrow {}^2E_g$ transition occurs and we here wish to report its characterization.

$Cr(CTH)Cl_2$ reacts with di-*tert*-butyl-*o*-benzoquinone in methanol, yielding after addition of $KPF_6$, a crystalline compound of formula $[Cr(CTH)(DTBSQ)]_2Cl(PF_6)_3$ (I). Under the same conditions tetrachloro-*o*-benzoquinone reacts, yielding $[Cr(CTH)(TCCat)]PF_6$ (II; TCCat = tetrachlorocatecholato). The formulation of I and II follows from elemental analysis, IR and EPR spectroscopy, and magnetic measurements.

I is EPR silent and is characterized by an effective magnetic moment of 2.9 $\mu_B$ at room temperature. No temperature dependence of the magnetic moment was observed; therefore, it must be concluded that the coupling is strongly antiferromagnetic with a ground state $S = 1$ and no excited state thermally populated. Since in an exchange Hamiltonian approach the energy separation between the ground triplet state and the first excited quintet state is $2J$, the isotropic coupling constant $J$ can be assumed to be larger than 350 cm$^{-1}$.

Electrochemical measurements in acetonitrile solution show that I undergoes a reversible one-electron redox process at 0.21 V vs SCE and an irreversible one at 1.3 V vs SCE. As supported by spectroscopic data and comparison with iron(III) and cobalt (III) analogues, both processes are associated with ligand-centered electron-transfer processes, i.e. catecholate-semiquinone and semiquinone-quinone.

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