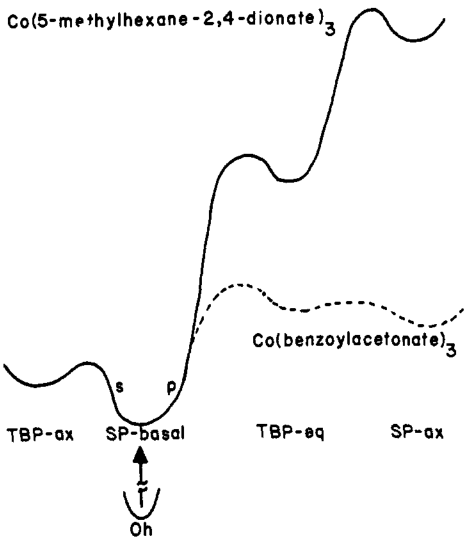
pushed too far because they were difficult to obtain and do contain significant uncertainties. However, the qualitative conclusions which could be drawn from this type of analysis might lead to the reaction profiles shown in Chart I.

Chart I



Factors which could affect the relative energies of the five-coordinate species are, as before, the relative electronegativities and π-accepting abilities of the two different ends of the bidentate ligands and, in addition, the relative *π-donating* abilities and the changes in ring strain in the six-membered chelate ring in its different orientations about the central metal ion (diequatorial *vs.* apical equatorial, etc.). These are difficult to evaluate at this time.

We have investigated the kinetics of stereoisomerization of Co((+)-3-acetylcamphorate)$_3$ where the chirality of the ligands causes all four octahedral stereoisomers to have different energies and allows us to make more direct measurements of the 12 microscopic rate constants than was possible in the above systems.[28] The results are similar to those in Table II and our analysis of their significance prompted, in part, the development of the method reported here.

The scheme described in this paper should be helpful in unifying and understanding the mechanistic results of many substitution and isomerization reactions of octahedral compounds which react *via* five-coordinate species. The same technique could be applied for other modes of five-coordinate rearrangement if it becomes apparent that processes other than the BPR are operable.

Acknowledgments. The author wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Foundation of the State University of New York for support of this work.

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(28) C. S. Springer, Jr., and C. Hinrichsen, unpublished results.

Stereochemically Nonrigid Eight-Coordinate Molybdenum and Tungsten Tetrahydrides

P. Meakin,* L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson

Contribution No. 1956 from the Central Research Department,
E. I. du Pont de Nemours and Company, Experimental Station,
Wilmington, Delaware 19898. Received August 24, 1972

Abstract: Stereochemical nonrigidity has been investigated for a class of eight-coordinate transition metal hydrides. Ten hydrides of the form H_4ML_4 were prepared with L tertiary phosphines, a bidentate phosphine, and a phosphonite for molybdenum(IV) and tungsten(IV) by reaction of $NaBH_4$ or $LiAlH_4$ with L_2MCl_4 and excess L. Limiting fast- and slow-exchange nmr spectra were observed for eight of these hydrides. Rearrangement barriers are relatively high ($\Delta G^{\ddagger}$ = 12–16 kcal mol^{-1}), with those for the tungsten set uniformly the higher. The structure of one hydride, $H_4Mo[P(C_6H_5)_2CH_3]_4$, was determined by single-crystal X-ray analysis. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions of a = 12.174 (4) Å, b = 22.057 (9) Å, c = 19.642 (11) Å, and β = 119.68 (4)° with four molecules per cell. Structure refinement by least squares led to a conventional R of 0.071. The H_4MP_4 framework is a dodecahedron with triangular faces; the hydrogen and the phosphorus atoms are at the A and B sites, respectively (*i.e.*, vertices of elongated and flattened tetrahedra, respectively). The implications of the structural information with regard to the rearrangement process and a comparison with similar processes in HML_4 and H_2ML_4 complexes are discussed. Studies of two nine-coordinate hydrides, H_6WL_3, are also presented.

Magnetic equivalence of ligand nuclei in eight-coordinate complexes has been a general observation.[1–6] In some instances, the magnetic equivalence has been ascribed to a rapid intramolecular rearrangement, and various stylized mechanisms have been considered.[1–3] Preliminary nmr studies[7,8] of eight-coordinate complexes of the type H_4ML_4 (M =

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(1) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

(2) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(3) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); *Rec. Chem. Progr.*, **31**, 51 (1970).

(4) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).

(5) P. G. Douglas and B. L. Shaw, *ibid.*, 334 (1970).

(6) M. Freni, R. Demichelis, and D. Giusto, *J. Inorg. Nucl. Chem.*, **29**, 1433 (1967).

(7) J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.*, **93**, 5261 (1971).

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Mo or W, and L is a phosphine ligand) indicated that complexes of this type are rigid on the nmr time scale at or just below room temperature. As the temperature is raised the nmr spectra undergo line shape changes characteristic of an intramolecular mutual exchange process and eventually a limiting high-temperature spectrum is obtained in which all the protons are in effect equally coupled to all of the ^{31}P nuclei.

In this paper, we describe the preparation of a series of H_4ML_4 complexes including a number of new members in the series, the hydride nmr spectral changes with temperature, the crystal structure of a representative member in the series, $H_4Mo[P(C_6H_5)_2CH_3]_4$, and possible mechanisms for the intramolecular rearrangement processes in these hydrides. The preparation and nmr studies of two nine-coordinate hydrides (H_6ML_3) are also reported.

Experimental Section

A. **Synthetic. General Preparative Procedures.** Reagent grade metal chlorides were used without further purification. All solvents were dried over neutral grade alumina or a molecular sieve and thoroughly degassed prior to use. Since most of the hydride complexes or the intermediates to the hydrides react with moisture and atmospheric oxygen, the majority of the reactions were run under rigorously oxygen-free conditions using a Vacuum Atmospheres Corporation Dri-Lab.

Preparation of the L_2MCl_4 Complexes. In a dry nitrogen atmosphere 0.021 mol of phosphorus ligand was added to 100 ml of dry, nitrogen-saturated methylene chloride with stirring.[9] Bis(acetonitrile)molybdenum or -tungsten tetrachloride (0.01 mol) (prepared by the reaction of acetonitrile with $MoCl_5$ or WCl_5)[10] was added with stirring continued for 1 hr. About 350 ml of petroleum ether (bp 38–50°) was added slowly to precipitate solids or oils. The solids were washed with an additional 400 ml of petroleum ether and then dried *in vacuo* for 15 min. When the addition of petroleum ether gave an oil, the petroleum ether was decanted, and an additional 50 ml of fresh petroleum ether was added and the flask was scratched. Another 200 ml of petroleum ether was added, and agitation was continued until solids precipitated. Finally, these solids were washed with 400 ml of petroleum ether and dried *in vacuo* for 15 min. The L_2MCl_4 complexes were not characterized before use in subsequent stages in the synthesis of the H_4ML_4 complexes. An infrared spectrum was run to determine that there was no coordinated acetonitrile.

Tetrakis(diethoxyphenylphosphine)molybdenum Tetrahydride. Diethoxyphenylphosphine (2.77 g, 0.014 mol) and sodium borohydride (1.89 g, 0.05 mol) were slurried in 80 ml of dry, hydrogen-saturated ethanol. Bis(diethoxyphenylphosphine)molybdenum tetrachloride (3.80 g, 0.006 mol) was slowly added in portions over a 10-min period while hydrogen gas was passed over the surface of the reaction mixture. After the addition was complete, the reaction was stirred for 16 hr at 25° with a hydrogen atmosphere[9] maintained. The deep yellow reaction mixture was then evaporated to dryness *in vacuo* at 25°. The resulting solid was dissolved in 250 ml of toluene, and the solution was evaporated to an oil on a Rinco evaporator. Methanol (150 ml) was added to the oil and the mixture then cooled to −40°. Yellow solids formed, and these were separated by filtration. Recrystallization was twice effected by dissolution of the solid in 10–15 ml of toluene, filtration, and methanol addition (100 ml) to the filtrate. In the final stage, the yellow crystals, which precipitated after cooling to −40° for 3 days, were collected and dried *in vacuo* for 4 hr at 50°. Yields varied between 0.50 and 1.5 g. In the infrared spectrum there were two bands at 1751 and 1818 cm^{-1} probably associated with Mo–H vibrations.

Anal. Calcd for $C_{40}H_{64}O_8P_4Mo$: C, 53.81; H, 7.22. Found: C, 53.98; H, 6.88.

Tetrakis(diethoxyphenylphosphine)tungsten Tetrahydride. Diethoxyphenylphosphine (5.15 g, 0.26 mol) and sodium borohydride (3.40 g, 0.09 mol) were slurried in 150 ml of dry, hydrogen-saturated ethanol. While maintaining the temperature at 25°, bis(diethoxyphenylphosphine)tungsten tetrachloride (8.80 g, 0.012 mol) was added in small portions over a 10-min period. The reaction mixture was stirred for 4 hr maintaining a hydrogen atmosphere[9] and then evaporated to dryness *in vacuo* at 25°. The residual gummy solid was dissolved in 200 ml of toluene, the slurry filtered, and the filtrate evaporated to an oil on a Rinco evaporator. Methanol (100 ml) was added to the oil. Cooling to −40° for 20 hr gave crystals which were separated by filtration. The crystals were dissolved in 15 ml of toluene, and 100 ml of methanol was added to the filtrate. After cooling for 4 hr at −40°, yellow crystals were collected and dried *in vacuo* at 25° for 48 hr (yield, 1.5 g). The infrared (Nujol mull) had W–H bands at 1808 and 1886 cm^{-1}.

Anal. Calcd for $C_{40}H_{64}O_8P_4W$: C, 48.99; H, 6.57. Found: C, 48.44; H, 6.74.

Tetrakis(ethyldiphenylphosphine)tungsten Tetrahydride. The reaction was run in a nitrogen-free argon atmosphere;[9] purification was done in a nitrogen atmosphere. Ethyldiphenylphosphine (6.41 g, 0.029 mol) was dissolved in 200 ml of dry, argon-saturated tetrahydrofuran. Bis(ethyldiphenylphosphine)tungsten tetrachloride (10.27 g, 0.014 mol) was added, and the mixture was stirred at 25° for 15 min. Lithium aluminum hydride (3.0 g, 0.08 mol) was added slowly in portions; when the addition was complete, the mixture was stirred 1 additional hr. Distilled water (10 ml) was added dropwise to the mixture causing gas evolution and a color change from red-yellow to chrome yellow. The mixture was filtered and the filtrate evaporated *in vacuo* to a gummy deep yellow oil which was extracted with 600 ml of refluxing petroleum ether (bp 38–50°). The filtered extracts were evaporated on a Rinco evaporator to a yellow oil, and solidification took place in 6 days. The solid was dissolved in 100 ml of petroleum ether, the solution was filtered, evaporated to 50% of its original volume, and then cooled to −40° for 1 day. Yellow crystals were separated by filtration and dried *in vacuo* for 24 hr at 25° (yield, 1.1 g). The infrared (Nujol mull) showed W–H bands at 1820 and 1875 cm^{-1}.

Anal. Calcd for $C_{56}H_{64}P_4W$: C, 64.73; H, 6.17. Found: C, 64.55; H, 6.32.

Tetrakis(methyldiphenylphosphine)molybdenum Tetrahydride.[11] The reaction was run in either argon or helium;[9] the product was worked up in a nitrogen atmosphere. Methyldiphenylphosphine (1.20 g, 0.0059 mol) and sodium borohydride (0.80 g, 0.02 mol) were slurried in 30 ml of dry argon-saturated ethanol. Bis(methyldiphenylphosphine)molybdenum tetrachloride was added over a 10-min period. After stirring the reaction mixture an additional 50 min, a yellow precipitate was separated by filtration. The yellow solids were twice slurried in 20 ml of argon-saturated methanol and recovered by filtration. Crude yield after drying *in vacuo* was 1.23 g. The yellow solids were dissolved in benzene (20 ml), and then methanol (30 ml) was slowly added dropwise to the filtered solution giving a precipitate of yellow crystals. The infrared spectrum showed Mo–H bands at 1714 and 1800 cm^{-1}.

Anal. Calcd for $C_{52}H_{56}P_4Mo$: C, 69.3; H, 6.27. Found: C, 69.2; H, 6.32.

Tetrakis(triethylphosphine)molybdenum Tetrahydride. The reaction was run in a hydrogen atmosphere;[9] purification can be done in a nitrogen atmosphere. Triethylphosphine (2.6 g, 0.022 mol) and sodium borohydride (3.0 g, 0.08 mol) were added to 80 ml of dry, hydrogen-saturated ethanol. After cooling to 0°, bis(triethylphosphine)molybdenum tetrachloride (4.74 g, 0.01 mol) was added over a 10-min period; the reaction mixture was stirred for 1 hr at 25° and for 15 min at 50°. The brown mixture was evaporated to dryness *in vacuo* at 25°. Residual brown solids were then dissolved in 250 ml of toluene; the solution was filtered and evaporated to dryness. The resulting brown oil was recrystallized three times by dissolution in a minimum amount of petroleum ether (25–50 ml) and methanol addition (50–75 ml) to the point of incipient precipitation. After cooling to −40° for 2 hr, the off-white crystals were separated by filtration. The crystals were dried *in vacuo* at 25° for 48 hr to yield 1.5 g of the desired compound. The infrared spectrum showed Mo–H bands at 1712 and 1808 cm^{-1}.

Anal. Calcd for $C_{24}H_{64}P_4Mo$: C, 50.34; H, 11.26. Found: C, 50.53; H, 11.25.

Tetrakis(ethyldiphenylphosphine)molybdenum Tetrahydride. In a nitrogen-free argon atmosphere,[9] tetrachlorobis(ethyldiphenylphosphine)molybdenum (6.66 g, 0.01 mol) was added slowly over a 10-min period to ethanol (120 ml) containing ethyldiphenylphos-

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[9] Solutions of the tetrahydrides themselves are stable in a nitrogen atmosphere. However, in some cases the yields were not high when the reaction was carried out under nitrogen. Accordingly an argon or hydrogen atmosphere was used.

[10] F. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 4531 (1964).

[11] F. Pennella, *Chem. Commun.*, 158 (1971).

phine (4.50 g, 0.021 mol) and sodium borohydride (3.02 g, 0.08 mol). After stirring at room temperature for 1 hr, the red-yellow solution was filtered and the filtrate evaporated to 60 ml. An equal volume of petroleum ether (bp 38-50°) was slowly added while vigorously scratching the walls of the flask; the flask was cooled to −40° overnight. The resulting yellow crystals were separated by filtration and dissolved in 25 ml of toluene (25°). Petroleum ether was slowly added to the solution as the side walls were scratched to induce crystallization. After cooling to −40°, the crystals were separated and dried *in vacuo* at 25° for 20 hr (yield, 1.51 g of yellow crystals). The infrared spectrum (Nujol mull) showed bands at 1782, 1818 s; 1835, 1848 w cm^{-1}.

Anal. Calcd for $C_{56}H_{64}P_4Mo$: C, 70.28; H, 6.74. Found: C, 70.51; H, 6.85.

Tetrakis(dimethylphenylphosphine)tungsten Tetrahydride. Bis(dimethylphenylphosphine)tungsten tetrachloride (6.02 g, 0.01 mol) and dimethylphenylphosphine (3.04 g, 0.022 mol) were added to 150 ml of dry argon-saturated tetrahydrofuran.[9] Lithium aluminum hydride (2.0 g, 0.05 mol) was mixed with 200 ml of tetrahydrofuran, the slurry was filtered, and the filtrate was added to the reaction mixture. This mixture was stirred at 25° for 2 hr, and after cooling to room temperature, it was filtered, and the filtrate was evaporated *in vacuo*. The resulting deep yellow oil was washed with 400 ml of petroleum ether to remove any excess dimethylphenylphosphine. Tetrahydrofuran (75 ml) was added to the remaining oil and 1-2 ml of water was carefully added dropwise with stirring. After gas evolution ceased, the mixture was evaporated to dryness on a Rinco evaporator to give a deep yellow oil. This oil was a mixture of hydrides including the desired tetrahydride. The latter was never obtained in pure form but was adequately characterized by ^{31}P and ^{1}H nmr data. Dissolution of the oil in 50 ml of petroleum ether followed by filtration, evaporation to 50% of the initial volume, and cooling to −40° for 20 hr yielded 1.0 g of crystals. The infrared spectrum (Nujol mull) showed W–H stretching bands at 1760 and 1820 cm^{-1}, and the nmr data suggested that the compound was $[(C_6H_5(CH_3)_2P]_3WH_6$ (*vide infra*).

Anal. Calcd for $C_{24}H_{39}P_3W$: C, 47.69; H, 6.50. Found: C, 47.80; H, 6.53.

Tetrakis(methyldiphenylphosphine)tungsten Tetrahydride. Bis(methyldiphenylphosphine)tungsten tetrachloride (7.26 g, 0.01 mol) and methyldiphenylphosphine (4.40 g, 0.022 mol) were added to 150 ml of dry, nitrogen-saturated ethanol in a nitrogen atmosphere for 10 min. To this mixture was added sodium borohydride (3.02 g, 0.08 mol), and after stirring for 20 hr at room temperature, it was cooled to −40° for 2 hr. Yellow solids (4.4 g) were separated by filtration and recrystallized by dissolution in a minimum (200 ml) of warm benzene followed by 80-90% evaporation of the filtrate on a Rinco evaporator. Ethanol (200 ml) was slowly added to the concentrate while the sides of the vessel were scratched to induce crystallization. Yellow crystals were separated by filtration and dried *in vacuo* at 25° for 4 hr (yield, 1.4 g). The infrared spectrum showed W–H bands at 1780 and 1820 cm^{-1}.

Anal. Calcd for $C_{52}H_{56}P_4W$: C, 63.16; H, 5.70. Found: C, 63.12; H, 5.83.

Bis[1,2-bis(diphenylphosphino)ethane]molybdenum Tetrahydride. In a dry nitrogen atmosphere, [1,2-bis(diphenylphosphino)ethane]molybdenum tetrachloride (6.80 g, 0.01 mol) and 1,2-bis(diphenylphosphino)ethane (4.78 g, 0.012 mol) were added to 150 ml of dry, nitrogen-saturated ethanol. After stirring for 30 min at 50°, sodium borohydride (3.0 g, 0.08 mol) was added over a 5-min period. Refluxing conditions were established for an additional 30 min, the reaction was cooled slowly to room temperature, and the solid which had precipitated was separated by filtration. This yellow solid was twice recrystallized by dissolution in benzene at 50° and addition of 200 ml of ethanol. The resulting yellow crystals were dried *in vacuo* at 25° for 5 hr (yield, 1.5 g). The infrared spectrum showed W–H bands at 1750 and 1830 cm^{-1}.

Anal. Calcd for $C_{52}H_{52}P_4Mo$: C, 69.64; H, 5.84. Found: C, 69.80; H, 5.88.

Bis[1,2-bis(diphenylphosphino)ethane]tungsten Tetrahydride. The reaction was run in a nitrogen-free argon box;[9] however, the work-up may be done under nitrogen. A slurry of [1,2-bis(diphenylphosphino)ethane]tungsten tetrachloride (3.62 g, 0.005 mol) and 1,2-bis(diphenylphosphino)ethane (2.39 g, 0.006 mol) in 300 ml of argon-saturated ethanol was stirred at room temperature for 10 min. After heating the reaction mixture to 50°, sodium borohydride (0.04 mol, 1.51 g) was added in portions over a 5-min period. On completion of the addition, yellow solids began to form. The reaction was then refluxed for 2 hr and cooled, and the yellow solids were separated by filtration. The solids were twice recrystallized by dissolution in benzene at 50° followed by slow ethanol addition (175 ml). Cooling to −40° produced yellow crystals which were separated and dried *in vacuo* at 25°. Yields varied between 0.60 and 1.1 g. The infrared spectrum (Nujol mull) showed W–H bands at 1790 and 1850 cm^{-1}.

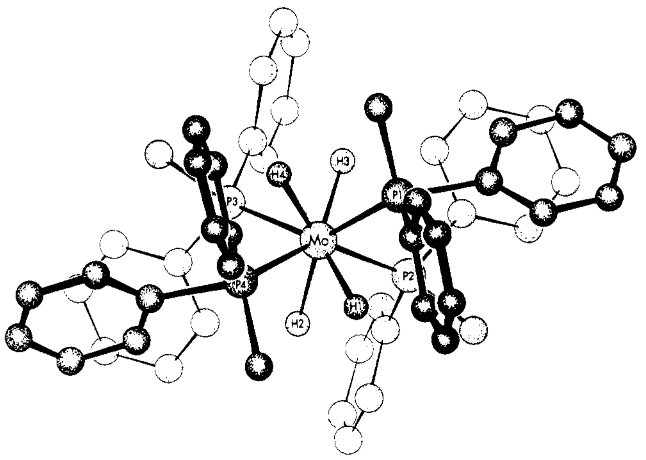

Figure 1. The molecular structure of $H_4Mo[P(C_6H_5)_2CH_3]_4$.

Anal. Calcd for $C_{52}H_{52}P_4W$: C, 63.42; H, 5.32. Found: C, 64.09; H, 5.54.

B. X-Ray. The crystal structure of $MoH_4[P(C_6H_5)_2CH_3]_4$ was determined to establish the molecular geometry in the solid state. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions of $a = 12.174$ (4) Å, $b = 22.057$ (9) Å, $c = 19.642$ (11) Å, and $\beta = 119.68$ (4)°. There are four molecules per cell, and hence there is no space group imposed molecular symmetry. The calculated density is 1.31 g/cm^3; no suitable solvent system could be found to obtain an experimental value of the density. About 4950 reflections were measured on a Picker four-circle automatic diffractometer. The structure was solved by heavy-atom techniques and refined by full-matrix least squares to a conventional R of 0.071 for 3670 observed reflections. All of the hydrogen atoms were located, and the hydride hydrogen positions were refined.

C. Nmr. Nmr samples were prepared in a nitrogen atmosphere (Vacuum Atmospheres Dri-Lab; less than 2 ppm O_2) using deoxygenated solvents except for those samples in which chlorodifluoromethane was the solvent. Variable temperature proton nmr spectra were recorded using a Bruker HFX-90 and Varian HR-220 spectrometers. The ^{31}P spectra (36.43 MHz) were measured with and without proton noise decoupling using the Bruker spectrometer. The ^{31}P samples were run in 10-mm tubes with 3-mm coaxial capillaries containing hexafluorobenzene or 1,2-dibromotetrafluoroethane for field-frequency stabilization. Temperatures for the spectra taken on the HR-220 were measured either by observing the chemical shift separation in methanol or ethylene glycol samples run before and after each trace or by means of a thermometer which fits inside the spinning nmr tube. For the HFX-90, temperatures were measured by means of a copper–constantan thermocouple located just beneath the sample tube and were calibrated using a similar thermocouple held coaxially in the spinning sample tube partially filled with solvent.

Results and Discussion

The Solid-State Molecular Structure of $H_4Mo[P(C_6H_5)_2CH_3]_4$. The molecular structure of $H_4Mo[P(C_6H_5)_2CH_3]_4$, illustrated in Figure 1, has a metal–ligand coordination sphere that is essentially a D_{2d} ($\bar{4}2m$) dodecahedron, with triangular faces, characterized by interpenetrating tetrahedra with hydrogen atoms forming an elongated tetrahedron (A sites[12]) and phosphine ligands a flattened tetrahedron (B sites[12]); both share a common idealized $S_4(\bar{4})$ axis which passes through the Mo atom and the H(1)–H(2) and H(3)–H(4) midpoints. This stereochemistry in dodecahedral geometry is that predicted by the Hoard–

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(12) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

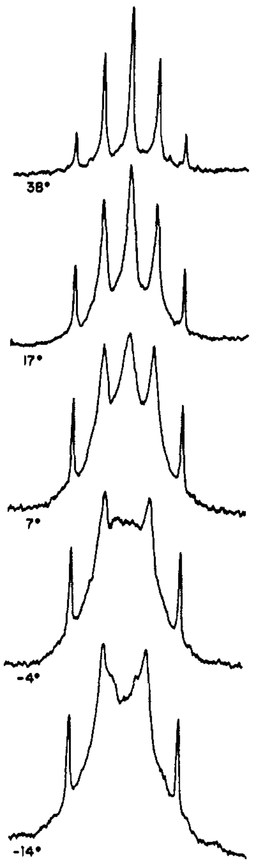

Figure 2. Temperature-dependent hydride region ^1H 90-MHz nmr spectra of $H_4Mo[P(C_2H_6)_3]_4$ in toluene-d_8.

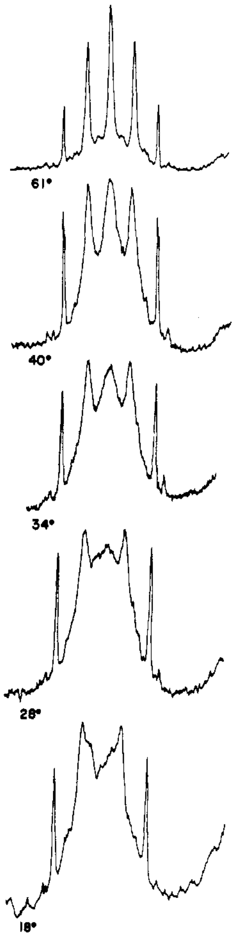

Figure 3. Temperature-dependent hydride region ^1H 90-MHz nmr spectrum of $H_4W[PC_6H_5(CH_3)_2]_4$ in toluene-d_8.

Silverton rules.[12] An alternative characterization of the dodecahedron is by the orthogonally equivalent trapezoids [P(1)H(1)H(2)P(3) and P(2)H(3)H(4)P(4)] with an observed dihedral angle of 88.7° between the trapezoids (average atomic deviation 0.03 Å). This clearly differentiates the coordination polyhedron from the square antiprism, the other common coordination polyhedron in eight-coordination, since an angle of 79.4° is the limit for a regular antiprism.[13] In Figure 1, the view is in the direction of what would be the $\bar{8}$ axis of a square antiprism, assuming equivalent ligands. The atomic coordinates of the atoms in the inner coordination sphere are listed in Table I.

Table I. Positions of the H_4MP_4 Atoms in $H_4Mo[P(C_6H_5)_2CH_3]_4$[a]

Mo	*x*	*y*	*z*
Mo	0.2729	0.0151	0.2522
P(1)	0.0572	−0.0233	0.1838
P(2)	0.2073	0.1227	0.2491
P(3)	0.4631	0.0289	0.2356
P(4)	0.3537	−0.0747	0.3343
H(1)	0.220	0.019	0.315
H(2)	0.371	0.045	0.348
H(3)	0.213	0.027	0.155
H(4)	0.279	−0.040	0.198

[a] Coordinates are in fractions of the cell edges.

Although the overall symmetry is idealized D_{2d}-($\bar{4}2m$), the molecular symmetry is more precisely $C_2(2)$; the twofold axis maintained in the crystal is one of the dihedral twofold axes of the idealized dodecahedron (the view direction of Figure 1). There are two types of Mo–P distances with 2.433 (2) Å for Mo–P(1) (Mo–P(4)) and 2.503 (3) Å for Mo–P(2) (Mo–P(3)); the average Mo–H distance is 1.70 (3) Å. The average H(1)–Mo–H(2) and P(1)–Mo–P(3) angles are 60.7 and 142.8°, respectively, giving dodecahedral shape parameters[12] of 30.3° for θ_A(H) and 71.4° for θ_B(P). These data are typical[2,14,15] of dodecahedral geometries even though there are no close comparisons for eight-coordinate complexes with either hydride or phosphine ligands. It is difficult to predict what an Mo–P single bond distance should be, but the data here are in reasonable agreement with 2.48 Å calculated from radii of 1.38 Å for Mo(IV)[14] and 1.10 Å for P. The Mo–H distances (1.70 (3) Å average) are in the range of other observed distances,[16] and a value of 1.8 Å was estimated for the Mo–H distance in $Mo_2H(\pi\text{-}C_5H_5)_2P(CH_3)_2(CO)_4$.[17]

The solid-state distortions from $D_{2d}(\bar{4}2m)$ symmetry are significant at least in a statistical sense. These deviations from the idealized symmetry, which probably prevails for the molecule in solution, may result

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(13) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7, 1686 (1968); 11, 1446 (1972).

(14) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 10 (1967).

(15) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).

(16) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., p 42.

(17) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2576 (1965).

Table II. Nmr Parameters for Some Eight-Coordinate Tetrahydrides at Room Temperature

Complex	ΣJ_{HP}[a]	δ_H[b]	δ_P[c]	Solvent	J_{HW}
$H_4W[P(C_6H_5)_2C_2H_5]_4$	127	1.82		Toluene-d_8	
$H_4W[PC_6H_5(OC_2H_5)_2]_4$	124	3.51		Toluene-d_8	31
$H_4W[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	114	10.7[d]		Chlorobenzene	
$H_4W[PC_6H_5(CH_3)_2]_4$	126	2.82		Toluene-d_8	30
$H_4W[P(C_6H_5)_2CH_3]_4$	123	1.78		Toluene-d_8	
$H_4Mo[P(C_2H_5)_3]_4$	137	5.57		Toluene-d_8	
$H_4Mo[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	119	10.84[d]		Chlorobenzene	
$H_4Mo[P(C_6H_5)_2C_2H_5]_4$	136	2.15		Toluene-d_8	
$H_4Mo[PC_6H_5(OC_2H_5)_2]_4$	127	3.44		Toluene-d_8	
	127[e]	2.48[e]	192.4[e]	Methylene chloride	
$H_4Mo[P(C_6H_5)_2CH_3]_4$	131	2.10		Toluene-d_8	
	131[e]	2.48[e]	37.9[e]	Methylene chloride	

[a] $J_{H_1P_1} + J_{H_1P_2} + J_{H_1P_3} + J_{H_1P_4}$. [b] Parts per million upfield from TMS. [c] Parts per million upfield from 85% H_3PO_4. [d] Parts per million upfield from chlorobenzene. [e] 0°.

from the usual packing effects which are mainly intramolecular in origin. In point of fact, all four hydride hydrogens have short contacts (2.20–2.32 Å) involving benzene hydrogen atoms.

The ^1H and ^{31}P Nmr Results for H_4ML_4 Complexes. In the low-temperature limit hydride region proton nmr spectrum of three of the five molybdenum tetrahydrides and all five tungsten tetrahydrides reported in this work, there is a symmetric pattern with two sharp outer lines and a broad central region attributed to the overlapping of many individual lines; see Figures 2, 3, and 4 and Figure 1 in ref 7 and 8. The two exceptional molybdenum complexes are discussed below. In the four cases where the low-temperature limit spectra have been recorded at both 90 and 220 MHz, the spectra are indistinguishable at these two frequencies. In addition, the low-temperature limit ^{31}P nmr spectrum of $H_4Mo[P(C_6H_5)_2CH_3]_4$ in which the ligand protons have been selectively decoupled consists of a symmetric pattern with two distinct outer lines (Figure 2 of ref 7). The symmetry of both the ^1H and ^{31}P spectra and the invariance of the ^1H spectra to the magnetic field indicate that in the solution structure of these complexes the hydride hydrogens and the ligand phosphorus atoms are chemically but not magnetically equivalent.

As the temperature is raised from the low-temperature limit, the shapes of the complex central parts of both the ^1H and ^{31}P spectra begin to change and eventually sharpen into the central three lines of a binomial quintet (Figures 2, 3, and 4, Figures 1 and 2 of ref 7 and Figure 1, of ref 8). The two outer lines remain sharp at all temperatures, a feature characteristic of intramolecular mutual exchange processes in systems of this type.[18,19] Since only the two outer lines out of the very many lines composing the spectrum are well resolved, unambiguous analysis of the low-temperature limit spectra is difficult. Chemical shifts and the sum of the H–P coupling constants are the only parameters that can be rigorously derived (Table II). In the hydride region of the proton nmr spectra of two of the tungsten complexes ($H_4W[PC_6H_5(CH_3)_2]_4$ and $H_4W[PC_6H_5(OC_2H_5)_2]_4$ (Figures 3 and 4)) the satellite lines corresponding to the 14.4% of molecules containing ^{183}W could be clearly seen and the ^1H–^{183}W coupling constants measured; the values are 31 and 30 Hz, respectively.

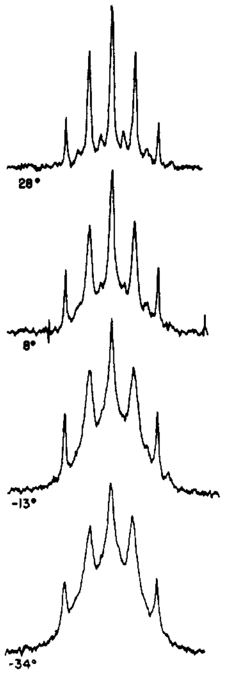

Figure 4. Temperature-dependent hydride region ^1H 90-MHz nmr spectra of $H_4W[PC_6H_5(OC_2H_5)_2]_4$ in toluene-d_8. The satellite lines arising from coupling of the hydride protons to ^{183}W (14.4% natural abundance, $I = ^1/_2$) can be clearly seen in the high-temperature limit spectra.

A quantitative determination of the exchange rates and mechanistic information cannot be obtained from the temperature dependence of the nmr line shapes in the absence of an analysis of the limiting slow-exchange spectra. Even if the latter were achieved, it is doubtful whether a complete density matrix line shape calculation[20] could be carried out even for a highly symmetric eight-spin system. There are 4! × 4! = 576 possible permutations which convert a labeled H_4ML_4 molecule into all possible labeled molecules with the same configuration (the product of all permutations of the hydrogens among themselves and all permutations of the ligands L among themselves). Decomposition of the group of all possible permutations of order 576 into

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(18) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *ibid.*, **92**, 1068 (1970).

(19) P. Meakin, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, L. J. Guggenberger, W. G. Peet, and E. L. Muetterties, *ibid.*, **92**, 3482 (1970).

(20) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971), and references therein.

double cosets with respect to the eight permutations which form a representation of the molecular symmetry group D_{2d} indicate that there are 20 permutational subclasses (or basic permutational sets)[20] including the identity set. Thus there are 20 different possible types of temperature dependence for the nmr line shapes including invariance to temperature change. Some of these 20 possibilities can be excluded as being solely responsible for the observed line shape effects because they do not average all of the H–P coupling constants and therefore do not lead to a calculated high-temperature limit hydride region ^1H nmr spectrum consisting of a binomial quintet. Even so we are left with a large number of basic permutational mechanisms which are *by themselves* consistent with the high-temperature limit spectra. Because of this large number of possibilities it is doubtful if a unique basic permutational mechanism could be picked out as being the only one consistent with the observed spectra. The situation is even further complicated by the fact that all linear combinations of the basic permutational mechanisms must also be considered[20] and at least several hundred such combinations would have to be tried. If the exchange process consists of two steps—(a) a fast averaging of the effective high-resolution nmr Hamiltonian to T_d symmetry on the nmr time scale even at low temperatures and (b) a slower process responsible for the observed nmr line shape effects near room temperature—the line shape analysis can be carried out as if the H_4ML_4 complexes had T_d symmetry. In this case there are only five basic permutational sets[7] (including the identity), and the chances of obtaining mechanistic information from the nmr line shapes would be much improved, provided the density matrix calculations could be carried out.[20] A crude estimate of the free energies of activation can be made by estimating the exchange rate from the appearance of the spectrum at some chosen temperature and calculating the free energy of activation, $\Delta G^{\ddagger}$, from the Eyring equation

$$R(T) = K(kT/h)e^{-\Delta G^{\ddagger}/RT} \tag{1}$$

where $R(T)$ is the exchange rate at temperature T and K is the transmission coefficient, assumed to have the value $K = 1$. Using this approach, the results shown in Table III were obtained. It should be noted that if the estimated rates are in error by a factor of 10, the resulting error in $\Delta G^{\ddagger}$ will be only about 1 kcal mol^{-1}. As has been observed previously for analogous HML_4[21,22] and H_2ML_4[19,23] complexes, the barriers are relatively insensitive to ligand variations; but there is a definite trend to higher barriers for higher atomic numbers of the central metal. The results obtained for the H_xML_4 (x = 1, 2, 4) are summarized in Table IV.

Table III. Estimated Free Energies of Activation for the Mutual Exchange Process in Some Eight-Coordinate Tetrahydrides

Complex	Temp, °C	Estimated rate, sec^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	Solvent
$H_4W[P(C_6H_5)_2C_2H_5]_4$	28	200	14.5	Toluene-d_8
$H_4W[PC_6H_5(OC_2H_5)_2]_4$	7	50	14.0	Toluene-d_8
$H_4W[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	60	100	16.5	Chlorobenzene
$H_4W[PC_6H_5(CH_3)_2]_4$	28	100	15.0	Toluene-d_8
$H_4W[P(C_6H_5)_2CH_3]_4$	28	200	14.5	Toluene-d_8
$H_4Mo[P(C_2H_5)_3]_4$	−4	200	13.0	Toluene-d_8
$H_4Mo[P(C_6H_5)_2C_2H_5]_4$	−15	200	12.5	Toluene-d_8
$H_4Mo[P(C_6H_5)_2CH_3]_4$	−15	200	12.5	CD_2Cl_2

Table IV. Barriers to Exchange[a] for Some H_xML_4 Systems

HML_4		H_2ML_4	H_4ML_4
$HFe(PF_3)_4^-$	$HCo(PF_3)_4$	H_2FeL_4	
<5	5.5	11.0–16.5	
$HRu(PF_3)_4^-$	$HRh(PF_3)_4$	H_2RuL_4	H_4MoL_4
7	9	16–>20	12–13.5
$HOs(PF_3)_4^-$	$HIr(PF_3)_4$	H_2OsL_4	H_4WL_4
8	10	>20	14–17

[a] $\Delta G^{\ddagger}$, kcal mol^{-1}.

$H_4Mo[PC_6H_5(OC_2H_5)_2]_4$ and $H_4Mo[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$. The hydride region ^1H nmr spectra of $H_4Mo[PC_6H_5(OC_2H_5)_2]_4$ and $H_4Mo[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ consist of binomial quintets at all temperatures attainable in CD_2Cl_2 and chlorobenzene as solvents, respectively. The ^{31}P nmr spectrum of $H_4Mo[PC_6H_5(OC_2H_5)_2]_4$ in CH_2Cl_2 is also a binomial quintet down to −50°. $H_4Mo[PC_6H_5(OC_2H_5)_2]_4$ was examined at lower temperatures in $CHClF_2$. At −75° the hydride region proton nmr spectrum is a sharp symmetric binomial quintet; below this temperature the spectra start to broaden (probably due to increasing viscosity of the solution) until at about −120° the quintet can no longer be resolved. There is no evidence in these spectra for a limiting low-temperature spectrum which is not a binomial quintet. Two plausible interpretations of these spectral data are the following: (a) the barrier to rearrangement is low and the mutual exchange process is fast on the nmr time scale at all attainable temperatures, thus averaging all the H–P coupling constants on the nmr time scale, (b) the barriers to exchange have a magnitude similar to those observed in the other molybdenum tetrahydrides but the low-temperature limiting spectra are accidentally binomial quintets (this may be due either to an accidental equality of all the H–P coupling constants or to large H–H and/or P–P coupling constants resulting in slow-exchange-limit quintets through a "virtual coupling" effect). Comparative data clearly identify the second interpretation as the more reasonable one. The two analogous tungsten complexes have barriers of about the same magnitudes as the other tungsten hydrides (Table III), and notably one of these, $H_4W[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$, has the highest barrier of the five tungsten hydrides. Distinctions between the low-temperature-limit spectra of the tungsten tetrahydrides and a binomial quintet are smaller for the two tungsten hydrides analogous to the molybdenum hydrides that have a binomial quintet spectrum than those for the other tungsten tetrahydrides. See especially the spectrum of $H_4W[PC_6H_5(OC_2H_5)_2]_4$ in Figure 4.

H_6ML_3 Complexes. In two cases (M = W, L = $P(CH_3)_2C_6H_5$, $P(C_6H_5)_2C_2H_5$) quartet hydride spectra

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(21) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1797 (1971).

(22) P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, **94**, 5271 (1972).

(23) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **95**, 75 (1973).

are observed which are assigned to H_6WL_3 species. One of these, $H_6W[P(CH_3)_2C_6H_5]_3$, has already been described in the literature[24] and the spectral data (τ 12.18, $J_{PH} = 35.7$) compare reasonably well with those reported (τ 11.94, $J_{PH} = 36.9$). The corresponding parameters for the second compound are τ 11.89 and $J_{PH} = 34$. No line shape effects are observed in these spectra even at very low temperatures. Rearrangement barriers in nine-coordinate complexes are expected to be low,[3] thus these data provide no stereochemical information. The expected stereoisomer, a trigonal prism of hydrogen atoms with phosphine ligands capping the square faces, would have environmental equivalence and magnetic inequivalence of the hydrogen set and of the phosphorus set.

Conclusion

Intramolecular rearrangements are much more facile in eight- than in six-coordinate complexes, at least for complexes in which all ligands are equivalent or nearly equivalent in steric and electronic character.[3] In the group of H_xML_4 molecules and ions all coordination classes examined to date are stereochemically nonrigid,[20,22,23] and there is no large difference[25] in rearrangement barriers between six- and eight-coordinate molecules. In fact, we have here the curious situation in which the eight-coordinate rearrangement barriers are surprisingly high and the six-coordinate barriers are surprisingly low. A rationale for the low barriers in H_2ML_4 molecules has been presented in the context of a tetrahedral jump mechanism in which barrier height is lowered as the MP_4 substructure approaches a regular tetrahedron.[20,22] A similar mechanism was assumed for the five-coordinate HML_4 molecules and ions; this class has the lowest rearrangement barriers of the group and has MP_4 substructures that more closely approach a regular tetrahedron than do those of the other classes.[23] The crystal structure of $H_4Mo[P(C_6H_5)_2CH_3]_4$ established a flattened MP_4 skeleton. It is reasonable that this specific structure is representative of the H_4ML_4 class. If the tetrahedral jump model is then assumed to be the dominant rearrangement path in H_4ML_4 molecules, a relatively high barrier becomes plausible because of the large motions required for the phosphorus ligands in the rearrangement process. This contribution to the barrier should be larger than in HML_4 and H_2ML_4 classes based on the available structural data. However, there is the implicit and perhaps unrealistic assumption in these comparisons that P–M–P bending force constants do not vary significantly. A further consideration in the tetrahedral jump model unique to the eight-coordinate class is that at least three hydride hydrogens must move in a concerted fashion. This latter factor, in addition to uncertainties in P–M–P bending force constants, makes it rather difficult to assess the rearrangement barriers in different classes of H_xML_4 complexes.

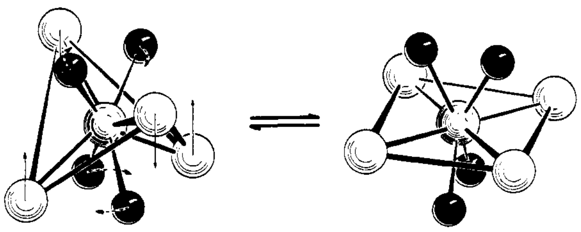

Figure 5. Possible alternative to tetrahedral jump mechanism for rearrangement in H_4ML_4 complexes.

The observation that the rearrangement barrier in H_4ML_4 molecules increases on substitution of bidentate for unidentate phosphine ligands is explicable in terms of a tetrahedral jump model. Bidentate ligands limit jump pathways and possibly require a concerted motion of all four hydrogen nuclei. We are seeking a more exacting test of the jump model through the synthesis of a tetrahydride which has a tetradentate phosphine ligand. Such a structure may well be rigid if the proposed jump process is the only relatively low energy pathway to intramolecular rearrangements.

The foregoing discussion leaves unanswered the question why the rearrangement barriers in H_4ML_4 molecules are so much higher than in ML_8 complexes with equivalent ligands (for H_2ML_4 relative to ML_6, the situation is reversed).[26] Many plausible physical rearrangement mechanisms may be considered for a dodecahedral eight-coordinate complex.[2,3,12] Some of these mechanisms such as a "breathing" motion would not remove the magnetic inequivalence of hydrogen atoms (and of phosphorus atoms) in the H_4ML_4 structure; a fast motion of this type only raises the effective molecular symmetry from D_{2d} to T_d. A fast traverse of D_{2d} dodecahedral and D_2 square-antiprismatic forms *via* the motion described by Hoard and Silverton[12] would have no effect on the nmr spectra. Achievement of magnetic equivalence in H_4ML_4 through stylized[27] mechanisms appears to require traverse of dodecahedral states in which some or all phosphorus atoms occupy sterically and electronically unfavorable A[12] sites (one exception is noted below).[28] Thus the high barriers in the H_4ML_4 class relative to ML_8 complexes are probably a reflection of these steric and electronic factors. Such factors can be substantive in rearrangement modes for coordination polyhedra that have inequivalent vertices, see especially the trigonal bipyramid in five coordination.[3]

There are 20 permutational mechanisms distinguishable in principle by the nmr line shape changes, but at this point in time permutational distinctions are not made for the reasons cited above. Physical mechanisms alternative to the tetrahedral jump have not been exhaustively explored, but one alternative, not previously considered in eight-coordination, is suggested by the X-ray crystal structure and is shown in Figure 5. This mechanism involves the inversion of the flattened P_4 tetrahedron and the simultaneous twisting of the elongated H_4 tetrahedron. In the tran-

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(24) J. R. Moss and B. L. Shaw, *Chem. Commun.*, 632 (1968).

(25) Precise comparisons cannot be made. Barriers for molybdenum and tungsten complexes fall in the same range as those found for the six-coordinate iron analogs.[20,22] However, we have consistently found that barriers increase in a given class as the atomic number of the central metal increases.[20,22,23] Only rough barrier estimates are available for ruthenium in six coordination. Using these estimates (16 to >20 kcal mol^{-1}) for a comparison with the barriers in eight-coordination molybdenum, it appears that rearrangement barriers are lower in H_4ML_4 than in H_2ML_4 complexes.

(26) Slow-exchange limit nmr spectra have not been observed for ML_8 complexes.[1-3]

(27) *I.e.*, based on traverse of polytopal forms, such as the dodecahedron, the square antiprism and the bicapped (square faces) trigonal prism.[1-3]

(28) These are multistep processes whereas the tetrahedral jump mechanism and the mechanism shown in Figure 5 are not.

sition state the four phosphorus atoms are coplanar with the central metal atom, and the H_4 tetrahedron was twisted through 45° with respect to the P_4 tetrahedron so that the former is staggered with respect to the latter. The transition state has S_4 symmetry. There was no indication in the solution nmr spectra of the departure from D_{2d} symmetry observed in the X-ray crystal structure. The deviation from D_{2d} symmetry is small, and even if the solution structure exhibited the same distortion the effective nmr Hamiltonian would probably have D_{2d} symmetry due to rapid intramolecular processes averaging the deviations to zero on the nmr time scale. In this physical process, the PP repulsions are maximized in the transition state, whereas they are minimized in the transition state for the tetrahedral jump mechanism.[29]

Acknowledgment. We wish to acknowledge the assistance of M. A. Cushing with the synthetic work, of L. F. Lardear with the X-ray work, and of G. Watunya and L. J. Rizzardi in obtaining some of the nmr spectra.

[29] The MP_4 skeleton in $H_4Mo[P(C_6H_5)_2CH_3]_4$ is about midway between a regular tetrahedron and a square plane. Hence the tetrahedral jump mechanism and this one physical alternative require phosphorus atom motions that are antipodal in character.

Nature of Phosphorus(V) Chloride in Ionizing and Nonionizing Solvents[1-3]

R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson, and S. G. Shore*

Contribution from the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

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Abstract: Laser Raman spectra in conjunction with freezing point depression measurements provide evidence for two competing equilibria in the ionizing solvents CH_3CN, CH_3NO_2, and $C_6H_5NO_2$, (1) $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$ and (2) $PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$, with (1) being predominant above about 0.03 *m* and (2) being predominant at lower concentrations. These observations resolve earlier conflicting reports on the ionization scheme in acetonitrile and nitrobenzene. The nature of phosphorus(V) chloride has also been studied in nonionizing solvents. When cryoscopic data are treated in the usual manner (neglect of possible solid solution formation) the apparent molecular weight in C_6H_6 supports the monomeric formulation PCl_5, while in CCl_4 the apparent molecular weight supports the dimeric formulation P_2Cl_{10}. This study has shown, however, that solid solution formation does occur in the carbon tetrachloride–phosphorus(V) chloride system and that it cannot be neglected. Application of the experimentally determined coefficient for the distribution of solute between solid and liquid phases (mole fraction of solute in solid phase:mole fraction of solute in liquid phase = 0.50 ± 0.02 at infinite dilution) to correct for solid solution formation gives an apparent molecular weight which is in excellent agreement with monomeric PCl_5.

Phosphorus(V) chloride is known to show a varied structural nature which depends upon the environment in which it is found. In the solid state[4-7] it is $[PCl_4^+][PCl_6^-]$ and molecular PCl_5 in the molten[8] and vapor[9-11] states. In polar solvents such as acetonitrile and nitrobenzene it is ionized while in nonpolar solvents such as benzene and carbon tetrachloride it is molecular in character.[9,12]

The nature of phosphorus(V) chloride in solution as a function of solvent has been a matter of contention in the literature. Conflicting reports have been given for its properties in both ionizing and nonionizing solvents.

In acetonitrile and in nitrobenzene, phosphorus(V) chloride is electrically conducting.[14] Although it seems certain that the tetrachlorophosphonium cation, PCl_4^+, exists in such solutions, the presence of the hexachlorophosphate anion, PCl_6^-, has been a source of dispute. Payne[14] has interpreted electrolysis experiments in nitrobenzene and acetonitrile to indicate that in these solvents PCl_5 is in equilibrium with PCl_4^+ and PCl_6^-. On the other hand, Fialkov and Buryanov[15] have interpreted the results of similar experiments in terms of an alternative scheme in which PCl_5 is in equilibrium with PCl_4^+ and Cl^-. Critical comments[16] on the proposals of Payne[14] and Fialkov and Buryanov[15] have claimed that phosphorus(V) chloride is in fact completely ionized as PCl_4^+ and PCl_6^- in acetonitrile and nitrobenzene. However, the presence of a "small" amount of molecular PCl_5 in solution was later acknowledged.[13]

An infrared study by Schmulbach and Ahmed[17] indicated the presence of PCl_5, PCl_4^+, and PCl_6^- in CH_3CN.

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