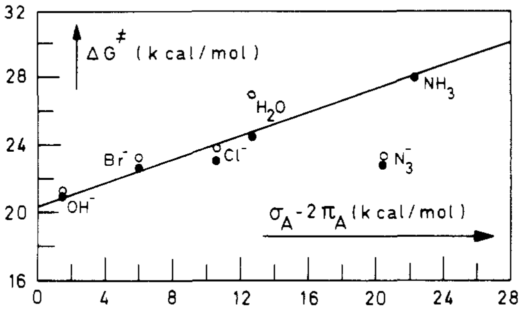

Figure 5. Linear relationship between the rate constants (Table II) for the cis → trans (○) and the trans → cis (●) isomerization reactions of $Co(en)_2A(H_2O)^{m+}$ and $\sigma_A - 2\pi_A$. The anomalous position of N_3^- is probably due to the fact that this ligand is characterized by π-acceptor as well as π-donor properties. The π-donor properties of N_3^- are therefore probably more important than would appear from the value π = 324 cm^{-1}; a larger π parameter would move the N_3^- result closer to the curve of Figure 5. The absence of NO_2^- and CN^- corresponds to the nonobservation of the isomerization process for those ligands (see also footnote 26).

and 2 are compared, it follows that ^5E is always π_A higher than $^5A_2$. Therefore, one expects the racemization to take place, not via TBP(A_{ax}) but rather via cis–trans isomerization. It is also clear now why the aquation of the cis complexes is never accompanied by racemization.

As stressed before, these expectations are borne out by the experimental data (Table II). The fact that $Co(en)_2NH_3(H_2O)^{3+}$ racemizes without cis–trans isomerization can hardly be considered as a counterexample. For A = NH_3, we predict the same activation energy for cis–trans isomerization and for racemization; the calculated value is very high though (7.5 kcal/mol), and therefore the racemization rate is very small. The difference in interligand repulsion alone might easily induce differences of the observed order of magnitude.

Conclusion

The simple reaction scheme of Figure 2 can be used to rationalize the role of the inert A ligand in the isomerizations and the substitutions of $Co(en)_2AX^{n+}$; it shows how the stereochemistry can be predicted and—for stereomobile reactions—how the reaction rate depends on the ligand field parameters of A.

Acknowledgment. Financial support of the Belgian Government (Programmatie van het Wetenschappsbeleid) is acknowledged. K.P. is indebted to the Belgian National Science Foundation (NFWO) for a predoctoral fellowship.

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Reinterpretations, Based on ^{183}W NMR Spectra, of Several Heteropolytungstates Derived from the Wells–Dawson "2:18" Structure. Preparation and Structure Proof for the First γ-Isomer of a 2:18 Complex[1]

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^{183}W NMR spectra prove the following: (1) The first γ-isomer of the 2:18 Wells–Dawson heteropoly structure has been isolated. γ-$[As_2W_{18}O_{62}]^{6-}$ differs from the α-isomer by 60° rotations of *both* W_3O_{13} caps about their 3-fold axes. (2) α-$[P_2W_{12}Mo_6O_{62}]^{6-}$, obtained quantitatively by reaction of molybdate with the P_2W_{12} complex, does not, as previously supposed, contain all the W's in the two W_6 belts but has the W's in a boatlike arrangement derived from the α-$[P_2W_{18}O_{62}]^{6-}$ structure by stripping a W from the W_3O_{13} cap on one end of the complex and the eclipsed W from the cap on the other end, plus those two eclipsed W's from each belt that were immediately adjacent to the W's removed from the caps. It is highly probable that the unsaturated P_2W_{12} species has the W's in the same arrangement and that its formula is $[P_2W_{12}O_{48}H_x]^{(14-x)-}$. (3) The complex previously formulated as α-$[P_2W_{16}Mo_2O_{62}]^{6-}$ is really α-$[P_2W_{15}Mo_3O_{62}]^{6-}$, wherein one Mo_3O_{13} cap has replaced a W_3O_{13} cap of the Wells–Dawson structure. The complex is prepared quantitatively from what was heretofore taken to be "α-$[P_2W_{16}O_{59}]^{12-}$", which is probably really a 15-tungsto species. (4) The currently accepted formulation of Preyssler's 6-tungstophosphate, "$[P_3W_{18}O_{66}]^{9-}$", cannot be correct. The simple NMR spectrum could reconcile with more highly polymeric structures.

Introduction

In recent papers[2-4] we demonstrated the power of ^{183}W NMR for unambiguous elucidation of the structures of polytungstate complexes in solution. Besides discussion of factors involved in the origin of ^{183}W NMR chemical shifts, band assignments, use of quadrupolar nuclei as structure probes, and use of coupling constants, numerous spectra were presented in those papers including, of pertinence here, those of the α- and β-isomers of $[P_2W_{18}O_{62}]^{6-}$, α_2-$[P_2W_{17}O_{61}]^{10-}$, and α_2-$[P_2W_{17}VO_{62}]^{7-}$.

It is worth noting that essentially all of the conclusions that were commonly accepted prior to our ^{183}W NMR data, about the specific structures and isomerisms in the sizable series of complexes derived from the well-known 2:18 Wells–Dawson structure[5-7] (Figure 1), have been proven incorrect by a combination of the ^{183}W NMR spectra we reported previously[2-4] and those reported in the present paper.[1] The earlier con-

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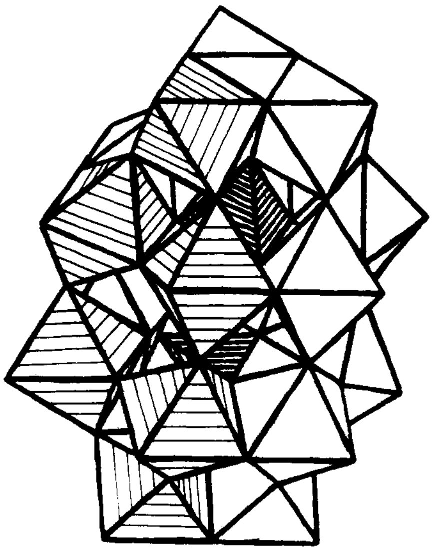

Figure 1. Wells-Dawson structure for α-$[P_2W_{18}O_{62}]^{6-}$ and its derivatives. Each vertex of a polyhedron locates the center of an oxygen atom. P (or As) atoms are at the centers of the interior (hatched) tetrahedra. In the parent complex every octahedron contains a W atom, displaced toward its unshared oxygen. β-Isomers result from 60° rotation, about the 3-fold axis, of one W_3O_{13} cap, while γ-isomers result from such rotation of both the top and bottom W_3O_{13} caps. The structure of α-$[P_2W_{12}Mo_6O_{62}]^{6-}$, made by reacting molybdate with 12-tungstodiphosphate, has Mo atoms replacing the W's in the six hatched octahedra, while 12-tungstodiphosphate presumably has vacant sites for the hatched octahedra. $[P_2W_{15}Mo_3O_{62}]^{6-}$, formerly misformulated as a 16-tungsto complex, has one 3-fold W_3O_{13} cap at the top of the α-isomer replaced by an isostructural Mo_3O_{13} cap.

clusions were based on ambiguous structural X-ray results in one case and on indirect arguments derived from polarographic[8] and ^{31}P NMR studies,[9] as well as on defectively incomplete cryoscopic[10] and analytical data. We have already pointed out[4] how ^{31}P NMR and polarographic studies easily reflect small movements of the central P^{5+} toward vacant or substituted W sites and therefore do not necessarily support the structural conclusions that had been proposed.

^{183}W NMR spectroscopy, on the other hand, by shifting the focus to the backbone of a complex, i.e. to its tungsten framework, can provide unambiguous structural information. For example, our earlier papers[2-4] proved, inter alia, that the origin of the α-β geometrical isomerism in the parent $[P_2W_{18}O_{62}]^{6-}$ complexes is a 60° rotation, about its 3-fold axis, of one of the W_3O_{13} caps on one end of the complex rather than a 60° rotation of an entire PW_9 half-unit about that axis, as had been accepted. It was also proven that the unsaturated α_2-$[P_2W_{17}O_{61}]^{10-}$ isomer and the substituted α_2-$[P_2W_{17}VO_{62}]^{7-}$ isomer had the vacancy and the V substitution, respectively, at the site of a "cap" W rather than a "belt" W.

When a parent 2:18 complex is subjected to controlled partial degradation by base in solutions of controlled pHs, a series of "unsaturated" tungsten-deficient polyanions can be obtained by removal of one or more WO^{4+} units from that parent's structure.[8,11] Unsaturated heteropolytungstate species can be made to react easily with a wide variety of other octahedrally coordinated heteroatoms (such as Mo^{6+}, Co^{2+}, Zn^{2+}, V^{5+}, etc.) so as to restore the overall "parent" structures but with various of the W's substituted by the other octahedral metal ion(s).[12] The partial structural relationships maintained between the substituted species and the parent complexes are responsible for comprehensive schemes of interconversions between them and must be related to the bonding and labilities of the addenda atoms in various structural sites. A basic objective of understanding the interconversion reactions, which has the potential of leading to identification of reactive sites in heteropoly species, has a prerequisite of accurate structural information about the complexes involved.

Experimental Section

Spectroscopy. All ^{183}W NMR spectra were obtained on a Bruker WH/HFX-90 FT NMR spectrometer operating at a magnetic field of 2.114 T, under conditions described previously.[4] Ultraviolet and visible spectra were recorded on a Cary-14 spectrometer, and IR spectra on a Perkin-Elmer Model 457 grating instrument using samples in KBr disks.

Preparation and Characterization of Compounds. Compounds were prepared as reported in the literature.[1,11] Specifically, dodecatungstodiphosphate and "α-hexadecatungstodimolybdodiphosphate" were made by the methods of Contant and Ciabrini[8,9] while polymeric hexatungstophosphate was prepared according to Preyssler's directions.[10] IR and ^{31}P NMR spectra agreed with those previously reported for the same compounds.[9,10,13,14]

The ammonium salt of α-$[As_2W_{18}O_{62}]^{6-}$ was prepared by a modification of the method of Baker and Tsigdinos.[15] A 140-g sample of arsenic(V) oxide was added to a solution of 100 g of $Na_2WO_4{\cdot}2H_2O$ in 600 mL of water. The mixture was boiled under reflux for 8 h. The solution soon became dark blue owing to formation of a little heteropoly blue species by reduction. Addition of a small amount of bromine water restored the lemon yellow color of the desired complex. The solution was concentrated to 300 mL by boiling and then cooled to 10 °C in an ice bath. A 100-g sample of solid NH_4Cl was added to precipitate the desired product by the common ion effect. The yellow crystalline product was filtered off and redissolved in a minimum of water at room temperature. It was reprecipitated by addition of three times the solution's volume of dioxane, to reduce the polarity of the solvent. This procedure removes excess NH_4Cl, which is soluble in water-dioxane mixtures. The product was filtered off and washed with a 3:1 dioxane-water mixture. Subsequent recrystallization from water gave, as first product, small amounts of an orange crystalline material (the ammonium salt of the γ-isomer), which was removed by filtration. The filtrate, upon slow evaporation, gave copious amounts of the more soluble lemon yellow ammonium salt of the α-isomer. The latter was recrystallized again from water. The Li salt of each isomer was obtained by use of a strong-acid cation-exchange resin in the Li form,[16] followed by vacuum evaporation of the effluent. Samples of the K salts were prepared by the same method. The orange potassium γ-octadecatungstodiarsenate(V) was analyzed for As and W. Anal. Calcd for $K_6[As_2W_{18}O_{62}]{\cdot}15H_2O$: As, 3.02; W, 66.78. Found: As, 3.08; W, 66.62.

NMR sample solutions contained the Na or Li salts of the respective complexes in 99.7 atom % D_2O. Those Na or Li salts were obtained from the less soluble but easily recrystallizable potassium or ammonium salts by use of a high-capacity sulfonic acid cation-exchange resin column in the appropriate form[16] or by metathesis with $LiClO_4$ or $NaClO_4$.

Results. Experimental results are summarized in Table I. The ^{183}W NMR spectra of γ-$[As_2W_{18}O_{62}]^{6-}$, α-$[P_2W_{12}Mo_6O_{62}]^{6-}$, α-

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Table I. ^{183}W NMR Chemical Shifts of Some Heteropolytungstate Complexes in D_2O Solution

complex	counterion	concn	resolution, Hz	shifts,[a] ppm ($^2J_{P-O-W}$ values, Hz)
α-$[P_2W_{18}O_{62}]^{6-}$	Na^+	0.4[b]	0.15	173.8 (d, 1.61, 12 W), 128.1 (d, 1.17, 6 W)
β-$[P_2W_{18}O_{62}]^{6-}$	Na^+	0.36[b]	0.15	191.2 (d, 1.61, 6 W), 171.1 (d, 1.61, 6 W), 131.1 (d, 1.17, 3 W), 111.6 (d, 1.32, 3 W)
α-$[As_2W_{18}O_{62}]^{6-}$	Li^+	0.55[b]	0.59	145.3 (12 W), 121.9 (6 W)
γ-$[As_2W_{18}O_{62}]^{6-}$	Li^+	0.2[b]	0.59	166.0 (12 W), 110.0 (6 W)
α-$[P_2W_{12}Mo_6O_{62}]^{6-}$	Li^+	0.35[b]	0.15	179.9 (d, 1.61, 4 W), 166.6 (d, 1.61, 4 W), 130.3 (d, 1.17, 4 W)
α-$[P_2W_{15}Mo_3O_{62}]^{6-}$	Li^+	0.38[b]	0.15	180.1 (d, 1.61, 6 W), 179.3 (d, 1.61, 6 W), 134.1 (d, 1.10, 3 W)
"6:1" tungstophosphate	Li^+	1.95[c]	0.29	287.8 (d, 1.17, 1*n* W), 275.5 (d, 1.47, 1*n* W), 209.7 (d, 1.47, 2*n* W), 207.6 (d, 1.47, 2*n* W)

[a] Relative to (upfield of) external saturated Na_2WO_4 solution in D_2O. [b] In mol/L. [c] In g/L as the potassium salt.

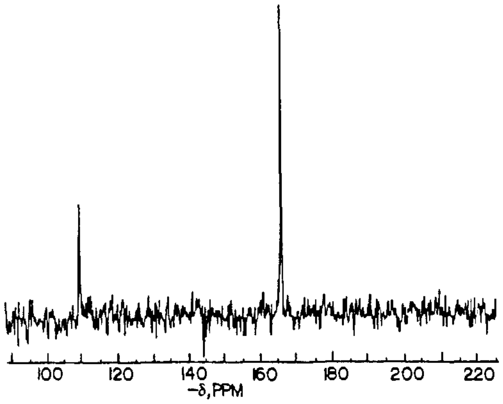

Figure 2. ^{183}W NMR spectrum of (orange) γ-$[As_2W_{18}O_{62}]^{6-}$.

$[P_2W_{15}Mo_3O_{62}]^{6-}$, and that of "Preyssler's 6-tungstophosphate(V)" are given in Figures 2–5.

Discussion

α- and γ-$[As_2W_{18}O_{62}]^{6-}$. The various possibilities for geometrical isomers of the Wells–Dawson structure (Figure 1) were postulated in some detail in 1970.[17] That most of these complexes have at least two isomers[11] has been known from the time of the first elucidation of the 2:18 compounds by Wu[18] in 1920. The most famous case of this isomerism is the α and β forms (Wu's "B" and "A" forms, respectively) of $[P_2W_{18}O_{62}]^{6-}$. The ^{183}W NMR spectrum of α-$[P_2W_{18}O_{62}]^{6-}$ consists[2] of just two very narrow doublets (splitting caused by $^2J_{W-O-P}$) with area ratio 1:2 for one doublet to the other, in accordance with the structure illustrated in Figure 1, which was determined by structural X-ray crystallography.[6,7] The four-line spectrum of β-$[P_2W_{18}O_{62}]^{6-}$ consists[3] of two narrow doublets downfield from two larger narrow doublets. The area ratios are 1:1:2:2. This can be reconciled only with the structure formed when one W_3O_{13} cap of the α structure is rotated 60° about the 3-fold axis.

The lemon yellow isomer, α-$[As_2W_{18}O_{62}]^{6-}$, like the α-isomer of its phosphorus analogue, gives a ^{183}W NMR spectrum consisting of just two resonances with area ratio 1:2 (Table I). The orange isomer also gives just two resonances (Table I) with area ratio 1:2, but these are at very different chemical shifts from those of the α-isomer. The spectrum is reproduced as Figure 2.

While a two-line spectrum with area ratio 1:2 could arise either from 60° rotations of both caps of the α-structure or from one AsW_9 half-unit of the α-structure being rotated 60° relative to the other one about the 3-fold axis, the evidence clearly supports the rotation of the two caps for the orange γ-isomer. Comparison of the spectra of α- and β-$[P_2W_{18}O_{62}]^{6-}$ shows that when just one cap is rotated, the NMR chemical shifts for one of the 6W (belt) resonances and for one of the 3W (cap) resonances remain unchanged and so both are assigned to the end with the unrotated cap. The 3W resonance for the other (rotated) cap is shifted downfield 16.5 ppm while the 6W resonance for the belt adjacent to the rotated cap is shifted upfield 17.4 ppm. For the arsenic isomers, the ^{183}W NMR spectrum of the orange complex shows a 12 ppm downfield shift for *each* cap and a 20.7 ppm upfield shift for *each* belt, relative to the spectrum of the α-isomer. This nicely fulfills the expectations for two caps being rotated. The IR spectra of the α- and γ-isomers are distinct from each other, but very similar, each being consistent with a Wells–Dawson related structure. Relative solubilities, yields of preparative reactions, and stabilities of the α- vs. γ-isomer parallel, in slightly accentuated degree, those factors for α- vs. β-isomers of $[P_2W_{18}O_{62}]^{6-}$. The less soluble orange γ-$[As_2W_{18}O_{62}]^{6-}$ undergoes, in water solution, slow isomerization, yielding a dark yellow solution (a β-isomer?) and finally the lemon yellow α-isomer.

12-Tungstodiphosphate Complexes. Contant and Ciabrini et al.[8,9] studied the 12-tungstodiphosphate complex made by controlled basic degradation of the α-$[P_2W_{18}O_{62}]^{6-}$ anion. Since ^{31}P NMR gives a single resonance, showing the two P's to be structurally identical, they concluded that the 12-tungsto species consists of a Wells–Dawson structure that has been stripped of both its W_3O_{13} caps, yielding $[P_2W_{12}O_{50}]^{18-}$.

All our attempts to obtain the ^{183}W NMR spectrum of the Na or Li salts of the 2:12 anion at pHs of 4.5, 6, and 8 were unsuccessful. Cyclic voltammograms and polarographic studies revealed that the 2:12 species is not stable in solution during the relatively long accumulation time[4] required to obtain the ^{183}W NMR spectrum. During the process of these NMR experiments, we observed that the D_2O solutions of the 2:12 complex deposited a white precipitate, the IR spectrum of which coincided with those of salts of α_2-$[P_2W_{17}O_{61}]^{10-}$. These observations are in agreement with the interconversion reactions proposed by Contant and Ciabrini.[8] We therefore had recourse to making the molybdate-substituted derivative, $[P_2W_{12}Mo_6O_{62}]^{6-}$, which forms quickly and quantitatively by reaction of molybdate with the 12-tungstodiphosphate and is stable for long periods.

The ^{183}W NMR spectrum of α-$[P_2W_{12}Mo_6O_{62}]^{6-}$ (Figure 3) consists of three equal-area resonances, each split into a narrow doublet by W–O–P coupling. This spectrum, together with the fact that the ^{31}P NMR spectrum of the 6-molybdo-12-tungstodiphosphate consists of a single resonance (as is also the case for the unsaturated 12-tungstodiphosphate), proves that the sites occupied by Mo atoms are one position in each cap of the Wells–Dawson structure (eclipsed) plus the two positions in each belt which are adjacent to those two eclipsed cap Mo atoms, as illustrated in Figure 1.

Although the possibility of rearrangement during substitution must always be considered, it is highly probable that the unsaturated 12-tungstodiphosphate has the same P_2W_{12} structure, with vacancies in the positions that get filled by Mo atoms in the reaction with molybdate. This would make the

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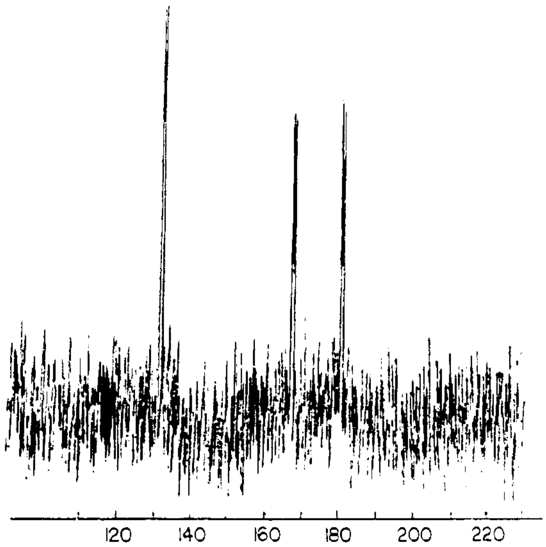

Figure 3. ^{183}W NMR spectrum of α-$[P_2W_{12}Mo_6O_{62}]^{6-}$.

correct formula of the unsaturated species $[P_2W_{12}O_{48}H_x]^{(14-x)-}$. This boat-shaped P_2W_{12} structure, formed by "peeling off" an entire $-WO-O_2-(W_2O_3-O_2-W_2O_3)-O_2-WO-$ group, is supported by (1) the clean and easy reaction with molybdate, (2) the structural identity of the two P atoms in the unsaturated species, and (3) the fact that the complex is easily and reversibly reduced to a heteropoly blue species. Further, the high negative charge on the anion and the fact that it retains a significant part of the Wells–Dawson structure of its parent are consistent with the observation that the 12-tungstodiphosphate easily changes first to α_2-$[P_2W_{17}O_{61}]^{10-}$ and, in acidic solution, to α-$[P_2W_{18}O_{62}]^{6-}$. We note that a 12-tungstodiphosphate consisting of just the Wells–Dawson structure with the caps removed, as originally proposed, should not be reducible to a heteropoly blue species,[19] which is contrary to our observation. The ability to form heteropoly blue species depends upon the presence of adjacent addenda octahedra that each have only one unshared oxygen atom. In a paper[20] based on analytical and polarographic data, subsequent to their original work on this subject,[8,9] Contant and Ciabrini stated they "intuitively consider" that all of the Mo atoms in α-$[P_2W_{12}Mo_6O_{62}]^{6-}$ are in adjacent sites, contrary to their earlier proposal. The data given above prove the correctness of their later intuition.

3-Molybdo-15-Tungstodiphosphate(V). The ^{183}W NMR spectrum of a species heretofore formulated[8,9,20] as α-$[P_2W_{16}Mo_2O_{62}]^{6-}$ (that is, as the substituted molybdate derivative of an unsaturated complex that has been formulated as α-$[P_2W_{16}O_{59}]^{12-}$) is given in Table I and Figure 4. The spectrum cannot be reconciled with any structure having that formulation.

The ^{183}W NMR spectrum consists of three narrow doublets with area ratios of 2:2:1, indicating that the complex is a 3-molybdo-15-tungstodiphosphate species, α-$[P_2W_{15}Mo_3O_{62}]^{6-}$. Such a complex derives from the Wells–Dawson structure by substitution of one W_3O_{13} cap group by one Mo_3O_{13} cap. The ^{183}W NMR chemical shifts (Table I) for this anion are only ~7 ppm upfield with respect to those observed for α-$[P_2W_{18}O_{62}]^{6-}$, reflecting the chemical similarity of W and Mo as well as the fact that a 2:18 heteropoly Wells–Dawson type structure has been restored. As in the previous case, the possibility of rearrangement during the reaction between molybdate and the unsaturated species must be borne in mind.

Figure 4. ^{183}W NMR spectrum of α-$[P_2W_{15}Mo_3O_{62}]^{6-}$.

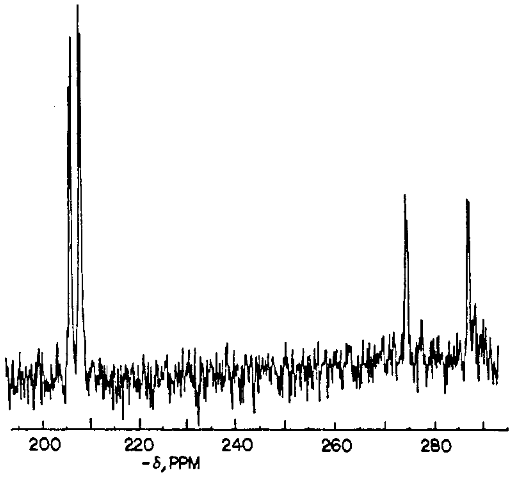

Figure 5. ^{183}W NMR spectrum of Preyssler's polymeric 6-tungstophosphate.

It seems improbable, however, that the unsaturated species does not consist of the Wells–Dawson structure minus one cap rather than the previously claimed 16-tungstodiphosphate. A hypothetical $[P_2W_{16}O_{59}]^{12-}$ species with two W atoms removed from neighboring sites in one cap of the Wells–Dawson structure would leave the remaining WO_6 octahedron of that cap with an improbably high electron density (three unshared oxygens), which has not been observed heretofore. Such species might, of course, be very short-lived intermediates in reactions, but occurrence as a major component is very improbable. A more likely structure for a 16-tungstodiphosphate species would be one derived from the Wells–Dawson structure by removal of two WO^{4+} units, one from a cap and the other either from a belt or from the other cap. But such a species would not be very likely to react with molybdate to replace just one entire cap. Therefore it is highly probable that the unsaturated 16-tungstodiphosphate which has been described is actually a 15-tungstodiphosphate.

The Formula of "Preyssler's Complex". In 1970 Preyssler[10] reported isolating a white crystalline byproduct from the mother liquor during the preparative procedure for α-$[P_2W_{18}O_{62}]^{6-}$. Investigation led to the conclusion[9,10] that the white complex is a trimeric 6-tungstophosphate, which was formulated $[P_3W_{18}O_{66}]^{9-}$.

The trimeric formula was adopted on the basis of cryoscopy in fused Glauber's salt, $Na_2SO_4{\cdot}10H_2O$. The straight line which indicated, upon extrapolation, an ionic weight corresponding to a trimer was drawn through only two data points. Baker and Tsigdinos[21] had found, however, that Glauber's salt cryoscopy often gives curved lines with Wells–Dawson type

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anions owing to the slightly basic nature of concentrated sulfate solutions, which leads to partial degradation of the polyanions, forming greater proportions of fragments of the complexes as dilution increases. Preyssler's data therefore really indicate that the complex is more highly polymeric than a trimer.

The ^{183}W NMR spectrum of Preyssler's 6-tungstophosphate is simple, containing just four well-resolved narrow doublets with area ratios of 1:1:2:2 (Figure 5). The ^{31}P NMR spectrum contains a single resonance indicating that the various P atoms are structurally identical. These results cannot be reconciled with the currently accepted formulation for this anion.[9,10] Various more highly polymeric structures can be devised that satisfy all the present data, so an X-ray crystal structure determination will probably be required.

Notes

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Rearrangement of *closo*-3,3-$(PPh_3)_2$-3-H-1-(R)-3,1,2-$IrC_2B_9H_{10}$ to *closo*-2,2-$(PPh_3)_2$-2-H-8-(R)-2,1,8-$IrC_2B_9H_{10}$. Synthesis and X-ray Structure of *closo*-2,2-$(PPh_3)_2$-2-H-8-(C_6H_5)-2,1,8-$IrC_2B_9H_{10}$

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During our continuing investigation of the chemistry of the known alkene hydrogenation and isomerization catalyst *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$[1] (Ia), the iridium congerner and its derivatives, *closo*-3,3-$(PPh_3)_2$-3-H-1-(R)-3,1,2-$IrC_2B_9H_{10}$, R = H (IIa),[1] R = C_6H_5 (IIb),[2] R = CH_3 (IIc)[2] and R = 1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$) (IId),[2] were prepared and notable differences between the reactivity of the Rh and Ir systems were observed. Syntheses of IIb-d, the exo-nido complexes derived from these compounds, and the dimeric complex derived from IIa will be reported in a future paper. Although thermally induced migration of carbon atoms over the surfaces of polyhedral cobaltacarboranes is a well-established phenomenon,[3] similar isomerization reactions are not so well-known for other metallacarboranes. The formation of 2,1,8 isomers of icosahedral metallacarboranes have been observed previously[3] only during high-temperature vapor-phase thermal isomerization of (η-C_5H_5)Co($C_2B_9H_{11}$) isomers. The 2,1,8 isomer of this system was observed as the dominant kinetic product (74%) arising from the 3,1,2 isomer during such reactions at temperatures near 500 °C; however, three other isomers were also detected in the reaction mixture. Here we report the ready polytopal rearrangement of IIb and IIc under mild thermolytic conditions in toluene solvent at the reflux temperature. In each of these examples the carbon atom bearing the substituent migrated in such a fashion as to produce the isomeric *closo*-2,2-$(PPh_3)_2$-2-H-8-(C_6H_5)-2,1,8-$IrC_2B_9H_{10}$ (IIIb) and *closo*-2,2-$(PPh_3)_2$-2-H-8-(CH_3)-2,1,8-$IrC_2B_9H_{10}$ (IIIc) species in 84% (30 h) and 33% (9 days) yields (heating time), respectively. None of the other possible isomers were produced in detectable quantities under the experimental conditions described. The rearranged species IIId was prepared by heating $[(COD)Ir(PPh_3)_2]^+$[*nido*-7-(1′-*closo*-1′,2′-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}]^-$ in the presence of cyclohexane at the reflux temperature (41%). The unsubstituted IIa was not observed to rearrange after 5 days at reflux in toluene. The order of relative ease of rearrangement is apparently IId > IIb > IIc, in agreement with the idea that relief of steric strain provides some driving force for rearrangement by moving the bulky carbon substituent to the second belt (vertex 8) of the icosahedron, thus relieving interaction with the metal vertex and its triphenylphosphine ligands.

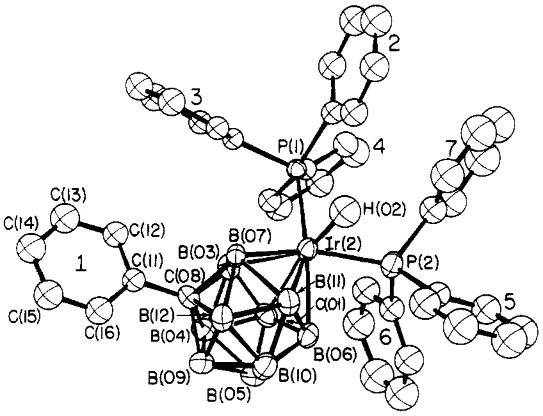

Figure 1. Molecular structure of *closo*-2,2-$(PPh_3)_2$-2-H-8-(C_6H_5)-2,1,8-$IrC_2B_9H_{10}\cdot{}^1/_2CH_2Cl_2$.

Below we describe the X-ray analysis of IIIb, upon which the foregoing structural arguments are based.

The structure of *closo*-2,2-$(PPh_3)_2$-2-H-8-(C_6H_5)-2,1,8-$IrC_2B_9H_{10}$ was determined by a single-crystal diffraction study. The molecule is illustrated in Figure 1.[4] Selected interatomic distances and angles are listed in Tables I and II. The crystal structure closely resembles that of the Rh congener of Ia in its conformation about the metal. The most striking feature of the structure is the relative positions of the two carbon atoms of the C_2B_9 carborane ligand, which defines this complex as a member of the 2,1,8-isomer series.[4] The phenyl-bearing carbon vertex of the carborane has migrated to a position on the lower pentagonal belt, nonadjacent to the other carbon atom, resulting in a decrease in both electrostatic repulsions and steric interactions among the two carbon atoms and the Ir atom. The iridium atom, as expected, exhibits pseudooctahedral coordination; the carborane ligand occupies three coordination sites and the two PPh_3 ligands and the hydride occupy the remaining sites. There is no fundamental distortion from the usual 12-vertex closo icosahedral geometry.

Experimental Section

All manipulations were carried out in an intert atmosphere with standard Schlenk techniques. Unless otherwise specified all solvents

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(1) (a) Paxson, T. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 4674. (b) Paxson, T. E. Ph.D. Thesis, University of California, Los Angeles, 1974.

(2) Doi, J. A. Ph.D. Thesis, University of California, Los Angeles, 1980.

(3) Kaloustian, M. K.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 6679.

(4) The cage numbering system in this paper is consistent with that favored by IUPAC for *closo*-carboranes. Commission on Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.* **1972**, *30*, 683.

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