caused the lengthening of two Rh–Rh distances from the average value of 2.87 Å to 3.33 Å. Another example is the hexacapped trigonal-antiprismatic cluster[55] (Chart XIV of ref 1b) $[\mathbf{Fe_6Pd_6}(CO)_{24}H]^{3-}$, which is predicted to have $B = 7$. The observed value is 8. The extra electron pair may be the cause of the long Pd–Pd distance of 2.88 (av) Å though it may also be due to the hydride in the trigonal-antiprismatic Pd_6 cage (proposed site). For the corner-sharing dicube $X = 1$ since each cube has $X = 0$. The B value is predicted to be 21, which is two electron pairs less than that of 23 observed in $Me_6\mathbf{Zn_7}O_8Me_8$.[56] The extra electron pairs may enter the antibonding Zn–O orbital framework.

The $[Pt_6(CO)_{12}]^{2-}$ dianion,[57] which has a slipped trigonal-prismatic structure, has a B value of 7 instead of the predicted value of 9. This may be due to the depopulation of the highest occupied e′ orbitals for a regular trigonal prism. It should be emphasized, however, that the electron deficiency in Pt clusters is probably related to its tendency to adopt a 16- rather than an 18-electronic configuration.

Conclusion

In summary, we have shown in this paper that the topological electron counting (TEC) theory developed recently by us[1] can be extended to include clusters containing both non-metal and metal atoms as well as clusters of lower dimensions (1- or 2-D).

A comparison is made, and a bridge established, between the skeletal electron pair (SEP) and the TEC theories, thereby providing an alternative (and sometimes complementary) way of calculating the number of skeletal electron pairs.

The correlation between the *cage* size and the number of *skeletal electron pairs* (B) is discussed. It is evident that larger encapsulated atoms require a larger B value and incomplete encapsulation can occur if B is not large enough. The difference between $T = 6V + B$ and $T = 6M + B'$ in calculating the number of topological electron pairs of close-packed high-nuclearity metal clusters is emphasized.

It is shown that, for a given structure, successive replacement of main-group elements by transition metals as vertices increases the topological electron counts (N) by 10 without affecting the number of skeletal electron pairs (B). It is also illustrated that as the number of faces of a cluster decreases, the electron count increases and vice versa.

Ways in which the TEC approach differs from other electron counting schemes (multiple electron counts, application to fused or connected polyhedra) are illustrated by examples. Reasons for "electron-rich" and "electron-deficient" clusters are also discussed.

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Bridge-Cleavage Reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ (Cy = Cyclohexyl) with Dimethyl Sulfoxide and Dibenzyl Sulfoxide. Conversion of Trans-S-Bonded and Trans-O-Bonded Sulfoxide Complexes to the Cis-S-Bonded Isomers

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The synthesis of the dimeric halide-bridged platinum(II) complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ from the reaction of $[K][PtCl_3(C_2H_4)]$ with PCy_3 under high-dilution conditions was reported in 1981.[1] This precursor allowed entry into the series of complexes *trans*-$[PtCl_2(PCy_3)(L)]$ (L = CO, CN-*t*-Bu, NC_5H_5, SMe_2, $AsPh_3$, tertiary phosphine; *t*-Bu = *tert*-butyl, Me = methyl, Ph = phenyl) via bridge cleavage with the appropriate nucleophile, L.[1] In all cleavage reactions, the trans isomer of the mixed-ligand complex is quantitatively produced and only in the case where L = CO could the cis isomer be generated (in trace amounts) by catalytic isomerization with free CO.[1] The exceptional stability of these complexes with respect to thermal trans → cis isomerization is demonstrated by a complete lack of isomerization upon heating solutions of *trans*-$[PtCl_2(PCy_3)(L)]$ (L = SMe_2, NC_5H_5) in the presence of a 10-fold excess of L at 55 °C for 2 h.[1]

As part of an electrochemical study[2-5] of geometric and ligand effects on the redox chemistry of platinum(II) complexes we have recently prepared[5,6] a series of mixed-ligand complexes, $[PtCl_2(PPh_3)(L)]$ (L = thioether, sulfur-bonded sulfoxide), via bridge cleavage of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$. In one case we were able to isolate separately both cis and trans isomers where L = thioether (Bz_2S (Bz = benzyl)) but in all cases where L = sulfur-bonded sulfoxide we were able to isolate only the cis isomers. The stability of the trans isomers of $[PtCl_2(PCy_3)(L)]$ with respect to isomerization led us to investigate further the cleavage reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ with sulfur-containing nucleophiles.

Experimental Section

$[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ was prepared by the literature method.[1] ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 89.56 MHz (^1H) and 36.2 MHz (^{31}P) on a JEOL FX90Q spectrometer operating in the Fourier transform mode. Chemical shifts are referenced to internal tetramethylsilane (^1H) and external 85% phosphoric acid (^{31}P) with more positive values of the chemical shift representing deshielding. Infrared spectra were obtained for solid solutions in KBr on a Nicolet 5DX Fourier transform IR spectrometer..

Cleavage reactions were performed by adding a stoichiometric amount of the nucleophile to a dichloromethane solution of the dimer (ca. 25 mg) and refluxing overnight. The solids were precipitated with hexane and dried in air. The ^1H and $^{31}P\{^1H\}$NMR spectra were recorded for the $CDCl_3$ solutions of these solids as a function of time. After each reaction was >85% complete, as estimated by peak heights in the $^{31}P\{^1H\}$ NMR spectra, the solvents were removed in vacuo and the products washed with hexane and dried for IR analysis.

Results and Discussion

It is reported[1] that $[Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2]$ is cleaved by SMe_2 to yield *trans*-$[PtCl_2(PCy_3)(SMe_2)]$, which resists isomerization at 55 °C for 2 h in the presence of excess SMe_2. The corresponding cleavage with Me_2SO forms a single new species observable in the $^{31}P\{^1H\}$ NMR spectrum with $\delta = 19.35$ and $^1J(^{195}Pt,^{31}P) = 3174$ Hz. The magnitude of the coupling constant is consistent with coordination of Me_2SO trans to PCy_3. The ^1H NMR spectrum shows that the methyl protons are substantially deshielded ($\delta = 3.20$; cf. $\delta = 2.49$ for Me_2SO itself) and coupled to platinum, $^3J(^{195}Pt,^1H) = 13$ Hz, as anticipated for an S-bonded sulfoxide.[7] The methyl proton resonance is considerably broadened, with a peak width at half-height of ca. 3.5 Hz, which we attribute to unresolved trans coupling, $^4J(^{31}P,^1H)$ (vide infra). When the compound is allowed to stand in $CDCl_3$ solution, in the presence of a trace amount of free Me_2SO, a very slow trans → cis isomerization occurs.[8] The $^{31}P\{^1H\}$ NMR spectrum shows a new species, with $\delta = 27.58$ and $^1J(^{195}Pt,^{31}P) = 3378$ Hz, appearing as resonances due to the trans isomer diminish in in-

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tensity. The magnitude of $^{1}J(^{195}Pt,^{31}P)$ in complexes of PCy_3 is known to follow the predicted trends due to trans-influence changes in supporting ligands in a systematic manner,[1] and an increase of ca 200 Hz on isomerization would be anticipated. The ^{1}H NMR spectrum similarly shows a decrease in intensity of the broadened resonance at 3.20 ppm and a new, sharp resonance, with a peak width at half-height of ca 1.1 Hz, at 3.63 ppm with $^{3}J(^{195}Pt,^{1}H) = 22$ Hz. This confirms that the sulfoxide remains bonded via sulfur and is further evidence for the cis geometry of the complex since the decrease in $^{4}J(^{31}P,^{1}H)$ upon isomerization (i.e. $^{4}J(^{31}P,^{1}H)_{cis} << {}^{4}J(^{31}P,^{1}H)_{trans}$) leads to line narrowing. After 8 months at room temperature, the $^{31}P\{^{1}H\}$ NMR spectrum indicates that isomerization is ca. 85% complete (by peak heights) and the IR spectrum of the isolated product shows $\nu(S{=}O) = 1135$ cm^{-1}, confirming S-bonding of the sulfoxide.[7] Thus, trans-$[PtCl_2(PCy_3)(L)]$ complexes can undergo trans → cis isomerization, as commonly encountered for analogues with less sterically demanding tertiary-phosphine ligands, but at an astonishingly slow rate under ambient conditions. With the PPh_3 analogue, for example, the isomerzation must be extremely rapid as we have been unable to isolate *trans*-$[PtCl_2(PPh_3)(Me_2SO)]$ by any method so far attempted, and indeed, addition of Me_2SO to a $CDCl_3$ solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$, followed by immediate examination by $^{31}P\{^{1}H\}$ NMR spectroscopy, shows only the presence of *cis*-$[PtCl_2(PPh_3)(Me_2SO\text{-}S)]$.

Cleavage of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ with the larger nucleophile Bz_2SO was investigated to see if the trans → cis isomerization could be completely retarded. In fact, a new isomerization process was found to occur. Thus, reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ with 2 equiv of Bz_2SO in refluxing CH_2Cl_2 for 20 h, followed by precipitation with hexane and examination of the solid produced by $^{31}P\{^{1}H\}$ NMR spectroscopy in $CDCl_3$ solution, shows the presence of unreacted dimer and a new species with $\delta = 19.64$ and $^{1}J(^{195}Pt,^{31}P) = 3206$ Hz. The value of $^{1}J(^{195}Pt,^{31}P)$ differs considerably from the value for the PCy_3 trans to Cl arrangement in *cis*-$[PtCl_2(PCy_3)(Me_2SO)]$ (3378 Hz) and implies formation of a trans cleavage product. The ^{1}H NMR spectrum, however, shows *no* deshielded resonances with coupling to ^{195}Pt for the diastereotopic benzylic protons of a S-bonded sulfoxide. Instead, a single peak at 3.89 ppm, with no coupling to ^{195}Pt, is observed. This peak position coincides with the resonance position for the benzylic protons of free Bz_2SO. Coordination of Bz_2SO to platinum via oxygen would be consistent with these data. Thus, O-bonding leads to very small or negligible deshielding of the α-protons of sulfoxides[7] and coupling of these protons to the metal center is not observed.[7] The value of $^{1}J(^{195}Pt,^{31}P)$ is also consistent with a trans arrangement of PCy_3 and $Bz_2SO\text{-}O$ ligands, although comparative data for platinum(II) phosphine complexes with oxygen-donor ligands are scarce. O-Bonding of sulfoxides to platinum(II) is observed in sterically congested systems[7] and may be promoted by tertiary-phosphine ligands with large cone angles.[9] The initial product of the cleavage of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ by Bz_2SO is thus formulated as *trans*-$[PtCl_2(PCy_3)(Bz_2SO\text{-}O)]$.

Upon standing in $CDCl_3$ solution, the complex undergoes a slow isomerization. In the $^{31}P\{^{1}H\}$ NMR spectrum, peaks associated with *trans*-$[PtCl_2(PCy_3)(Bz_2SO\text{-}O)]$ are replaced by a resonance at 23.28 ppm with $^{1}J(^{195}Pt,^{31}P) = 3396$ Hz. The magnitude of $^{1}J(^{195}Pt,^{31}P)$ indicates a geometry with PCy_3 trans to Cl and so implies a trans → cis isomerization. In the ^{1}H NMR spectrum, however, new resonances appear for the benzylic protons, which are substantially deshielded, $\delta(H_A) = 5.61$ and $\delta(H_B) = 4.41$, and exhibit coupling, $J(H_A,H_B) = 12.3$ Hz. The more shielded resonance is observably coupled to platinum, with $^{3}J(^{195}Pt,H_B) = 31$ Hz while the less shielded proton is not. This pattern for the diastereotopic protons is typical of an S-bonded benzylic sulfoxide, as observed previously in related complexes by both ourselves[6] and others.[10] After 8 months in $CDCl_3$ solution, $^{31}P\{^{1}H\}$ NMR spectroscopy indicates that isomerization to the cis-S-bonded isomer is ca. 90% complete (by peak heights). The IR spectrum of the isolated product shows $\nu(S{=}O) = 1130, 1184$ cm^{-1} as shoulders on the bands at 1119 and 1177 cm^{-1} due to the PCy_3 group, confirming S-bonding of the sulfoxide.

The reactions of Me_2SO and Bz_2SO with $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ thus differ considerably. The initially formed cleavage product is the *trans*-$[PtCl_2(PCy_3)(L)]$ complex in both cases, but Me_2SO is S-bonded while Bz_2SO is O-bonded. Both complexes undergo slow isomerization to the corresponding cis-S-bonded isomers. The Bz_2SO system is exceptional since the geometric isomerization is accompanied by a change in the mode of coordination of the ambidentate sulfoxide ligand. We are not aware of any related examples of such phenomena in sulfoxide coordination chemistry, and it is clear that a fine balance of steric and electronic effects must control product formation. Thus, the initially formed cleavage product contains the sterically favored, but electronically disfavored,[11] O-bonded sulfoxide trans to the bulky PCy_3 group while the isomerization product contains the electronically favored,[11] but sterically disfavored, S-bonded sulfoxide cis to the bulky PCy_3 ligand. Systematic studies of steric and electronic effects may shed light on the factors governing such processes.[6] The detailed mechanism of the unusual isomerization process has not been investigated but, in view of the steric congestion at the metal center, a dissociative pathway may be possible.[12,13]

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Registry No. $[Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2]$, 76156-54-2; *trans*-$[PtCl_2(PCy_3)(Me_2SO\text{-}S)]$, 98858-84-5; *cis*-$[PtCl_2(PCy_3)(Me_2SO\text{-}S)]$, 98920-55-9; $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$, 15349-80-1; *cis*-$[PtCl_2(PPh_3)(Me_2SO\text{-}S)]$, 63863-24-1; *trans*-$[PtCl_2(PCy_3)(Bz_2SO\text{-}O)]$, 98839-72-6; *cis*-$[PtCl_2(PCy_3)(Bz_2SO\text{-}S)]$, 98858-85-6.

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Synthesis and Structure of Hexaaquanickel(II) Tris(1,8-naphthyridine-2,7-dicarboxylato)dinickelate(II) Pentahydrate

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The 1,8-naphthyridine (1,8-napy) ring can function as either a monodentate, bidentate, or binuclear ligand.[1] The binuclear mode is particularly interesting since the two metal ions are in close proximity and metal–metal interactions can occur.[2-4] However, in the majority of the 1,8-napy complexes the ligand

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