$$E_{0\text{-}0}(^3\text{d}-\pi^*) = \tfrac{1}{2}[E^{\text{abs}}_{\text{max}}(^1\text{d}-\pi^*) - 1000 + E^{\text{em}}_{\text{max}}(^3\text{d}-\pi^*)] \qquad (1)$$

$E^{\text{abs}}_{\text{max}}(^1\text{d}-\pi^*)$ and $E^{\text{em}}_{\text{max}}(^3\text{d}-\pi^*)$ are the energy maxima in cm^{-1} from the CT absorption and emission spectra, respectively. As illustrated in Figure 3, Δ is defined as the energy difference between the $^3\text{d}-\pi^*$ and the $^3\pi-\pi^*$ excited states. The estimates based on eq 1 are approximate; for example, we have neglected the complications that occur if the CT band envelopes reflect more than one state.[6] Nevertheless, the numbers are useful because the discussion is based on *trends* rather than the absolute energies themselves.

Inductive Effect. The most obvious energy trends are that the $^1\text{d}-\pi^*$ absorption and the $^3\text{d}-\pi^*$ emission energies decrease as the para substituents on the phosphine range from Cl to H to CH_3. This correlates with the trend of increasing basicity established by Tolman:[14]

$$\text{P}(p\text{-Cl-Ph})_3 < \text{PPh}_3 < \text{P}(p\text{-Me-Ph})_3 \qquad (2)$$

Thus, the variation in the band energies can be explained as a simple inductive effect: Stronger phosphine donors increase the electron density at copper and lower the energy of the CT excited states.

The ordering in (2) is based on the effect that phosphine variation has on the carbonyl stretching frequencies of $\text{Ni(CO)}_3(\text{PR}_3)$ systems.[14] A similar phosphine-induced perturbation of the ring-stretching mode(s) of the dmp ligand is apparent in the $^3\pi-\pi^*$ phosphorescence spectra (Table I). In line with high-resolution studies of the phosphorescence spectrum of the free 1,10-phenanthroline ligand,[15,16] the high-frequency modes in the $^3\pi-\pi^*$ emission are assigned to totally symmetric ring-stretching modes as well as overtones and combination bands involving the same. Since dmp is a π-acceptor ligand, the frequencies are expected to decrease on complex formation just like the carbonyl stretching frequencies in $\text{Ni(CO)}_3(\text{PR}_3)$ complexes.[14] Consistent with this reasoning, the higher the donor strength of the phosphine, the greater the observed frequency shift. Parenthetically, we may note that the same synergistic interaction between the ligands has previously been invoked to explain the favorable formation constants of $\text{Cu(NN)(PPh}_3)_2^+$ species.[17]

Although the effect is quite small, the data in Table II also suggest that the energy of the $^3\pi-\pi^*$ state tends to decrease with increasing donor strength of the phosphine.[18] This trend can be understood in terms of the configurational mixing alluded to earlier. In the insert to Figure 3 the zero-order, i.e., noninteracting, $^3\pi-\pi^*$ and $^3\text{d}-\pi^*$ excited states differ in energy by δ at the equilibrium geometry of the $^3\pi-\pi^*$ configuration. When mixing is accounted for, the energy of the (preponderantly) $^3\pi-\pi^*$ state and, as a result, the energy of the $^3\pi-\pi^*$ emission decrease. Therefore, δ and $E_{0\text{-}0}(^3\pi-\pi^*)$ are expected to decrease as more basic phosphines are introduced into the complex. Although configurational mixing between the charge-transfer and intraligand excited states is a well-recognized phenomenon,[4-6,19,20] the $\text{Cu(dmp)(PR}_3)_2^+$ systems are noteworthy because it is possible to assess the energies of each state involved.

Dynamic Effects of Mixing. There is also a concomitant decrease in lifetime of the $^3\pi-\pi^*$ emission as the energy of the $^3\text{d}-\pi^*$ state decreases. Although a variety of processes may affect the lifetime, this trend is probably due to the increasing importance of configuration interaction as well. Configurational mixing should promote relaxation because spin-orbit interactions at the metal center facilitate the spin change that is formally required for crossing to the ground state. In the same way the $^3\pi-\pi^*$ lifetimes are shorter for $\text{Cu(NN)(PR}_3)_2^+$ systems than for the corresponding Ag(NN)_2^+ systems because the $^3\text{d}-\pi^*$ states occur at much higher energies in the silver systems.[6]

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-8414267.

Registry No. $\text{Cu(dmp)(P(}p\text{-Cl-Ph)}_3)_2^+$, 105061-79-8; $\text{Cu(dmp)(PPh}_3)_2^+$, 78809-58-2; $\text{Cu(dmp)(P(}p\text{-Me-Ph)}_3)_2$, 105061-77-6.

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(18) A reviewer has pointed out that the bands in Figure 2 may equally reasonably be interpreted in terms of a $^3\text{d}-\pi^*$ state that is much as 1000 cm^{-1} *below* the $^3\pi-\pi^*$ state. Although we agree that eq 1 provides only an approximation to the zero-zero energy, the changes in the energies of the $^3\pi-\pi^*$ states, albeit slight, are at least consistent with the proposal that the $^3\text{d}-\pi^*$ states are the higher energy states.

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Electronic Spectra of High-Nuclearity Cluster Carbonyls

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Received October 22, 1986

The study of the physicochemical properties of high-nuclearity clusters consisting of several metal atoms is of considerable interest. Fundamental questions concerning the changes in physical and chemical properties as the number of metal atoms increases need to be resolved. In this paper we report studies of the electronic spectra of several high-nuclearity osmium cluster carbonyls. These are compounds in which polyhedral arrangements of metal atoms are surrounded by a shell or sheath of CO ligands.[1] Solution visible/UV spectra for a set of high-nuclearity osmium carbonyls are shown in Figures 1-4, and a schematic energy level diagram for such clusters, adapted from ref 1, is shown in Figure 5.

Some physical properties of $\text{Os}_6(\text{CO})_{18}$ were reported earlier,[2] and the solution spectra of the clusters $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ (n = 2-6) (Figure 6) have been discussed by Chang and Woolley.[3] It is convenient to begin by reviewing these findings before discussing the spectra shown in Figures 1-4.

Gas-phase photoemission studies of $\text{Os}_6(\text{CO})_{18}$ show that the ionization threshold ($\approx$8 eV) occurs in the metal cluster d band, which extends down to about 12 eV; as usual in these systems, the carbonyl "5σ" and "1π" features overlap and peak at $\approx$14.5 eV ($\pm$1.5 eV).[4] Transmission and optical spectroscopy suggest that this compound is a semiconductor with a band gap of $\approx$1 eV, in agreement with the resistivity measurements. The first strong electronic transitions peak at $\approx$2.7 eV ($\pm$0.2 eV) in both crystals and solution.[2] The platinum cluster carbonyl dianions $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ (see Figure 6, for example) all show strong optical absorptions in the visible range. All of them are colored with the energy of the first intense absorption maximum in the visible, decreasing steadily as the cluster size increases (from 3.3 eV for n = 1 to 1.6 eV for n = 6). Early calculations by Chang and Woolley[3] have been improved by Bullett,[5] who also extended them to the Pt_9 species (n = 3). Bullett's results give a significant improvement to the description of the levels at the HOMO-LUMO gap and suggest that the HOMO of the dianion is an in-phase combination of carbonyl $2\pi^*$ levels split off from the main group of $2\pi^*$ levels, which remain empty, as suggested by Lauher.[6] This unusual feature arises from the particular geometry of these platinum carbonyls, which is based on the stacking of nearly planar layers of $\text{Pt}_3(\text{CO})_6$ moieties (Figure 6). The normal energy level pattern for cluster carbonyls is shown schematically in Figure 5; the metal cluster d levels lie in the gap between the M-CO bonding

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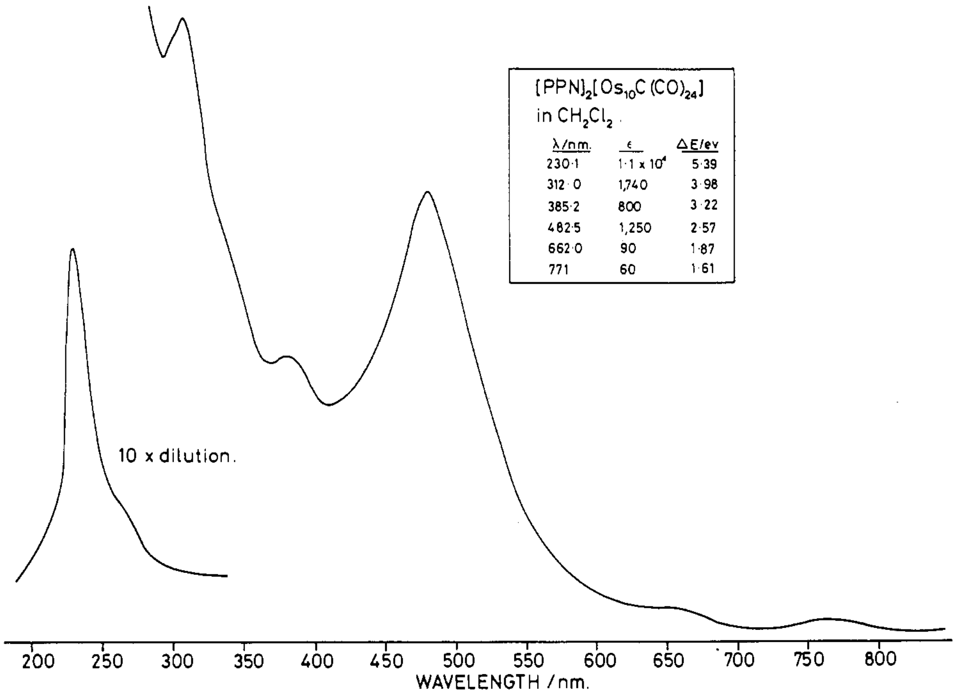
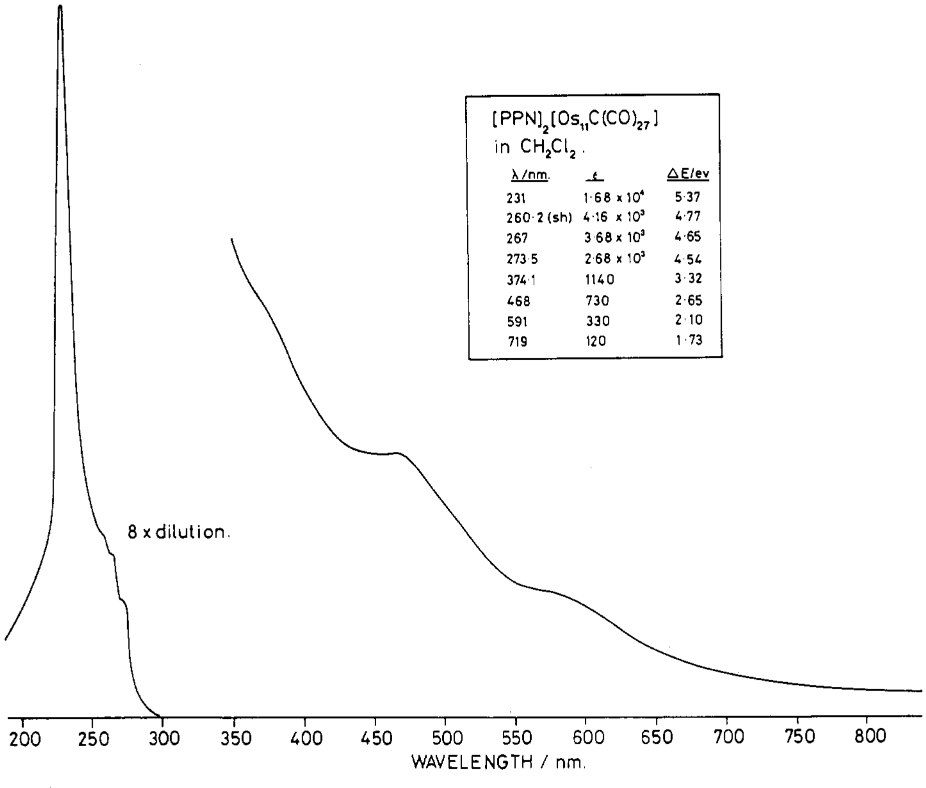


$[PPN]_2[Os_{10}C(CO)_{24}]$ in CH_2Cl_2.

λ/nm.	ε	ΔE/ev
230·1	$1{\cdot}1 \times 10^4$	5·39
312·0	1,740	3·98
385·2	800	3·22
482·5	1,250	2·57
662·0	90	1·87
771	60	1·61

Figure 1. UV/vis spectra of $[PPN]_2[Os_{10}C(CO)_{24}]$ in CH_2Cl_2 at room temperature.



$[PPN]_2[Os_{11}C(CO)_{27}]$ in CH_2Cl_2.

λ/nm.	ε	ΔE/ev
231	$1{\cdot}68 \times 10^4$	5·37
260·2 (sh)	$4{\cdot}16 \times 10^3$	4·77
267	$3{\cdot}68 \times 10^3$	4·65
273·5	$2{\cdot}68 \times 10^3$	4·54
374·1	1140	3·32
468	730	2·65
591	330	2·10
719	120	1·73

Figure 2. UV/vis spectra of $[PPN]_2[Os_{11}C(CO)_{27}]$ in CH_2Cl_2 at room temperature.

orbitals ("5σ") and the empty perturbed CO "2π*" levels. The position of E_{HOMO} depends on the transition metal; Figure 5 has been drawn for the osmium clusters. Whether or not there is a small gap between the *empty* 5d levels and the CO 2π* band is

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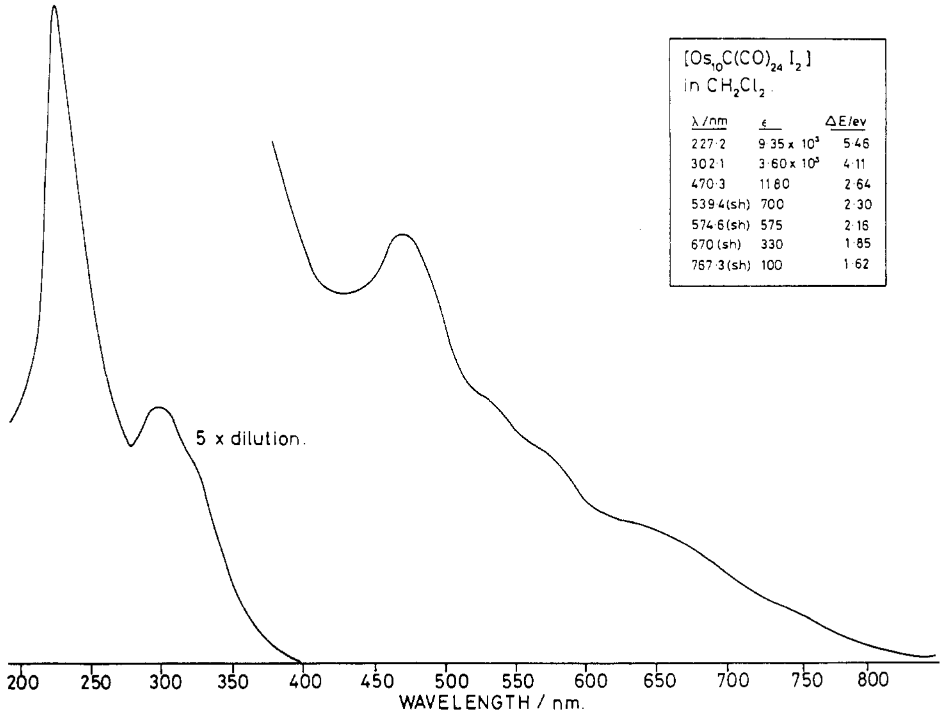
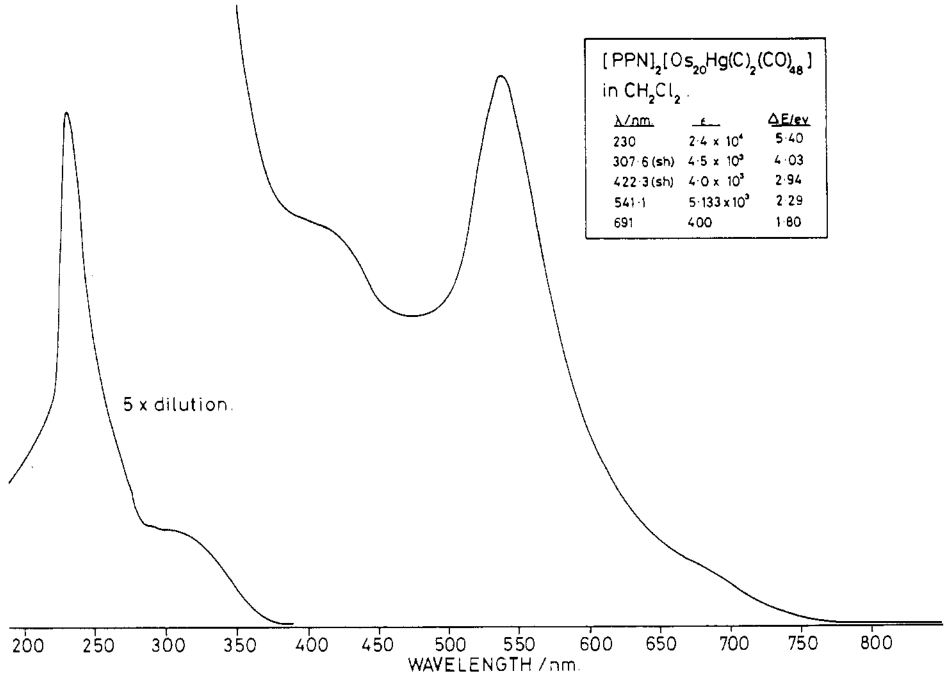
(12) The following materials were made according to the literature: $[PPN]_2[Os_{10}C(CO)_{24}]$,[8] $[Os_{10}C(CO)_{24}I_2]$,[9] $[PPN]_2[Os_{11}C(CO)_{27}]$,[10] $[PPN]_2[Os_{20}Hg(C)_2(CO)_{48}]$.[11] The solution visible/UV spectra were run on a Pye Unicam PU8800 spectrometer, at 20 °C in CH_2Cl_2.



[$Os_{10}C(CO)_{24}I_2$]
in CH_2Cl_2.

λ/nm	ε	ΔE/ev
227·2	9·35 x 10^3	5·46
302·1	3·60 x 10^3	4·11
470·3	1180	2·64
539·4(sh)	700	2·30
574·6(sh)	575	2·16
670(sh)	330	1·85
767·3(sh)	100	1·62

Figure 3. UV/vis spectra of [$Os_{10}C(CO)_{24}I_2$] in CH_2Cl_2 at room temperature.



[$PPN]_2[Os_{20}Hg(C)_2(CO)_{48}$]
in CH_2Cl_2.

λ/nm.	ε	ΔE/ev
230	2·4 x 10^4	5·40
307·6(sh)	4·5 x 10^3	4·03
422·3(sh)	4·0 x 10^3	2·94
541·1	5·133 x 10^3	2·29
691	400	1·80

Figure 4. UV/vis spectra spectra of $[PPN]_2[Os_{20}Hg(C)_2(CO)_{48}]$ in CH_2Cl_2 at room temperature.

determined by the specifics of the cluster compound considered.[13]

Apart from the new assignment of the HOMO, Bullett's overall description of the electronic structure[5] is much the same as in the earlier calculations.[3] Both sets of calculations suggest that the levels in the d band divide roughly into two groups that can be described as metal–metal bonding and metal–metal antibonding combinations; for example, in the basic building block for these clusters, $Pt_3(CO)_6$, Bullett finds nine "d levels" with energies between −9.4 and −10.8 eV and six "d levels" between −8.7 and −6.3 eV. This division of the d levels into two groups is commonly found in calculations on small transition-metal clusters and their compounds;[7] the compactness of the bonding orbitals is particularly noteworthy. In the bulk metals a similar division is found in the bcc structure, but it is not apparent in other close-packed structures (fcc, hcp, etc.).

On the basis of this energy level diagram, Chang and Woolley proposed that there should be two sets of strong transitions in the visible/UV region and numerous far-UV transitions. The lowest energy transitions are from the *top* of the occupied part of the d band (the M–M* levels in Figure 5) into the empty carbonyl "$2\pi^*$" levels on the carbonyl groups, and in $Pt_3(CO)_6^{2-}$ these were calculated to peak at $\Delta E_{max} \approx 3.3$ eV (with a spread of ±0.2 eV). At higher energies there should be strong UV absorptions involving transitions from the M–M bonding orbitals in the *lower* part of the d band to the empty "$2\pi^*$" levels with $\Delta E_{max} \approx 5.8$ eV (with a spread of ±0.2 eV). Transitions from the d band into the carbonyl "$6\sigma^*$" levels should occur with transition energies ΔE between 6 and 9 eV. Although the d-band energy levels extend over a range of several eV, the nonuniform level spacing is re-

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[13] Bullett, D. W. *Chem. Phys. Lett.* **1987**, *135*, 373.

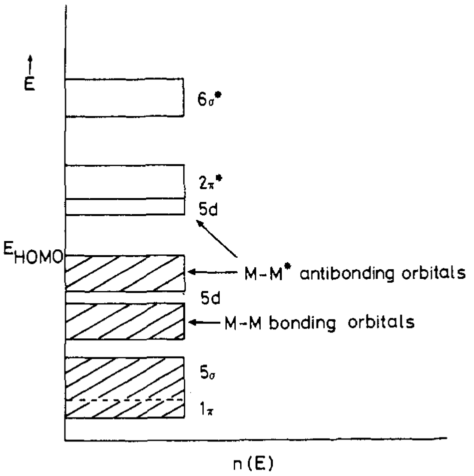

Figure 5. Energy level diagram of small transition-metal carbonyl clusters.

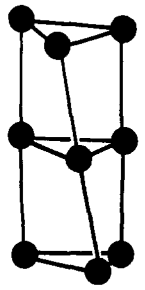

Figure 6. Metal framework of $[Pt_3(CO)_6]_n^{2-}$ ($n = 3$).

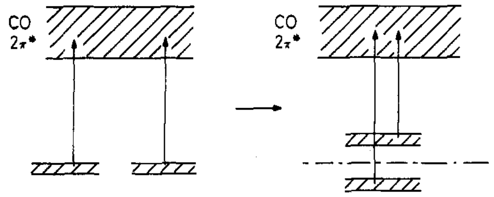

Figure 7. Splitting of the energy bands upon "dimer formation" in large transition-metal carbonyl clusters, e.g. $[Pt_3(CO)_6]_5^{2-}$ and $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$.

sponsible for the absorption maxima being fairly narrow. As the planar moieties are stacked on top of each other (increasing n), new bonding/antibonding combinations are formed and so the energy gaps tend to decrease (see Figure 7). The calculations show that this occurred particularly with some of the M–M* antibonding levels at the top of the d band, hence the decrease in the ΔE_{max} associated with transitions from these levels (the lowest energy visible absorptions) as n increases.[3,5,14] These remarks should be applicable to other high-nuclearity metal cluster carbonyls, and they form the basis for our discussion of the osmium species reported here.

The strong absorption in $Os_6(CO)_{18}$ with $\Delta E_{max} \approx 2.7$ eV is assigned[2] to transitions from the Os–Os* d levels into empty carbonyl "2π*" levels. The higher lying transitions predicted for optical spectroscopy were not reported although spiky fine structure can be seen superimposed over the broad plasmon peak measured in electron energy loss experiments on $Os_6(CO)_{18}$ in the region 10–15 eV.[2] Presumably these are mainly transitions between filled and empty carbonyl levels. If we turn now to the spectra of the larger osmium cluster carbonyls,[8-12] it can be seen from Figures 1–4 that there is substantial absorption in the range 200–600 nm on top of which two absorption peaks are superimposed. The spectra fit into the pattern proposed by Chang and Woolley. In all cases there is an intense absorption with $\Delta E_{max} \approx 5.4$ eV that can be assigned to transitions from Os–Os bonding orbitals in the lower half of the d band into the carbonyl "2π*" levels. The increased nuclearity of these clusters compared with the Os_6 cluster does not greatly increase the average connectivity of each Os center with respect to other metal atoms, and so this absorption peak is expected to remain at fairly constant wavelength as the nuclearity varies. On the other hand, the transitions from the upper part of the d band (the Os–Os* levels) into the carbonyl "2π*" levels have $\Delta E_{max} \approx 2.6$ eV in the $[Os_{10}C(CO)_{24}]^{2-}$, $[Os_{10}C(CO)_{24}I_2]$, and $[Os_{11}C(CO)_{27}]^{2-}$ species, but this absorption peak is split into two features in the spectrum of the $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ cluster with $\Delta E_{max} \approx 2.9$ and 2.3 eV (Figure 8). This splitting is due to the orbital interactions, associated with "dimer" formation, shown in Figure 7. In all cases the optical absorption becomes negligible for wavelengths >770 nm ($\Delta E \approx 1.6$ eV), which indicates that the HOMO–LUMO gap is probably on the order of 1 eV, as in $Os_6(CO)_{18}$. On this basis, the larger osmium clusters would be expected to give materials (powders or crystals) that are insulators.

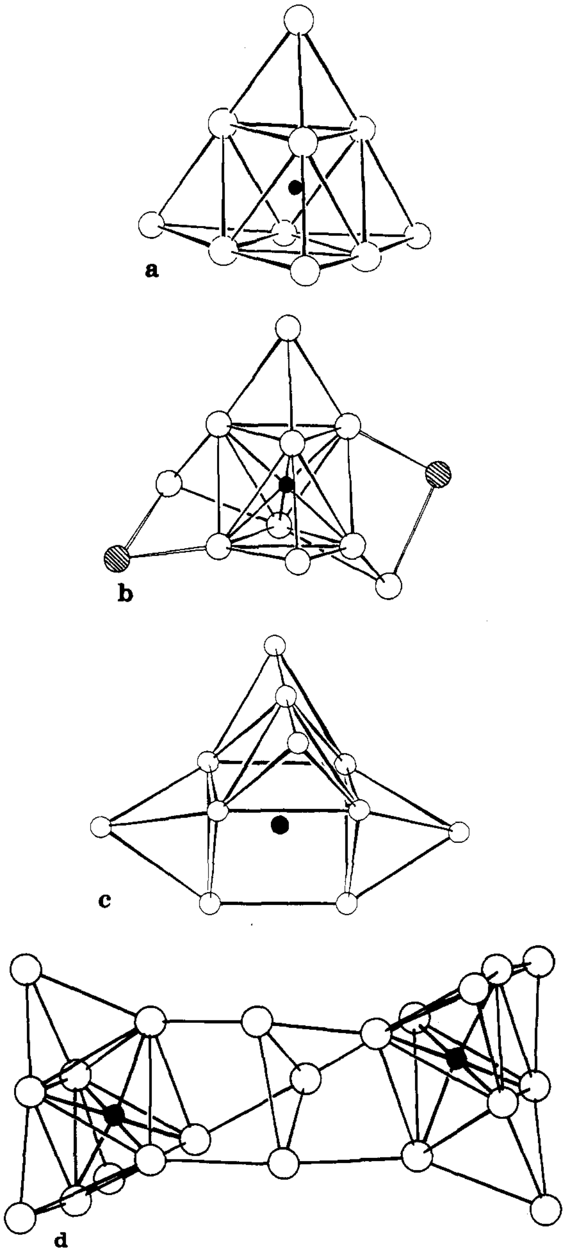

Figure 8. Metal frameworks: (a) $[PPN]_2[Os_{10}C(CO)_{24}]$, (b) $[Os_{10}C(CO)_{24}I_2]$, (c) $[PPN]_2[Os_{11}C(CO)_{27}]$, (d) $[PPN]_2[Os_{20}Hg(C)_2(CO)_{48}]$.

Finally, we should like to emphasize that the spectra reported here, and their interpretation in terms of the energy level diagram in Figure 5, are consistent with recent chemical pseudopotential

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calculations on a group of osmium cluster carbonyls.[13] These calculations confirm the validity of the schematic energy level diagram, Figure 5, and provide quantitative information about the distribution of molecular orbital energy levels in these cluster species. While it is possible that there are transitions in the low-energy part of the visible spectrum that are associated purely with the metal cluster (M–M → M–M* transitions), the calculations on both Pt[1,3,5] and Os[13] cluster carbonyls provide strong support for assigning the main visible/UV bands to metal cluster carbonyl $2\pi^*$ transitions. In view of the quantitative features of the energy level diagrams for these clusters[13] and our experience with the platinum cluster carbonyls,[3,5,14] we suggest that the transitions between filled and empty M–M 5d levels, if they occur, should be associated with the background absorption shown in Figures 1–4 but that the two main peaks in the spectra involve carbonyl $2\pi^*$ levels. The observed absorption coefficients of these main peaks, which are typical of fully allowed electric dipole transitions, are consistent with this interpretation. A more refined interpretation of cluster spectroscopy must await further experiments; single-crystal measurements and/or MCD could be particularly helpful.

In summary, the optical absorption spectra of these high-nuclearity osmium cluster carbonyls show a strong parallel with those found and predicted for the dianions, $[Pt_3(CO)_6]_n^{2-}$.[3,5] This should not be surprising since both sets of compounds have metal cluster cores that are columnar rather than globular. The Os_{20} cluster for example can be thought of as having a metal core built up as a stack of five M_3 triangles with additional Os atoms bonded to the top and bottom layers (the central M_3 unit containing the heteroatom Hg)—see Figure 8d.

Acknowledgment. We are grateful to the SERC for financial support (S.R.D.) and thank Dr. D. W. Bullett for sending us a preprint of his osmium cluster calculations.

Registry No. $[PPN]_2[Os_{10}C(CO)_{24}]$, 75117-74-7; $[PPN]_2[Os_{11}C(CO)_{27}]$, 110589-42-9; $[Os_{10}C(CO)_{24}I_2]$, 81181-60-4; $[PPN]_2[Os_{20}Hg(C)_2(CO)_{48}]$, 106466-56-2.

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Dissociative Substitution in Four-Coordinate Planar Platinum(II) Complexes. 3. Kinetics of the Displacement of Sulfur Donors from *cis*-Dimethylbis(dimethyl sulfoxide)- and *cis*-Dimethylbis(dimethyl sulfide)platinum(II) by Bidentate Ligands

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Received January 6, 1987

The usual mode of ligand substitution in four-coordinate planar d^8 metal complexes involves associative activation and considerable discrimination between the different nucleophiles.[1] The dissociative mode of activation is a rarity. A dissociative pathway has been characterized for the cis → trans isomerization of *cis*-$[Pt(PEt_3)_2(R)X]$ (where R is an alkyl or aryl group),[2,3] but in every case there is a more facile associatively activated pathway for ligand substitution.[4] Recently we showed that the displacement of dimethyl sulfoxide from *cis*-$[PtPh_2(Me_2SO)_2]$ by bidentate ligands in benzene solution occurred by a dissociatively activated pathway, with an intermediate that could discriminate between different nucleophiles[5] and have ruled out the alternative possibility that the sulfoxide, functioning temporarily as a bidentate, promotes this behavior by showing that *cis*-$[PtPh_2(Me_2S)_2]$ behaves in a similar way, albeit with an intermediate of much lower nucleophilic discrimination ability.[6] In both cases, stronger nucleophiles can also use a parallel associatively activated pathway.

In order to test the generality of the observation and to rule out the possibility that the dissociative mode of activation arises from some assistance from the ortho hydrogen of the phenyl group, we have extended our studies to the reactions

$$cis\text{-}[PtMe_2L_2] + \text{L-L} \rightarrow [PtMe_2(\text{L-L})] + 2\text{L}$$

(L = Me_2SO, Me_2S; L-L = a bidentate N, S, or P donor) and report the results in this paper.

Experimental Section

Preparation of Complexes. *cis*-Dimethylbis(dimethyl sulfoxide)platinum(II) was prepared by reacting *cis*-$[PtCl_2(Me_2SO)_2]$ with $SnMe_4$ in Me_2SO according to the method of Eaborn et al.[7]

cis-Dimethylbis(dimethyl sulfide)platinum(II) could not be isolated from solution and was prepared in situ by adding a sufficient excess (at least 50-fold) of dimethyl sulfide to a solution of the Me_2S-bridged dimer $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in accordance with the method of Scott and Puddephatt.[8]

$[PtMe_2(\text{L-L})]$. The syntheses of most of the complexes of this type that were postulated as reaction products have already been described in the literature. Displacement of the diolefin from $[PtMe_2(COD)]$ (COD = 1,5-cyclooctadiene) by L-L (L-L = 2,2′bipyridine (bpy),[9] 1,10-phenanthroline (phen),[9] 1,3-bis(diphenylphosphino)propane (dppp)[10] or of the sulfoxide from *cis*-$[PtMe_2(Me_2SO)_2]$ (L-L = bipyrimidine (bpym),[11] 1,2-bis(diphenylphosphino)ethane (dppe)[7]) has previously been described. The last method was also used to prepare the hitherto unknown complex where L-L = 1,2-bis(phenylthio) ethane (dpte). ^1H NMR ($CDCl_3$): δ(MePt) 0.789 (t, ^2J(PtH) = 86.36 Hz), $\delta(CH_2S)$ 2.91 (t, ^3J(PtH) = 18 Hz).

All complexes were characterized through elemental analysis, infrared spectroscopy, ^1H NMR spectroscopy and, where relevant, ^{31}P NMR and electronic spectroscopy. 1,2-Bis(phenylthio)ethane was prepared according to the literature method.[12] 1,10-Phenanthroline hydrate was dehydrated by heating under vacuum for 24 h at 80 °C, mp 117 °C. Other compounds were the best available commercial materials purified by recrystallization or distillation where necessary.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 783 spectrometer; ^1H and ^{31}P NMR spectra were recorded at 80 MHz on a Bruker WP 80 spectrometer using C_6D_6, $CDCl_3$, or $(CD_3)_2CO$ as solvent and tetramethylsilane and H_3PO_4 (externally), respectively, as standards.

Kinetics. Slower reactions were followed spectrophotometrically by measuring spectral changes of the reaction mixture with time in the visible and near-UV regions by means of a Perkin-Elmer Lambda 5 or a Cary 219 spectrophotomer. The reactions were started by mixing known volumes of prethermostated standard solutions of reagents in the thermostated (±0.05 °C) cell compartment of the spectrophotometer. Using at least a 10-fold excess of nucleophile over complex ensured first-order kinetics in any run. The reactions with dppe and dppp required the use of a HI-TECH SF3 stopped-flow spectrophotometer equipped with a Gould 054100 oscilloscope and a Radiometer REC 61

[†] Università di Messina.

[‡] University College London.

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