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Interconversion of Cis–Trans Isomers in $MX(CO)_2$(unsymmetric, bidentate phosphine)$_2$

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The compounds $MX(CO)_2(L\text{-}L')_2$ (M = Mo(II), Ta(I); X = halogen; L-L′ = the unsymmetric, bidentate phosphines 1-dimethylphosphino-2-diethylphosphinoethane (dmdepe), 1-dimethylphosphino-2-diisopropylphosphinoethane (dmdppe)) are shown to have a monocapped trigonal-prismatic structure and exist in two isomeric forms, cis and trans with respect to "labeled" ends of the bidentate phosphines, which occupy the capped quadrilateral face sites. The ligand methyl groups factor into two NMR differentiable sets, those directed toward the capping halide and those directed toward the unique edge. These sites exchange: $TaBr(CO)_2(dmpe)_2$ $\Delta G^\ddagger = 16.2 \pm 0.4$, $TaI(CO)_2(dmpe)_2$ $\Delta G^\ddagger = 16.7 \pm 0.5$, $[MoI(CO)_2(dmpe)_2]I$ $\Delta G^\ddagger = 12.6 \pm 0.6$, $TaI(CO)_2(dmdepe)$ $\Delta G^\ddagger = 17.1 \pm 0.4$, $[MoI(CO)_2(dmdepe)_2]I$ $\Delta G^\ddagger = 13.5 \pm 0.4$, $TaCl(CO)_2(dmdppe)_2$ $\Delta G^\ddagger = 19.4 \pm 0.4$, $TaI(CO)_2(dmdppe)_2$ $\Delta G^\ddagger = 20.0 \pm 0.4$ kcal/mol. Methyl resonances from cis and trans forms are resolved or partially resolved; exchange occurs with the same barriers as does that for cis–trans equilibration in the ^{31}P NMR spectra. An increasing $\Delta G^\ddagger$ with increasing steric hindrance suggests a nondissociative mechanism. $\Delta S^\ddagger$ for methyl group exchange in $[MoI(CO)_2(dmpe)_2]I$ is consistent with a polytopal rearrangement (2.8 ± 1.5 eu). However, the value for $TaI(CO)_2(dmpe)_2$ is substantially larger, 9.0 ± 1.1 eu. Least motion considerations suggest only two favorable mechanisms for site exchange in seven-coordinate species, if transit through idealized geometries is presumed. These mechanisms account for cis–trans exchange via a two-step process. The data, however, do not distinguish between this and mechanisms which do not pass through idealized forms.

Facile rearrangements are commonly encountered for seven-coordinate complexes.[1] Calculations based on ligand repulsion models[2] conclude that ground-state geometry is strongly dependent on the magnitude of the repulsive potential chosen and that for moderate to hard potentials the energy differences between the three idealized geometries (D_{5h} pentagonal bipyramid, C_{2v} monocapped trigonal prism, and C_{3v} monocapped octahedron) are minimal.[2d] Extended Hückel treatments support the latter conclusion and find little or no electronic barriers for interconversion between the limiting, idealized forms.[3]

DNMR, the primary tool for the study of seven-coordinate systems, has revealed no stereochemically rigid ML_7 complex.[1a,b] With inequivalent or chelating ligands, several examples of quenched exchange are known.[1e–h,j–n,p] However, except for $TaCl(dmpe)_2(\eta^4\text{-}C_{10}H_8)$ and related derivatives (dmpe = 1,2-bis(dimethylphosphino)ethane), the intimate details of these processes are poorly understood.

Prompted in part by an earlier report of an undefined process equilibrating ligand methyl groups in $[MoI(CO)_2(dmpe)_2]I$[4] and, in part, by our work on related systems,[1q,5,6] we set out to investigate dynamic processes in the C_{2v} monocapped trigonal-prismatic geometry using $MX(CO)_2$(bidentate phosphine)$_2$ (M = Mo(II), Ta(I); X = halogen) as a model. The ground-state geometry is firmly established for $TaX(CO)_2(dmpe)_2$[5] and $[MoI(CO)_2(dmpe)_2]I$[4] by spectroscopic methods, as well as by x-ray crystallography for the analogous $[MoCl(CO)_2(diars)_2]I_3$[7] (diars = *o*-phenylenebis(dimethylarsine)). Additionally, the system is easily modified to accomplish systematic variation of ligands and ^{31}P NMR allows observation of atoms directly bonded to the metal.

Experimental Section

Solvents were purified by distillation from sodium benzophenone ketyl except for methylene chloride and pentane which were distilled from phosphorus pentoxide. Tantalum pentachloride,[8] 1,2-bis(dimethylphosphino)ethane,[9] and $[MoI(CO)_2(dmpe)_2]I$[4] were prepared by literature methods. Sodium naphthalene was prepared by direct reaction and titrated immediately before use.[10]

Manipulations were performed in vacuo or under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ^1H and 40.5-MHz ^{31}P NMR, and mass spectra were obtained on Perkin-Elmer 457A and Varian XL-100 and AEI MS-9 spectrometers, respectively. ^{31}P NMR chemical shifts are relative to external 85% phosphoric acid. Elemental analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

1-Dimethylphosphino-2-diethylphosphinoethane (dmdepe). Et_2PH[11] (23.9 g, 0.266 mol) and 31.9 g (0.266 mol) of dimethylvinylphosphorus sulfide[12] were dissolved in 500 mL of THF and treated with 1 g of potassium *tert*-butoxide. After refluxing for 25 h, GLC analysis indicated complete consumption of the dimethylvinylphosphorus sulfide. The reaction mixture was evaporated to dryness, treated with 50 mL of water, and extracted with 5 × 100 mL of ether. Removal of volatile components in vacuo from the dried ($MgSO_4$) ethereal extract gave a low-melting solid, which was dissolved in 250 mL of dioxane, treated with 8 g of $LiAlH_4$, and refluxed for 24 h.

At the end of that period, sufficient water was added to quench the excess $LiAlH_4$, and the resulting suspension was extracted with 5 × 150 mL of ether. The ethereal extract was dried ($CaCl_2$) and fractionally distilled. The product distilled at 65 °C (0.5 mm) as a colorless liquid (11 g, 23%): mass spectrum *m/e* 178 $(^{12}C_8{}^1H_{20}{}^{31}P_2)^+$, 163 $(P - Me)^+$, 149 $(P - Et)^+$.

Anal. Calcd for $C_8H_{20}P_2$: C, 53.92; H, 11.31. Found: C, 53.36; H, 11.15.

1-Dimethylphosphino-2-diisopropylphosphinoethane (dmdppe). Dimethylvinylphosphorus sulfide[11] (30.0 g, 0.25 mol), 35.0 g of $i\text{-}Pr_2PH$[13] (0.30 mol), and 2 g of NaH were combined with 250 mL of THF in a 1-L autoclave. After heating for 24 h at 150 °C GLC analysis indicated nearly complete consumption of dimethylvinylphosphorus sulfide. The solvent was removed in vacuo, and the residue was treated with 250 mL of water and then extracted with 4 × 200 mL of ether. The pooled ethereal extracts were dried ($CaCl_2$) and freed of volatile components by vacuum distillation. The resulting dark, low-melting solid was refluxed in 200 mL of dioxane with 10 g of $LiAlH_4$ (0.26 mol). After 36 h, the reaction mixture was treated with ethanol until hydrogen evolution ceased (ca. 25 mL). Ether (200 mL) was added to the resulting suspension and the mixture filtered. The solid residue was washed with additional ether (3 × 200 mL), and the combined filtrates were fractionally distilled. The product was collected at 50 °C (0.1 mm) as a colorless liquid (13 g, 25%): mass spectrum *m/e* 206 $(^{12}C_{10}{}^1H_{24}{}^{31}P_2)^+$, 191 $(P - Me)^+$, 163 $(P - i\text{-}Pr)^+$. Analytical data were unsatisfactory; characterization rests on the mass spectral and NMR data (Table I) and the complexes below.

$TaI(CO)_2(dmpe)_2$ (1). A solution of 219 mg (0.38 mmol) of $TaCl(CO)_2(dmpe)_2$[5] (**2**) in 25 mL of THF was reduced at 0 °C with 0.76 mmol of sodium naphthalene and then treated with 97 mg (0.38 mmol) of iodine in 20 mL of THF. Removal of solvent and naphthalene in vacuo (70 °C, 5 μ) and crystallization of the residue by slow evaporation of a filtered benzene–heptane extract afforded yellow crystals in essentially quantitative yield: IR (THF solution) ν_{CO} 1838 (vs), 1769 (s) cm^{-1}; mass spectrum *m/e* 664 $(^{12}C_{14}{}^1H_{32}{}^{127}I^{16}O_2{}^{31}P_4{}^{181}Ta)^+$, 638 $(P - CO)^+$, 608 $(P - 2CO)^+$.

Anal. Calcd for $C_{14}H_{32}IO_2P_4Ta$: C, 25.32; H, 4.86. Found: C, 25.38; H, 4.51.

$TaCl(CO)_2(dmdepe)_2$ (3). To a solution of 4.00 g of freshly sublimed $TaCl_5$ (11.0 mmol) and 3.95 g (22.8 mmol) of dmdepe in

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Table I. NMR Data for Mo(II) and Ta(I) Complexes

Compd	$^{31}P\{^1H\}$ NMR, ppm	$^1H\{^{31}P\}$ NMR, τ
dmdepe	-24.7 (d), -53.8 (d) ($J_{AB} = 20.6$ Hz) 30 °C[e]	PCH_3: 9.05 (s) PCH_2CH_3: 9.03 (t, $J = 7.0$ Hz) PCH_2CH_3: 8.96 (br m) PCH_2CH_2P: 8.64 (br m) 30 °C[a]
dmdppe	1.0 (d), -54.8 (d) ($J_{AB} = 25.2$ Hz) 30 °C[e]	PCH_3: 9.29 (s) $PCHCH_3$: 9.23 (d, $J = 7.2$ Hz), 9.25 (d, $J = 7.2$ Hz) $PCHCH_3$: 8.57 (septet, $J = 7.2$ Hz) PCH_2CH_2P: 8.85 (br s) 30 °C[a]
$TaI(CO)_2(dmpe)_2$[b]	14.0 (s) 30 °C[b]	PCH_3: 8.41 (s), 8.62 (s) 20 °C[b,c]
$TaCl(CO)_2(dmdepe)_2$	Trans: $\delta_A = 45.8$, $\delta_B = 21.4$[i] Cis: $\delta_A = 44.7$, $\delta_B = 21.8$[i] -30 °C[b]	PCH_3: trans 8.24 (s), 8.38 (s); cis 8.27 (s), 8.36 (s) PCH_2CH_3 trans 8.70 (t, $J = 7.4$ Hz); cis 8.67 (t, $J = 7.4$ Hz) 30 °C[b,c]
$TaI(CO)_2(dmdepe)_2$	Trans: $\delta_A = 38.0$, $\delta_B = 10.0$[i] Cis: $\delta_A = 37.2$, $\delta_B = 11.7$[i] -40 °C[b]	PCH_3: trans 8.32 (s), 8.53 (s); cis 8.40 (s), 8.56 (s) PCH_2CH_3:[d] 9.04 (q, $J = 6$ Hz) 30 °C[c,e]
$TaCl(CO)_2(dmdppe)_2$	Trans: $\delta_A = 60.9$, $\delta_B = 12.0$[i] Cis: $\delta_A = 59.7$, $\delta_B = 14.3$[i] 30 °C[b]	PCH_3:[d] 8.46 (s), 8.50 (s) $PCHCH_3$:[d,f] 8.64 (d, $J = 7$ Hz), 8.82 (d, $J = 7$ Hz), 8.96 (d, $J = 7$ Hz), 9.02 (d, $J = 7$ Hz) 30 °C[c,e]
$TaI(CO)_2(dmdppe)_2$	Trans: $\delta_A = 38.6$, $\delta_B = 10.4$[i] Cis: $\delta_A = 37.8$, $\delta_B = 11.9$[i] -50 °C[b]	PCH_3:[d] 8.26 (s), 8.47 (s) $PCHCH_3$:[d,f] 8.63 (d, $J = 7$ Hz), 8.85 (d, $J = 7$ Hz), 9.05 (d, $J = 7$ Hz), 9.07 (d, $J = 7$ Hz) 30 °C[c,e]
$[MoI(CO)_2(dmdepe)_2]I$	Trans: $\delta_A = 46.9$, $\delta_B = 24.7$[i] Cis: $\delta_A = 55.7$, $\delta_B = 20.2$[i] -50 °C[g]	PCH_3: trans 8.00 (s), 8.17 (s); cis 8.04 (s), 8.22 (s) PCH_2CH_3:[d] 8.84 (t, $J = 7$ Hz) -50 °C[c,h]

[a] In $CHCl_3$. [b] In toluene. [c] Methylene resonances broad and unresolved. [d] Resonances from cis and trans forms unresolved. [e] In benzene. [f] In addition to inequivalence arising from orientation of groups with respect to the capping halide, the isopropyl methyl groups are diastereotopic. [g] In acetone. [h] In methanol. [i] AA′BB′ patterns, see text.

125 mL of 90:10 benzene/THF was added 3 equiv of sodium naphthalene. A further 1.5 equiv of sodium naphthalene was added over a period of 30 min under a stream of CO. The brown solid obtained by removal of solvent and sublimation of naphthalene in vacuo was chromatographed on a short silica gel column (THF eluent) to give an orange solution. Evaporation of solvent yielded a yellow-orange solid which was recrystallized from benzene–heptane (1.20 g, 18%): IR (THF solution) ν_{CO} 1829 (vs), 1760 (s) cm^{-1}; mass spectrum *m/e* 628 $(^{12}C_{18}{}^1H_{40}{}^{35}Cl^{16}O_2{}^{31}P_4{}^{181}Ta)^+$, 600 $(P - CO)^+$, 572 $(P - 2CO)^+$.

Anal. Calcd for $C_{18}H_{40}ClO_2P_4Ta$: C, 34.37; H, 6.41. Found: C, 35.30; H, 6.50.

$TaCl(CO)_2(dmdppe)_2$ (4). The reduction of 4.00 g of freshly sublimed $TaCl_5$ (11.0 mmol) and 4.53 g of dmdppe (22 mmol) with sodium naphthalene, as in the preparation of **3**, gave **4** after recrystallization from benzene–heptane: IR (THF solution) ν_{CO} 1825 (vs), 1757 (s) cm^{-1}; mass spectrum *m/e* 684 $(^{12}C_{22}{}^1H_{48}{}^{35}Cl^{16}O_2{}^{31}P_4{}^{181}Ta)^+$, 656 $(P - CO)^+$, 628 $(P - 2CO)^+$.

Anal. Calcd for $C_{22}H_{48}ClO_2P_4Ta$: C, 38.57; H, 7.06. Found: C, 39.05; H, 7.40.

$TaI(CO)_2(dmdepe)_2$ (5). **3** (441 mg, 0.702 mmol) and 178 mg (0.701 mmol) of I_2 were reacted as in the preparation of **1** to yield, after crystallization from benzene–heptane, yellow-orange crystals of **5**: IR (THF solution) ν_{CO} 1834 (vs), 1767 (s) cm^{-1}; mass spectrum *m/e* 720 $(^{12}C_{18}{}^1H_{40}{}^{127}I^{16}O_2{}^{31}P_4{}^{181}Ta)^+$, 692 $(P - CO)^+$, 664 $(P - 2CO)^+$.

Anal. Calcd for $C_{18}H_{40}IO_2P_4Ta$: C, 30.01; H, 5.60. Found: C, 30.13; H, 5.96.

$TaI(CO)_2(dmdppe)_2$ (6). **4** (583 mg, 0.852 mmol) and 216 mg of I_2 (0.852 mmol) were reacted as in the preparation of **1** to yield, after crystallization from benzene–heptane, orange crystals of **6**: IR (THF solution) ν_{CO} 1834 (vs), 1763 (s) cm^{-1}; mass spectrum *m/e* 776 $(^{12}C_{22}{}^1H_{48}{}^{127}I^{16}O_2{}^{31}P_4{}^{181}Ta)^+$, 748 $(P - CO)^+$, 720 $(P - 2CO)^+$.

Anal. Calcd for $C_{22}H_{48}IO_2P_4Ta$: C, 34.03; H, 6.23. Found: C, 33.88; H, 6.33.

$[MoH(CO)_2(dmdepe)_2][SO_3F]$ (7). A 50-mL Hoke bomb containing 3.96 g of $Mo(CO)_6$ (15.0 mmol) and 6.23 g (35.0 mmol) of dmdepe was heated for 40 h at 200 °C with occasional venting of evolved CO. Extraction of the contents of the vessel with 4 × 25 mL of THF gave a dark, viscous oil after removal of volatile components in vacuo (1 μ) at 80 °C. The material was dissolved in 25 mL of ether, filtered, and treated with 0.87 g (8.7 mmol) of HSO_3F while stirring vigorously. The resulting off-white precipitate was collected by filtration, washed with 4 × 6 mL of ether, and dried in vacuo (4.58 g, 50%): IR (THF solution) ν_{CO} 1863 (vs) cm^{-1}.

Anal. Calcd for $C_{18}H_{41}FMoO_5P_4S$: C, 35.53; H, 6.79. Found: C, 35.31; H, 6.35.

$[MoI(CO)_2(dmdepe)_2]I$ (8). **7** (942 mg) was dissolved in 8 mL of THF and treated with 2.5 mL of a 1.00 M solution of potassium in *tert*-butyl alcohol. The yellow solution was stirred for 30 min, the solvent removed in vacuo, and the residue extracted with ether. The ethereal extract was evaporated to dryness and the resulting solid was refluxed in hexane for 24 h. Filtration of the cloudy solution and evaporation of the solvent gave a yellow oil, which was dissolved in 30 mL of CH_2Cl_2 and treated with 330 mg of I_2 (1.30 mmol) in 25 mL of CH_2Cl_2 at −50 °C. Evaporation of the solvent after warming to 25 °C afforded a yellow solid, which was recrystallized from acetone–heptane to yield off-white crystals of **8**: IR (CH_2Cl_2 solution) ν_{CO} 1952 (vs), 1888 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{40}I_2MoO_2P_4$: C, 28.37; H, 5.29. Found: C, 28.28; H, 5.53.

Results

^{31}P NMR. Under the C_{2v} constraint established for $MX(CO)_2(dmpe)_2$ (M = Mo(II), Ta(I); X = halogen),[4,5,7] all phosphorus atoms are chemically equivalent (Figure 1) and no information concerning dynamic processes is contained in their ^{31}P NMR spectra (Table I). However, use of the unsymmetric phosphines dmdepe (1-dimethylphosphino-2-diethylphosphinoethane) and dmdppe (1-dimethylphosphino-2-diisopropylphosphinoethane) lowers the effective symmetry. These unsymmetric ligands were prepared by King's base-catalyzed P–H addition procedures.[12,14] In principle, two isomers are expected from either dmdepe or dmdppe complexes, cis (C_s) and trans (C_2), as shown in Figure 1. For either isomer, an AA′BB′ spectrum is anticipated.

The ^{31}P NMR spectrum of $TaCl(CO)_2(dmdepe)_2$ (**3**), a representative example, at −90 °C exhibits two partially overlapping AA′BB′ spectra in the ratio of 1.8:1.0 (Figure 2).

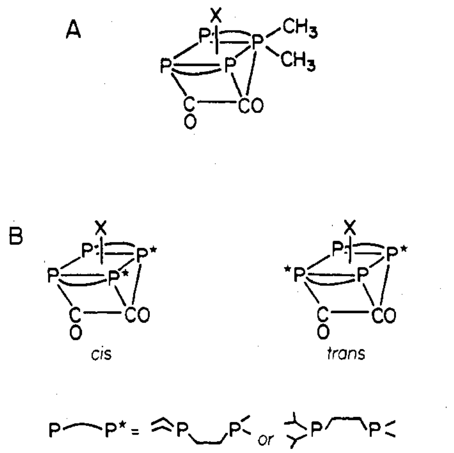


Figure 1. (A) Stereochemistry of $MX(CO)_2$(bidentate phosphine)$_2$ ($X \neq H$). (B) Possible isomers for $MX(CO)_2$(unsymmetric, bidentate phosphine)$_2$.

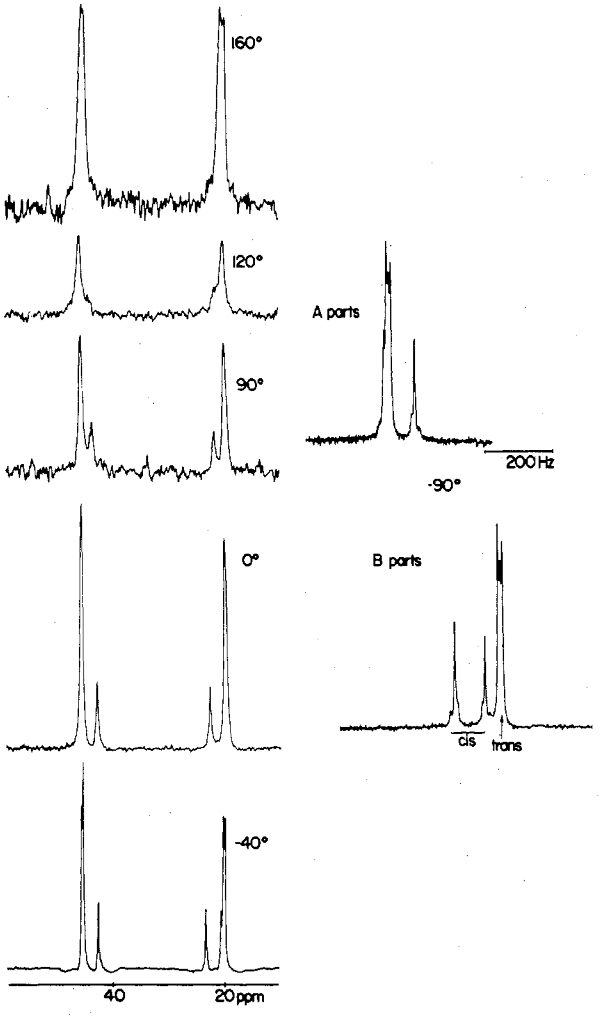


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $TaCl(CO)_2(dmdepe)_2$ in toluene-d_8/decalin.

Although the resolution does not permit solution of the spectra, tentative assignments can be made on steric grounds. The more crowded cis isomer is presumed to be the less abundant species (trans/cis = 1.8/1.0). On warming to ambient temperatures, a small linear dependence of chemical shifts on temperature[15] affords a deceptively simple spectrum in which the low- and high-field portions of the A and B parts of *cis*-**3** are obscured by the A and B parts of *trans*-**3**, respectively.

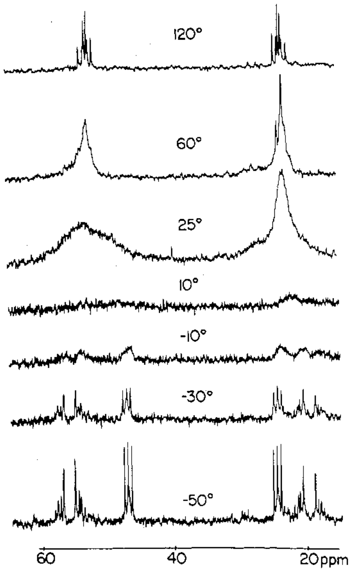
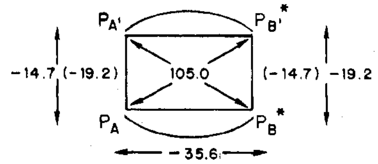


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[MoI(CO)_2(dmdepe)_2]I$. The low-temperature spectra were measured in acetone; Me_2SO was used for those at high temperatures.

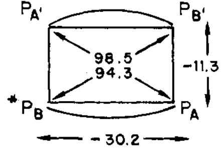
Nonetheless, two discrete isomers are observable. Coalescence of the resonances for cis and trans forms occurs at ca. 120 °C; T_c is not measurably dependent on concentration. The high-temperature limit could not be reached because of decomposition (appearance of free ligand, which does not exchange with *cis*- or *trans*-**3**), which is rapid at temperatures greater than 160 °C. Spectra of $TaCl(CO)_2(dmdppe)_2$ (**4**) were qualitatively similar. Although the onset of coalescence could be observed, T_c could not be reached below the decomposition point. Similar behavior was noted for **6**, although the isomer ratio was substantially more perturbed (trans/cis = 2.1/1.0).

The ^{31}P NMR spectra of $[MoI(CO)_2(dmdepe)_2]I$ (**8**) show two well-separated AA'BB' patterns (Figure 3), indicating the presence of cis and trans isomers. In contrast to the Ta(I) analogues, the isomer ratio is essentially unity (trans/cis = 1.1/1.0). Further, coalescence of the A parts and B parts of *cis*- and *trans*-**8** occurs at substantially lower temperatures, despite larger chemical shift separations ($T_c \simeq 10$ °C). Moreover, the high-temperature limiting spectrum is a single well-resolved AA'BB' pattern.

Solution of the low-temperature spectra[16,17] gives the values $|J_{AB}(cis) + J_{AB'}(cis)| = 69.4$, $|J_{AB}(cis) - J_{AB'}(cis)| = 140.6$, $|J_{AA'}(cis) + J_{BB'}(cis)| = 33.9$, $|J_{AA'}(cis) - J_{BB'}(cis)| = 4.5$, $|J_{AB}(trans) + J_{AB'}(trans)| = 41.5$, $|J_{AB}(trans) - J_{AB'}(trans)| = 18.9$, $|J_{AA'}(trans) + J_{BB'}(trans)| = 192.8$ and $|J_{AA'}(trans) - J_{BB'}(trans)| = 4.2$ Hz. Investigations of J_{PP} for $Mo(CO)_4(PR_3)_2$ and related derivatives[18] have established that trans P–P couplings are generally larger than cis couplings.[18c-f,19] Further, in those cases examined, J_{PP} for a trans arrangement was found to be positive and opposite in sign to that for cis couplings.[18e-g,19] The assignment of coupling constants most consistent with these trends is as shown:



cis-**8**



trans-**8**

Averaging *cis*- and *trans*-**8** leads to the values[20] (vide infra) $J_{AB} = \chi_{cis}J_{AB}(cis) + \chi_{trans}J_{AB}(trans) = -32.8$, $J_{AB'} = \chi_{cis}J_{AB'}(cis) + \chi_{trans}J_{AB'}(trans) = 44.5$, $J_{AA'} = \chi_{cis}J_{AA'}(cis) +$

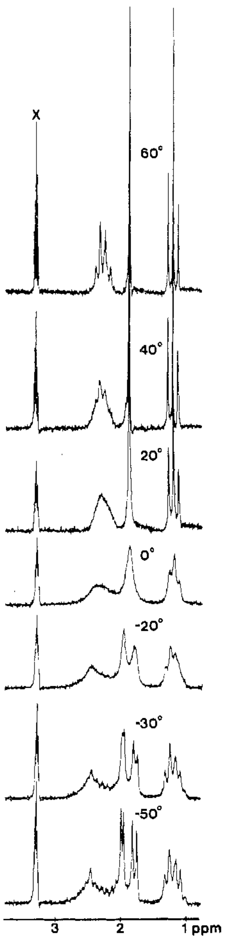


Figure 4. Variable-temperature $^{1}H\{^{31}P\}$ NMR spectra of $[MoI(CO)_2(dmdepe)_2]I$ in methanol-d_4.

$\chi_{trans}J_{AA'}(trans) = 42.0$, $J_{BB'} = \chi_{cis}J_{BB'}(cis) + \chi_{trans}J_{BB'}(trans) = 42.0$ Hz, in reasonable agreement with the values obtained from the limiting high-temperature spectrum:[17] $J_{AB} = \pm32.4$, $J_{AB'} = \mp47.0$, $J_{AA'} = \pm38.7$, $J_{BB'} = \pm38.7$ Hz.

With no assumptions regarding the assignment of coupling constants for *cis*- and *trans*-**8**, averaging of cis and trans isomers results in eight distinguishable sets of coupling constants for the high-temperature limit. Of the eight possibilities only the set quoted is in reasonable agreement with the experimental values. The unique fit supports the illustrated assignments in that it determines that the sign of the couplings for phosphorus atoms cis to one another is opposite that for phosphorus atoms trans to one another in both isomers. Moreover, the only interchange of the magnitudes of the J values allowed is one in which one isomer has a large trans coupling and a small cis coupling while the other isomer has the reverse ordering, an unlikely possibility.

We note that the similar coupling constants provide indirect evidence that the observed spectra result from cis and trans isomers and are not derived from isomers with different idealized geometries.

Spectral behavior was not measurably dependent on solvent (acetone, Me_2SO, methanol).

^{1}H NMR. As first noted by Connor et al.,[4] the dmpe methyl groups of $[MoI(CO)_2(dmpe)_2]I$ form two NMR differentiable sets, those directed toward the halogen and those directed away. Rapid exchange occurs above −30 °C. The same observations are valid for the isostructural Ta systems, $TaBr(CO)_2(dmpe)_2$ (**9**) and **1**. Further, **7**, **4**, and **6** all exhibit chemically inequivalent methyl groups which average to a single resonance in their $^{1}H\{^{31}P\}$ NMR spectra. For the unsymmetric Ta complexes, **4**, **5**, and **6**, spectra of the cis and trans isomers were only partially resolved. However, the low-temperature $^{1}H\{^{31}P\}$ NMR spectrum of **8** (Figure 4) indicates two pairs of equally intense resonances, consistent with equally populated cis and trans forms. On warming to −20 °C, the spectrum collapses to a single pair of resonances. Further heating averages this pair to a single methyl resonance. $\Delta G^{\ddagger}$ calculated for isomer interconversion (13.3 kcal/mol) is equal to that calculated for methyl group exchange (13.5 kcal/mol). The coalescence temperatures were unaffected by the presence of excess lithium iodide (50 equiv of LiI/Mo).

Table II. Barriers for Methyl Group Exchange in $MX(CO)_2[(CH_3)_2PC_2H_4PR_2]_2$

M	X	Parameter[g]	R		
			CH_3	C_2H_5	$CH(CH_3)_2$
Ta(I)	Cl	$\Delta G^{\ddagger}$			$19.4^{a,b,e}$
		T_c			358
	Br	$\Delta G^{\ddagger}$	$16.2^{a,e}$		
		T_c	293		
	I	$\Delta G^{\ddagger}$	$16.7 \pm 0.5^{d,e}$	$17.1^{a,b,e}$	$20.0^{a,b,e}$
		$\Delta H^{\ddagger}$	19.6 ± 0.3		
		$\Delta S^{\ddagger}$	9.0 ± 1.1		
		T_c	320	332	388
Mo(II)	I	$\Delta G^{\ddagger}$	$12.6 \pm 0.6^{d,f}$	$13.5^{a,c,f}$	
		$\Delta H^{\ddagger}$	13.3 ± 0.4		
		$\Delta S^{\ddagger}$	2.8 ± 1.5		
		T_c	253	273	

[a] Evaluated by the Gutowsky-Holm equation.[26] $\Delta G^{\ddagger}$ is quoted at the coalescence temperature. The values are reproducible to within ±0.4 kcal/mol. [b] Resonances from cis and trans forms were unresolved. [c] $\Delta G^{\ddagger}{}_{253\,K}$ for equilibration of the methyl resonances from cis and trans isomers = 13.3 kcal/mol. [d] Activation parameters determined from an Eyring plot of rate constants deduced by line shape analysis (DMNR-3) using an uncoupled two site model. Error limits are the standard errors derived from the least-squares fit. [e] Spectra accumulated in methanol-d_4. [f] Spectra accumulated in acetone-d_6. [g] Units: $\Delta G^{\ddagger}$, kcal/mol; T_c, K; $\Delta H^{\ddagger}$, kcal/mol; $\Delta S^{\ddagger}$, eu.

The barriers for methyl group exchange are tabulated in Table II. Inspection of the table reveals three trends. For a homologous series, $\Delta G^{\ddagger}$ increases with increasing halide size, although the increase is of minimal statistical significance. Second, $\Delta G^{\ddagger}$ is strongly dependent on phosphine bulk. In fact, for the series $TaI(CO)_2(bidentate\ phosphine)_2$ (i.e., **1**, **5**, and **6**), $\Delta G^{\ddagger}$ linearly depends on the cone angle[21] of the more hindered end of the unsymmetric ligand (cone angles: dmpe 107°,[22] dmdepe 116°,[23] dmdppe 135°[23]).[24] We note that the same trend is manifested in the isomer distributions. Additionally, the barriers to methyl group exchange are lower and the isomer distributions are nearer unity for the Mo(II) complexes than for the Ta(I) analogues.

Discussion

The ^{31}P NMR results above establish that cis–trans isomer exchange does occur (i.e., exchange of the capped quadrilateral face sites) within the monocapped trigonal-prismatic geometry. Additionally, the same process is responsible for the ligand methyl group exchange observed in the ^{1}H NMR spectra, since the barrier for methyl group exchange is identical, within experimental error, with that for equilibration of methyl resonances from cis and trans forms of **8** and since an estimate of $\Delta G^{\ddagger}$ for the cis–trans exchange observed in the ^{31}P NMR of **8** is the same as that for methyl group exchange.[25]

As minimal differences in electronic effects are anticipated for the groups $-PMe_2$, $-PEt_2$, and $-P(i\text{-}Pr)_2$,[27] the observed steric trends, an increase in ligand size effects an increase in barrier, strongly suggest exchange is a result of a polytopal rearrangement and is not due to an "arm-off, arm-on" or bond-rupture mechanism. $\Delta G^{\ddagger}$ for intramolecular pseudorotation in $MR(diene)(PR_3)_2$ (R = CH_3, H; M = Ir(I), Rh(I))

Table III. The C_{2v}–D_{5h} Paths

Path	D_{5h} ligands[a] Axial	Equatorial	Discoincidence index	Symmetry preserved	Edges in C_{2v} structure lost
I	24	13765	0.242	C_2	
II	17	23456	0.375	C_s	25
III	27	13654	0.529		15, 34
IV	17	26345	0.571		23, 56
V	27	14365	0.584		13, 45

[a] The labels refer to the sites illustrated in Figure 5.

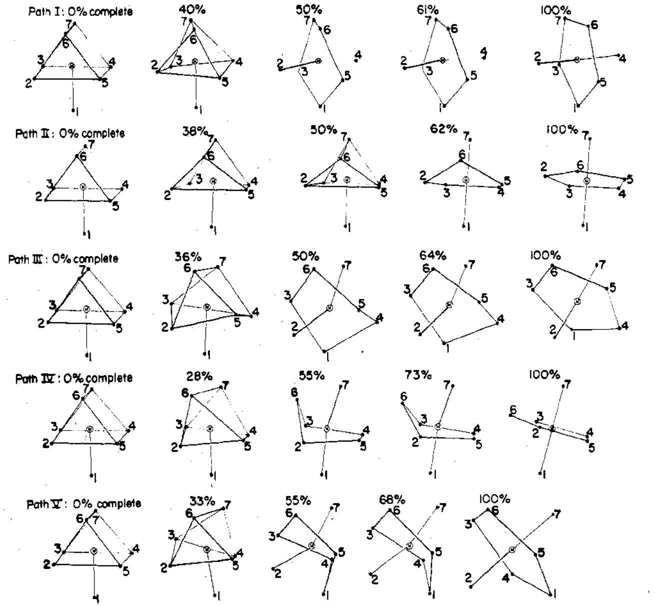


Figure 5. The C_{2v} to D_{5h} coordinate for paths I–V.

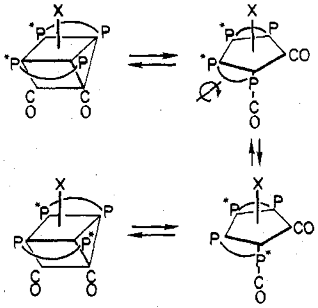


Figure 6. Possible mechanism for interconversion of cis–trans isomers. Conversion to pentagonal bipyramid follows path II. Exchange of chelate ends within the pentagonal-bipyramidal structure is repeated application of path I.[42]

is increased by an increase in the cone angle of PR_3.[28] For $Rh[P(OR)_3]_5^+$ increasing the bulk of R increases $\Delta G^\ddagger$ of *intramolecular* ligand exchange[29] but does not affect $\Delta G^\ddagger$ of *intermolecular* exchange.[30]

The lack of measurable dependence of $\Delta G^\ddagger$ on solvent supports a nondissociative mechanism, although not conclusively.[31]

Considering the substitutional inertness of the Ta(I) complexes[5] and the charge of the Mo(II) species, dissociation of halide is unlikely as a rate determining or other step in the exchange process.

Studies of site exchange in octahedral tris(bidentate chelate) complexes have established that $\Delta S^\ddagger$ generally lies in the range −8.0 to +5.0 eu for polytopal rearrangements and +7.0–15.0 eu for bond-rupture mechanisms.[31,32] Substantially more negative values have been reported for nondissociative paths,[32e,f] including some values from gas-phase measurements.[33] $\Delta S^\ddagger$ for pseudorotation in five-coordinate complexes tends to be near zero.[29,34] By these criteria the magnitude of $\Delta S^\ddagger$ for exchange in $[MoI(CO)_2(dmpe)_2]I$ is consistent with a nondissociative mechanism.[35] $\Delta S^\ddagger$ for the Ta(I) analogue, **1**, is somewhat large. Given the low accuracy of activation parameters determined by line-shape analysis and the problems inherent in assigning mechanism solely on the basis of $\Delta S^\ddagger$,[32f,g] the magnitude of the entropy of activation for **1** appears to be such that distinction between bond-rupture and polytopal mechanisms cannot be made on these grounds alone. We favor a nondissociative process on the basis of the steric effects discussed above, but note that $\Delta S^\ddagger$ for **1** is suggestive of an "arm-on, arm-off" mechanism.

A large number of nondissociative mechanisms are capable of accounting for the observed sequential exchange of chelate ends, i.e., an effective ligand twist. In order to determine plausible paths, we have considered motion requirements for the D_{5h} to C_{2v} traverse.

The five least-motion paths for the C_{2v}–D_{5h} transformation are shown in Table III in order of increasing motion. Two ligands in the C_{2v} structure must be chosen as axial ligands for the D_{5h} structure. It is obvious from considerations of least motion that these two ligands should not be adjacent. We thus have three unique choices: 17, 24, and 27 (see Table III).

For the 17 selection, considerations of motion and adjacency suggest only two unique equatorial arrangements, 23456 and 26345. For the 24 choice, only one arrangement seems plausible, 13765. These ligands are already adjacent in the requisite order. For the 27 axial choice, examination of a model shows only the 13654 and 14365 equatorial choices to be appealing. However, we did examine ten other unique paths with 2 and 7 as axial ligands.

Using unit ML bond lengths and bond angles as given by Thompson and Bartell for the potential r_{ij}^{-6},[2d] we have computed the discoincidence index[36] (the rms difference in matched Cartesian coordinates) for the various C_{2v}–D_{5h} rearrangements (Table III).

The least-motion advantage of path I is likely to persist with most reasonable geometries since, of all C_{2v}–D_{5h} paths, only path I leaves all edges of a C_{2v} structure intact in the course of the transformation. Path II, the next least-motion path, loses only one C_{2v} edge in the transformation, while paths III–V each lose two such edges.

Figure 5 shows transits of the five paths listed in Table III, using Halgren and Lipscomb's method of synchronous transits[36] to generate the intermediate points. We note that a C_2 axis is preserved in the course of path I and a mirror plane is conserved in the course of path II. Path I bears a striking resemblence to the Berry mechanism.[37] In both mechanisms the equatorial ligands become axial ligands in the course of the transformation. Moreover, path I has been experimentally established for $TaCl(dmpe)_2(\eta\text{-}C_{10}H_8)$.[1q] Path II, which passes near the C_{3v} monocapped octahedron, appears to be supported by solid-state evidence[38] and has been detected in $MoH(CO)_2$(bidentate phosphine)$_2^+$.[39] Both path I and path II are diamond–square–diamond rearrangements[40] and are equivalent to those suggested elsewhere.[3,38a,41] Exchange of arsenic methyl groups in $MoBr_2(CO)[P(OCH_3)_2C_6H_5]_2[cis\text{-}(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2]$, which is thought to have a monocapped octahedral structure derived from the carbonyl ligand capping a BrP_2 face of a *trans*-dibromo octahedron, may occur by path II.[1p]

The simplest nondissociative mechanism consistent with the NMR data for the compounds described in this work is a ligand twist. However, in contrast to a ligand twist in the D_{5h} pentagonal bipyramid, this system requires a transition state which is unrelated to any of the commonly found geometries.[42] Inasmuch as $TaX(dmpe)_2L_2$ (X ≠ H) chooses only a pentagonal-bipyramidal arrangement or a monocapped trigonal-prismatic structure, depending on the nature of L,[1q,5,43] it would appear that the most favorable path for isomer exchange would involve passage through a pentagonal bipyramid. If the results for $MX(CO)_2$(bidentate phosphine)$_2$ are to be explained by transit through idealized geometries, they are best accounted for by a two-step process shown in Figure 6. The same process rationalizes the methyl group exchange found for *rac*-$MoI_2(CO)_3[o\text{-}(As(CH_3)(C_6H_5))_2C_6H_4]$.[1n]

Our data establish only that sequential exchange of chelate ends does occur for **1**–**8** and that exchange likely occurs by a nondissociative path. We point out that paths I and II, generated by the least-motion calculations, provide models which rationalize these findings and account for exchange in other systems.

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Registry No. **1**, 65015-81-8; **2**, 61916-36-7; *cis*-**3**, 65084-87-9; *trans*-**3**, 65015-80-7; *cis*-**4**, 65015-79-4; *trans*-**4**, 65058-50-6; *cis*-**5**, 65058-49-3; *trans*-**5**, 65015-78-3; *cis*-**6**, 65058-48-2; *trans*-**6**, 65015-77-2; **7**, 65015-76-1; *cis*-**8**, 65058-47-1; *trans*-**8**, 65015-74-9; **9**, 61966-89-0; $[MoI(CO)_2(dmpe)_2]I$, 52587-01-6; dmdepe, 23936-60-9; dmdppe, 64999-60-6; Et_2PH, 627-49-6; *i*-Pr_2PH, 20491-53-6; I_2, 7553-56-2; $TaCl_5$, 7721-01-9; $Mo(CO)_6$, 13939-06-5; dimethylvinylphosphorus sulfide, 42495-78-3.

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