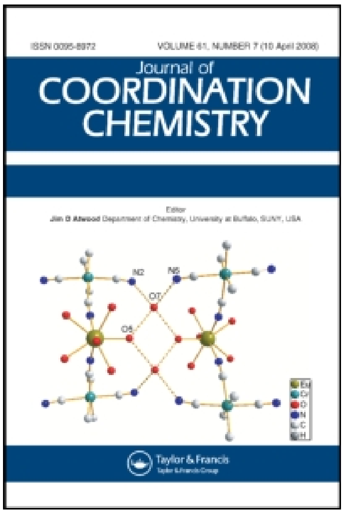

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Ph_2PPy REPLACEMENT OF THE 1,5-COD LIGAND IN THE SULFIDO-CAPPED CLUSTER $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$. X-RAY DIFFRACTION STRUCTURE AND REDOX BEHAVIOR OF $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

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Ph_2PPy REPLACEMENT OF THE 1,5-COD LIGAND IN THE SULFIDO-CAPPED CLUSTER $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$. X-RAY DIFFRACTION STRUCTURE AND REDOX BEHAVIOR OF $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

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The replacement of the 1,5-cyclooctadiene (COD) ligand in the cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$ (**1**) with the pyridylphosphine ligand Ph_2PPy (2.0 equiv) occurs readily at room temperature to give the phosphine-substituted cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ (**2**). Cluster **2** was isolated by preparative chromatography and characterized in solution by IR and ^{31}P NMR spectroscopy. The solid-state structure was established by X-ray diffraction analysis. $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ crystallizes in the monoclinic space group C_2/c, a = 19.8781(5) Å, b = 13.4603(3) Å, c = 16.3304(4) Å, β = 108.828(2) °, V = 4135.6(2) Å^3, Z = 4, d_{calc} = 1.711 g cm^{-3}; R = 0.0232, R_w = 0.0258 for 2212 observed reflections with $I > 3\sigma(I)$. The X-ray structure confirms the square planar geometry at the platinum center and coordination of the phosphorus centers to the platinum center in cluster **2**. The *arachno* polyhedral shape adopted by cluster **2** is not consistent with PSEP theory, with the deviation from PSEP theory being attributed to the strong propensity for the platinum center in **2** to maintain a square planar geometry. Cyclic voltammetric studies in CH_2Cl_2 indicate that **2** undergoes a reversible, one-election oxidation at $E_{1/2}$ = 0.39 V. The composition and energy of the HOMO and LUMO levels in the model cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ have been determined by carrying out extended Hückel molecular orbital calculations, and the data are discussed with respect to the observed electrochemistry.

Keywords: Heterometallic; iron; platinum; sulfide; cluster

INTRODUCTION

Many biologically important enzymes and proteins are known to contain polynuclear cluster compounds with an ancillary sulfido ligand(s).[1] The rich and

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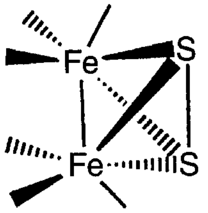
diverse chemistry exhibited by sulfido-capped clusters is not limited to the biological realm but also includes the areas of hydrodesulfurization[2] and synthesis of extended molecular arrays.[3] One particular challenge that still remains is the directed and high-yield synthesis of such cluster compounds, especially if detailed reactivity studies are to be carried out. In order to tackle these important areas of study, an easily prepared and readily available starting material is required. In this regard, the sulfido-bridged iron dimer $Fe_2(CO)_6(\mu_2\text{-}S)_2$, which was first described in a dissertation by Brendel[4] and in the journal literature by Hieber,[5] has been shown to function as an ideal building block for the construction of sulfido-capped mixed-metal *nido* and *arachno* polynuclear clusters.[6–10] These synthetic studies are also complemented by theoretical investigations on the bonding in the ligand-bridged dinuclear compounds $Fe_2(CO)_6(\mu_2\text{-}X)_2$ (where X = S, Se).[11] The molecular structure of the key dinuclear building block $Fe_2(CO)_6(\mu_2\text{-}S)_2$ is shown below.



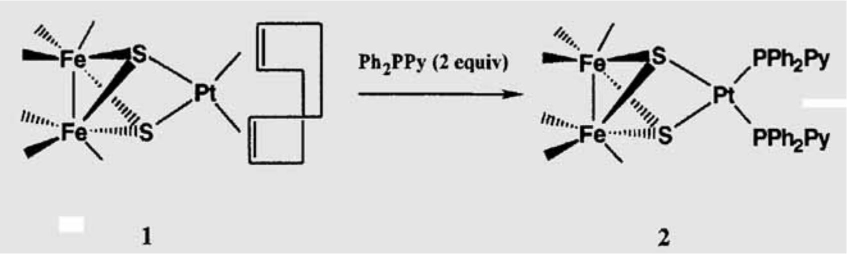
Herein we report our results on ligand substitution of added Ph_2PPy with $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$ to give $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$. The X-ray diffraction structure and the cyclic voltammetric behavior of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ are described, and the extended Hückel MO data on this new cluster compound are reported.

RESULTS AND DISCUSSION

Synthesis and Spectral Data

The reaction between $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$ (**1**)[12] and added Ph_2PPy (2.0 equiv) readily affords the phosphine-substituted cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ (**2**) at room temperature. Cluster **2** may be isolated as a red-black solid in yields on the order of 70–85% by chromatography over silica gel using CH_2Cl_2 as the eluant. $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ is very soluble in THF, and halogenated and aromatic solvents but is essentially insoluble in common saturated hydrocarbons such as petroleum ether and pentane. While samples of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

appear to be relatively stable in the solid state (< 5% decomposition after 1 month), fairly extensive decomposition of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ occurs in solution samples that have come in contact with oxygen. The reaction leading to cluster **2** is shown in equation 1.



$Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ was characterized in solution by IR and ^{31}P NMR spectroscopy. The IR spectrum of **2** (in CH_2Cl_2) exhibits three terminal ν(CO) bands at 2048 (s), 2007 (vs), and 1969 (s) cm^{-1}, which is typical of other clusters and dinuclear compounds containing the $Fe_2(CO)_6$ fragment.[6–10] The ν(CO) bands of cluster **2** are shifted to lower energy (*ca.* 40 cm^{-1}) with respect to the sulfido-bridged dimer $Fe_2(CO)_6(\mu_2\text{-}S)_2$, which signals the presence of a greater amount of electron density associated with cluster **2** relative to the dimeric building block $Fe_2(CO)_6(\mu_3\text{-}S)_2$.[3, 4] The single ^{31}P resonance observed at δ 16.68 is fully consistent with the structure of cluster **2**, and the value of the observed ^{195}Pt satellites ($J_{P\text{-}P}$ = 1380 Hz) supports a *cis*-substituted diphosphine platinum center.[13]

X-Ray Diffraction Data for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

The molecular structure of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ was established by X-ray crystallography. Single crystals of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ exhibit no unusually short inter- or intra-molecular contacts in the unit cell. The X-ray data collection and processing parameters for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ are given in Table I with the final fractional coordinates being listed in Table II. The ORTEP diagram in Figure 1 shows the molecular structure of the title cluster compound and serves to establish the ligation of the Ph_2PPy ligands at the platinum center *via* the phosphorus atoms. Selected bond distances and angles for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ are given in Table III.

The Fe-Fe bond length of 2.501(2) Å and the symmetry equivalent Fe—S bond distances of 2.273(2) Å are not unusual when compared with values reported for other structurally characterized sulfido-substituted iron compounds.[6e, 9a, 14] The non-bonded S—S distance of 2.86(3) Å is *ca.* 0.82 Å longer than the reported S—S bond distance for S_8,[15] supporting the absence of

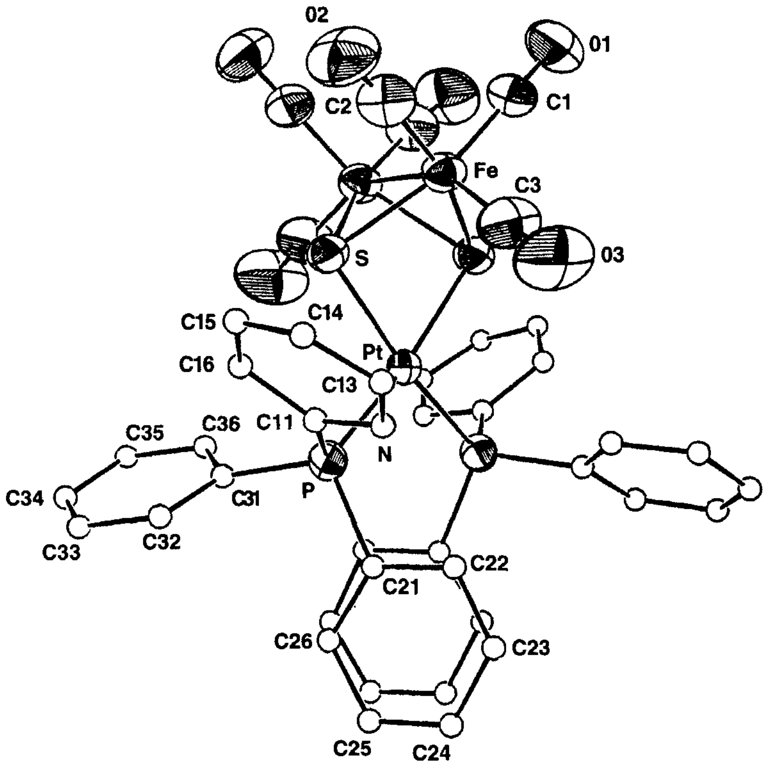


FIGURE 1 ORTEP diagram atoms of the non-hydrogen af $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ showing the thermal ellipsoids at the 50% probability level. The phenyl and pyridine rings are drawn with arbitrary thermal ellipsoids for clarity.

TABLE I X-ray crystallographic data and processing parameters for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

space group	C_2/c, monoclinic
a, Å	19.878(5)
b, Å	13.4603(3)
c, Å	16.3304(4)
β deg	108.828(2)
V, Å^3	4135.6(2)
mol formula	$C_{40}H_{28}Fe_2N_2O_6P_2PtS_2$
fw	1065.54
formula units per cell (Z)	4
ρ, g · cm^{-3}	1.711
abs coeff (μ), cm^{-1}	43.21
λ (Mo K α), Å	0.71073
collecn range, deg	$2.0 \leq 2\theta \leq 44.0$
tot. no. of data collcd	2746
no. of indep data, $I > 3\sigma(I)$	2212
Numb. of Parameters	249

TABLE I *(Continued)*

R	0.0232
R_w	0.0258
GOF	1.51
weights	$[0.04F^2 + \sigma F)^2]^{-1}$

TABLE II Fractional coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3) for the non-hydrogen atoms in $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Pt	0.000	0.23647(2)	0.750	2.454(5)
Fe	0.00031(4)	0.46587(6)	0.67355(6)	3.69(2)
S	0.07603(6)	0.3731(1)	0.7803(1)	3.58(3)
P	0.09096(6)	0.1286(1)	0.76465(9)	2.97(3)
O(1)	−0.1057(3)	0.6213(4)	0.6103(4)	7.4(2)
O(2)	0.1226(2)	0.5886(5)	0.6781(4)	8.4(2)
O(3)	−0.0143(4)	0.3561(6)	0.5147(4)	9.9(2)
N	0.1241(3)	0.1719(8)	0.6199(5)	9.8(2)
C(1)	−0.0642(3)	0.5607(5)	0.6338(5)	4.9(2)
C(2)	0.0733(3)	0.5425(6)	0.6747(5)	5.5(2)
C(3)	−0.0078(4)	0.4000(6)	0.5760(5)	6.2(2)
C(11)	0.1466(2)	0.1783(5)	0.7046(4)	4.1(1)
C(13)	0.1624(5)	0.220(1)	0.5751(6)	11.2(3)
C(14)	0.2194(4)	0.270(1)	0.6099(6)	12.1(3)
C(15)	0.2385(3)	0.2860(8)	0.6965(7)	10.7(3)
C(16)	0.2035(3)	0.2408(8)	0.7459(6)	7.8(2)
C(21)	0.0686(2)	0.0042(5)	0.7179(4)	3.5(1)
C(22)	0.0252(3)	0.0039(5)	0.6359(4)	4.0(1)
C(23)	0.0071(4)	−0.0851(8)	0.5954(5)	7.3(2)
C(24)	0.0299(4)	−0.1725(7)	0.6355(5)	7.1(2)
C(25)	0.0725(4)	−0.1708(6)	0.7191(6)	6.5(2)
C(26)	0.0921(3)	−0.0825(5)	0.7625(5)	4.7(2)
C(31)	0.1515(3)	0.1106(5)	0.8742(4)	4.1(1)
C(32)	0.2171(3)	0.0659(7)	0.8893(5)	6.7(2)
C(33)	0.2619(4)	0.0532(9)	0.9712(7)	9.0(3)
C(34)	0.2421(4)	0.085(1)	1.0397(7)	9.6(3)
C(35)	0.1788(4)	0.130(1)	1.0261(6)	8.7(3)
C(36)	0.1325(3)	0.1420(7)	0.9419(5)	6.1(2)

[a] Anisotropically refined atoms are give in the form of the isotropic equivalent displacement parameter defined as: (4/3) *[a^2*B(1, 1) + b^2*B(2, 2) + c^2*B(3, 3) + ab(cos γ)*B(1, 2) + ac(cos β)*B(1, 3) + bc(cos α)*B(2, 3)].

TABLE III Selected bond distances (Å) and angles (deg) in $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$[a]

Bond Distances			
Fe—Fe	2.501	Pt—S	2.330(1)
Pt—P	2.270(1)	Fe—S	2.273(2)
Fe—C(1)	1.776(6)	Fe—C(2)	1.776(7)
Fe—C(3)	1.784(8)	O(1)—C(1)	1.137(8)
O(2)—C(2)	1.144(9)	O(3)—C(3)	1.133(13)
S—S	2.86(3)	Fe—PT	3.331(1)

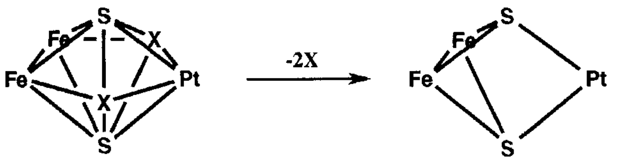
TABLE III *(Continued)*

Bond Distances			
P—C(11)	1.825(7)	P—C(21)	1.835(6)
P—C(31)	1.821(6)		
Bond Angles			
S—Pt—S'	75.67(5)	S—Pt—P	92.43(5)
S—Pt—P'	165.21(5)	P—Pt—P'	100.50(5)
S—Fe—C(1)	153.6(3)	S—Fe—C(2)	88.5(2)
S—Fe—C(3)	105.0(2)	C(1)—Fe—C(2)	94.4(3)
C(1)—Fe—C(3)	100.6(3)	C(2)—Fe—C(3)	97.8(4)
Pt—S—Fe	92.71(4)	Fe—C(1)—O(1)	178.2(8)
Fe—C(2)—O(2)	176.6(6)	Fe—C(3)—O(3)	177.9(8)
P—C(11)—N	118.9(5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

any significant interaction between the two capping sulfido groups. The observed 2.330(1) Å and 2.270(1) Å bond distances for the Pt—S and the Pt—P, bonds respectively, are in good agreement with PtP_2S_2 complexes that possess *trans* phosphorus and sulfur groups.[16] The *cis* bond angles (S—Pt—S', S—Pt—P, and P—Pt—P') and the *trans* bond angle (S—Pt—P') around the platinum atom are close to the idealized values of 90° and 180°, respectively, for a 16-electron, square planar platinum center. Clearly visible from the ORTEP diagram of cluster **2** is the fact that the Ph_2PPy ligands are bound to the platinum atom by the phosphorus atoms and not the two available nitrogen centers. Two of the aryl rings in the X-ray structure are parallel to within 5° and exhibit an average inter-ring distance of 3.50(6) Å, suggesting the presence of parallel π-π cloud interactions in the solid state.[17] Conventional electron-counting formalism dictates that the platinum center be regarded as a Pt^{2+} site, making it a soft acid center within the context of HSAB theory.[18] The coordination mode exhibited by the bifunctional Ph_2PPy ligands is in agreement with the coordination of the softer phosphorus donor center rather than the harder nitrogen atom. All other bond distances and angles are unexceptional.

The adopted *arachno* polyhedral structure by cluster **2** is of interest when viewed by Polyhedral Skeletal Electron Pair (PSEP) Theory.[19] As a formal five-vertex cluster containing seven skeletal electron pairs (SEP), PSEP theory predicts that $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ should exhibit a *nido* polyhedral structure, whose make-up may be theoretically considered as being derived from an octahedron with one missing vertex. However, the *arachno* structure exhibited by $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ is more easily considered as the loss of two vertices from the corresponding *closo* pentagonal bipyramid cluster shown below. The discrepancy between theory and experiment resides in the fact that the platinum center resists incorporation into the polyhedral core of **2**, preferring to remain four-coordinate and square planar. This behavior on the part of the platinum center serves to lower the vertex count in cluster **2** by one. Such a preference has its origin in the large platinum d-p promotion energy, which effectively removes the requisite platinum 6*p* orbital from entering into the delocalized bonding scheme.[20]



Seven vertex *closo* cluster

Five vertex *arachno* cluster

Cyclic Voltammetric Data for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

The redox properties of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ were examined by cyclic voltammetry at a platinum electrode in CH_2Cl_2 solvent containing 0.25 M tetra-n-butylammonium perchlorate (TBAP) as the supporting electrolyte. The cyclic voltammogram of **2** (not shown) reveals the presence of a reversible oxidation at $E_{1/2}$ = 0.39 V (vs SCE) when scanned over the potential range from 0.60 V to −1.60 V at a scan rate of 0.1 V/s. No evidence for a reduction process(es) was observed. An additional irreversible oxidation wave at E_{p^a} = 0.76 V was also recorded in the CV of **2** upon scanning out to a potential of 1.0 V. This second oxidation remained irreversible under all conditions examined (low temperatures and fast scan rates) and was not explored further.

The reversible oxidation response has been assigned to the 0/1+ redox couple based on the peak current (I_{p^c}/I_{p^a}) ratios of unity and linear plots of the current function (I_p) as a function of the square root of the scan rate (μ) over scan rates of 0.1 to 1.0 V/s.[21] The electron stoichiometry associated with this redox couple has been verified by comparison of the forward peak current of **2** with that of the known one-electron standard Cp^*_2Fe (internally added) in CH_2Cl_2/TBAP using Walden's Rule.[21a] The peak-to-peak separation (ΔE_p) of 84 mV for the **2/2+** redox couple is comparable to that of internally added Cp^*_2Fe (78 mV), suggesting that the heterogeneous charge transfer step (k_{het}) is rapid.

Extended Hückel Molecular Orbital Calculations

In order to gain information pertaining to the composition of the HOMO and LUMO in $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ we have carried out extended Hückel calculations on the model compound $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$. Figure 2 shows the CACAO drawings of the important HOMO and LUMO levels in $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$.[22]

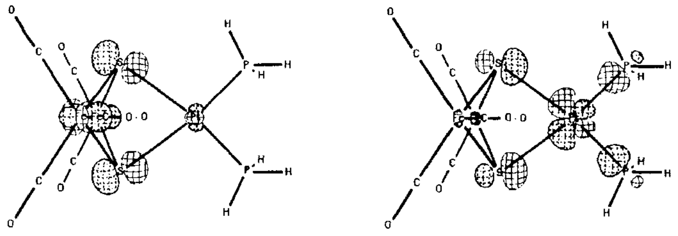


FIGURE 2 CACAO drawings of the HOMO (left) and LUMO (right) levels in F $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$.

The HOMO in $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ occurs at −10.85 eV and possesses a_1 symmetry. The HOMO exhibits bonding interactions between the two $Fe(CO)_3$ centers (52%) and the capping sulfido ligands (22%), with the iron orbital contribution to the HOMO best viewed as originating from a d_{yz} orbital that has been hybridized with added d_{z^2}, p_z, and p_x character. This particular hybridization serves to shape the HOMO for maximum overlap between the $Fe_2(CO)_6(\mu_3\text{-}S)_2$ centers. Each sulfido ligand consists of an in-phase arrangement of p_z orbitals, with minor contributions to the HOMO coming from the platinum p_z and s orbitals (5%) and the ancillary CO groups (6%). These MO data suggest that the 0/1+ redox couple found in the cyclic voltammetric studies on $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ involves electron removal from a cluster/ligand bonding orbital that is localized on the $Fe_2(\mu_3\text{-}S)_2$ centers.

The model cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ reveals a LUMO at −9.76 eV that possesses b_1 symmetry and whose orbital contributions derive from the antibonding overlap of the sulfido and PH_3 ligands with the platinum center. The two $Fe(CO)_3$ centers contribute less than 1% to the LUMO. Figure 2 (righthand side) clearly shows the platinum d_{xz} orbital and its hybridization with added p_x character, which allows diminished antibonding overlap with the shorter Pt—P bonds *vs* the Pt—S bonds (*vide supra*). The overall composition of the LUMO found for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ is not unlike the LUMOs reported for a wide variety of mononuclear, square-planar complexes of platinum.[23]

The LUMO found for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ does provide valuable data pertaining to the site of reduction in $Fe_2(CO)_6(\mu_3\text{-}S)_2PtL_2$ clusters. When the ancillary ligand on the platinum center contains a low-lying acceptor orbital, such as in bipyridine or 1,10-phenanthroline, we have found that a readily accessible one-electron reduction exists at a potential of *ca.* –1.2 V.[24] In the present case with phosphine ligands (PH_3 and Ph_2PPy) a low-lying orbital is not available and no reduction behavior is observed in CH_2Cl_2.

EXPERIMENTAL

The compounds Pt(1,5-COD)Cl_2[25] and $Fe_2(CO)_6(\mu_3\text{-}S)_2$[6b] were synthesized by using the available literature methods. The cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$ was prepared from $[Fe_2(CO)_6(\mu_2\text{-}S)_2]^{2-}$ and Pt(1,5-COD)Cl_2 by the published procedure.[26] The phosphine ligand Ph_2PPy was prepared from 2-bromopyridine and Ph_2PLi.[27] The solvents THF and CH_2Cl_2 were distilled from sodium/benzophenone ketyl and CaH_2, respectively. All synthetic operations were conducted under argon using Schlenk techniques.[28] The C and H microanalysis was performed by Atlantic Microlabs, Norcross, Ga.

Infrared spectra were recorded on a Nicolet 20-SXB FTIR spectrometer, using a PC and the available OMNIC software program. The ^{31}P NMR spectrum was recorded at 121 MHz on a Varian 300-VXR spectrometer, and the reported ^{31}P data were referenced relative to external H_3PO_4 (85%), taken to have $\delta = 0$. The positive chemical shift represents a resonance that is to low field of the external standard.

Synthesis of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$

To 1.00 g of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$ (1.55 mmol) in 100 mL of THF was added 0.81 g (3.10 mmol) of Ph_2PPy under argon flush. The reaction solution was stirred overnight at room temperature. TLC analysis using CH_2Cl_2 revealed the presence of the desired product along with a small amount of material that remained at the origin. The sulfido-capped cluster was isolated by preparative chromatography over silica gel using the same solvent system employed in the TLC analysis. The sample for microanalysis and single crystals of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ suitable for X-ray diffraction analysis, were grown from a CH_2Cl_2 solution of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ that had been layered with a small amount of heptane. Yield: 1.27 g (77%) of red-black $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$. IR ($CH_2Cl_2$) : ν_{co} = 2048(s), 2007(vs), 1969(*s*) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.68 ($J_{Pt\text{-}P}$ = 1380 Hz). *Anal.* Calcd. (found) for $C_{40}H_{28}Fe_2N_2O_6P_2PtS_2$: C, 45.05 (45.24); H, 2.63 (2.64).

X-ray Diffraction Data

A single crystal of $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(Ph_2PPy)_2$ suitable for X-ray diffraction analysis, having dimensions $0.42 \times 0.11 \times 0.08\ mm^3$, was selected and sealed inside a Lindemann capillary, followed by mounting on the goniometer of an Enraf-Nonius diffractometer. The radiation employed was Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromatized by a crystal of graphite. Cell constants were obtained from a least-squares refinement of 25 reflections with $2\theta > 40°$. Intensity data in the range $2.0 \leq 2\theta \leq 44.0°$ were collected at room temperature using the ω-scan technique in the variable-scan speed mode and were corrected for Lorentz, polarization, and adsorption (DIFABS). Three reference reflections [(12 0 0), (0 8 0), and (0 0 12)], showing variations of less than ±1%, were monitored periodically during the data collection. A careful check of equivalent reflections suggested a monoclinic symmetry, with a twofold crystallographic symmetry axis. The structure was solved by using Patterson techniques. All hydrogen atoms were located in the final difference maps, but were allowed to ride at a fixed distance from the attached carbon atoms with a single fixed isotropic temperature factor. All non-hydrogen atoms were refined anisotropically. Refinement converged at $R = 0.0232$ and $R_w = 0.0258$ for 2212 unique reflections with $I > 3\sigma(I)$.

Electrochemistry

All cyclic voltammograms were obtained with a PAR Model 273 potentiostat/galvanostat, equipped with positive feedback circuitry to compensate for *iR* drop. The air-tight cyclic voltammetry cell was based on a three-electrode design, and the electrochemical experiments employed a platinum disk as the working and auxiliary electrode. The reference electrode employed in all experiments consisted of a silver wire quasi-reference electrode, with all potential data reported relative to the formal potential of $Cp^*_2Fe/Cp^*_2Fe^+$ (internally added) redox couples, taken to have $E_{1/2} = -0.20$ V (vs SCE).[29]

Extended Hückel MO Calculations

The extended Hückel calculations performed on the model compound $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ were carried out with the program developed by Hoffmann,[30] as modified by Mealli and Proserpio,[22] with weighted Hij's.[31] The input Z-matrix for $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ was confined to having idealized C_{2v} symmetry using the bond distances and angles available from the X-ray data of **2**. The PH_3 groups used in the model cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(PH_3)_2$ were available as predefined groups in the CACAO package.

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