

six-coordinate cobalt(II) complexes. It is possible that one or more of the phosphines should be replaced with zeolitic oxygens.

The disproportionation of $\text{Co}_4(\text{CO})_{12}$ appears to take place for the cluster both inside and on the surface of the zeolite as judged by its reactions with phosphines. The disproportionation of adsorbed $\text{Co}_4(\text{CO})_{12}$ with phosphines represents a departure from the expected chemistry of this cluster. It is apparent that the adsorbed species is somehow activated for disproportionation.

Location and Structure of $\text{Co}_4(\text{CO})_{12}$ (ads). In addition to the unique chemistry for adsorbed $\text{Co}_4(\text{CO})_{12}$ the infrared spectrum for the adsorbed species on Na-Y zeolite is unusual. This has been noted by Watters et al.,²³ and their conclusion was that the cluster must reside within the supercage of the zeolite. Briefly the assignment is that the bridging carbonyl is shifted to lower wavenumber by interaction with a Lewis acid site on the zeolite. There is then a corresponding shift to higher wavenumber for the terminal carbonyls. This, in fact, is well established for carbonyl clusters adsorbed on alumina surfaces.¹⁷ It was argued that this type of interaction for $\text{Co}_4(\text{CO})_{12}$ could best be achieved in the supercage. We have shown here that the identical spectrum can be achieved for $\text{Co}_4(\text{CO})_{12}$ adsorbed directly on the surface of NaY zeolite (vide supra). Thus the infrared spectrum alone is not sufficient to locate the cobalt carbonyl cluster.

The observation of identical spectra for $\text{Co}_4(\text{CO})_{12}$ adsorbed on the surface and on the interior of Na-Y zeolite is unexpected. For $\text{Rh}_6(\text{CO})_{16}$ adsorbed on the surface of a zeolite a different infrared spectrum is observed compared to that for $\text{Rh}_6(\text{CO})_{16}$ that is postulated to occur within the zeolite.^{4,33} In the case of $\text{Co}_4(\text{CO})_{12}$ similar sites for adsorption must exist on the surface and in the interior of Na-Y zeolite. It was postulated that a site of 3-fold symmetry could be found in the supercage.²³ This allows the C_{3v} structure of $\text{Co}_4(\text{CO})_{12}$ to retain its symmetry upon adsorption. Certainly sites of 3-fold symmetry will also exist on the surface of the zeolite particle. This is easily seen from models of the faujasite structure; the α -cage may be terminated in such

a fashion to give 6 β -cages in a chair conformation that has 3-fold symmetry.

It should be noted that Watters et al.²³ observe that when $\text{Co}_4(\text{CO})_{12}$ is added to Na-Y zeolite by sublimation overnight, a spectrum consistent with crystalline $\text{Co}_4(\text{CO})_{12}$ is obtained. The cluster in this case lies on the surface of the zeolite.

The argument above does not address the fact that the spectrum for $\text{Co}_4(\text{CO})_{12}$ adsorbed on Na-Y is significantly simpler than that observed in solution. As indication of this is given in Table I. In solution, three intense absorptions are seen for $\text{Co}_4(\text{CO})_{12}$ at 2062 s, 2054 s and 1868 cm^{-1} . The adsorbed species gives only one intense band at $\sim 2080 \text{ cm}^{-1}$ and a weak band at 2056 cm^{-1} . An intriguing possibility is that the adsorbed cluster adopts a structure different from the C_{3v} structure observed in solution. One possibility is the D_{2d} structure with four bridging carbonyls first suggested by Cotton.³⁴ Raman studies are underway in an attempt to further elucidate the structure for the adsorbed cluster.

Furthermore it is clear that Na-X and Na-Y zeolite stabilize different cobalt carbonyl species. On the Na-X zeolite the dimer, $\text{Co}_2(\text{CO})_8$, is observed to give substantially more disproportionation to $\text{Co}(\text{CO})_4^-$. Also the cluster $\text{Co}_4(\text{CO})_{12}$ when adsorbed on the surface of Na-X gives a spectrum that is identical with the solution spectrum. Then there must be different sites for $\text{Co}_4(\text{CO})_{12}$ adsorption on Na-X and Na-Y zeolite, or the structure for the adsorbed cluster is different on the two supports.

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Registry No. $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{Co}_4(\text{CO})_{12}$, 17786-31-1; $\text{Co}(\text{C}-\text{O})_4^-$, 14971-27-8; $[\text{Co}(\text{CO})_3(\text{PEt}_3)_2][\text{Co}(\text{CO})_4]$, 54438-20-9; PEt_3 , 554-70-1; $\text{P}(t\text{-Bu})_3$, 13716-12-6.

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Chemistry and Stereochemistry of Reactions of Organophosphorus Ligands in Chiral $\text{Mo}(\text{CO})_5\text{L}$ Complexes¹

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$[\text{Me}(\text{EtO})(\text{HO})\text{P}]\text{Mo}(\text{CO})_5$ (**3**), a coordination complex with a chiral organophosphorus ligand, was synthesized and resolved. The OH group on the ligand of the (-) complex was esterified to give (+)- $[\text{Me}(\text{EtO})(i\text{-Pr}_2\text{NCH}_2\text{CH}_2\text{O})\text{P}]\text{Mo}(\text{CO})_5$ (**7**), which was then converted into its *N*-methiodide derivative, (+)-**8**, with retention of configuration at the phosphorus atom in each step. Compound (+)-**8**, when treated with sodium methoxide in methanol, gave a nearly equal mixture of (-)- $[\text{Me}(\text{EtO})(\text{MeO})\text{P}]\text{Mo}(\text{CO})_5$ (**9**) and the original (-)-**3**. Since (+)-**9** was obtained directly with retention of configuration from the reaction of (-)-**3** and diazomethane, the formation of (-)-**9** by the reaction of methoxide ion with (+)-**8** must occur with inversion of the phosphorus configuration. This reaction is highly if not completely stereospecific, but some racemization of the (-)-**9** product does occur under the experimental conditions. The unexpected formation of the (-)-**3** byproduct is due to a competing elimination reaction, which apparently occurs via the formation of a nitrogen ylide intermediate under the basic reaction conditions.

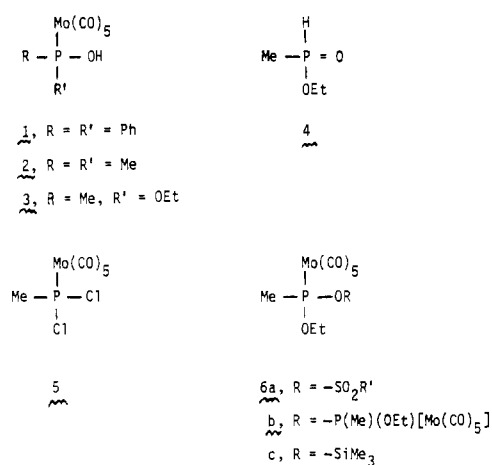
While an extensive literature exists on metal coordination compounds that contain one or more phosphorus ligands,² the chemistry and especially the stereochemistry of reactions of these species from the standpoint of the complexed ligand has received rather limited attention.³ Kraihanzel and his students recently

studied phosphorus ligand chemistry using species mainly of the general formula $\text{Mo}(\text{CO})_5\text{L}$ and $\text{Mo}(\text{CO})_4\text{L}_2$.⁴ Here,⁵ the syn-

- (1) Presented in part at the 189th National Meeting of the American Chemical Society, Miami, FL, April 1985, and the 19th Middle-Atlantic Regional Meeting, West Long Branch, NJ, May 1985.
- (2) (a) Verkade, J. G.; Coskran, K. J. *Organic Phosphorus Compounds*; Kosolopoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 2, p 1. (b) Booth, G. *Ibid.*; Vol 1, p 443. (c) Stelza, O. *Top. Phosphorus Chem.* 1977, 9, 1.

- (3) Optically active organometallic species in which the metal is the center of chirality are well-known, and the stereochemistry of their reactions has been reviewed, e.g.: (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967; p 302. (b) Brunner, H. *Top. Curr. Chem.* 1975, 56, 67. (c) Brunner, H. *Adv. Organomet. Chem.* 1980, 18, 151. In addition, numerous catalytic studies of organometallic species containing a chiral organophosphorus ligand have also been reported, e.g.: (d) Capler, V.; Comisso, G.; Sunjic, V. *Synthesis* 1981, 85. (e) Brunner, H. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 249. (f) Bogdanovic, B. *Ibid.* 1973, 12, 954. (g) Knowles, W. S. *Acc. Chem. Res.* 1983, 16, 106.

Chart I. Structures of 1-6



thesis of **1** and **2** (Chart I) and the isolation of a crystalline triethylamine salt of **1** were of particular interest to us, since it was apparent that an extension of this chemistry to an unsymmetrically substituted ligand would produce a chiral species (e.g. **3**), which should be resolvable by classical methods. Thus, this route might serve as a prototype to resolved organometallic catalysts of new and varied structures. Alternately, new types of resolved trivalent organophosphorus compounds would be obtained, if the ligand could be chemically modified and then decomplexed without racemization. This elegant technique was recently described for some resolved copper(I)⁶ and platinum(II)⁷ complexes (the latter without any chemical modification) of phosphorus(III) ester ligands.

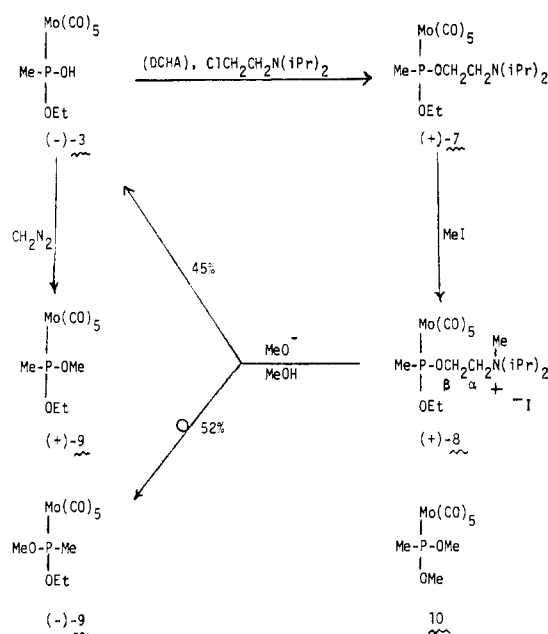
Results

The chiral $[\text{Me}(\text{EtO})(\text{HO})\text{P}]\text{Mo}(\text{CO})_5$ complex (**3**) selected for this study was synthesized from ethyl methylphosphinate (**4**) and molybdenum hexacarbonyl, by the procedure reported for **1** and **2**. However, due to the low yields obtained, an alternate synthesis was desired. Initially, a molybdenum pentacarbonyl pyridine complex⁸ was prepared and used in place of $\text{Mo}(\text{CO})_6$ in the reaction with **4**, but no improvement in yield was obtained. $[\text{Me}(\text{Cl})_2\text{P}]\text{Mo}(\text{CO})_5$ (**5**) was then synthesized, and the stepwise displacement of its chlorine substituents was explored. Here, an NMR study of the ethanolysis of **5** indicated that $[\text{Me}(\text{EtO})(\text{Cl})\text{P}]\text{Mo}(\text{CO})_5$, the initial product, apparently reacted with ethanol even faster than did **5** and hence could not be obtained in this way for subsequent hydrolysis to **3**. Further experimentation revealed that solvolysis of **5** in a 95/5 mol % ethanol/water solution produced an optimum yield of the desired **3**, which was readily separated from accompanying $[\text{Me}(\text{HO})_2\text{P}]\text{Mo}(\text{CO})_5$ and $[\text{Me}(\text{EtO})_2\text{P}]\text{Mo}(\text{CO})_5$ side products by preparation and recrystallization of its dicyclohexylamine (DCHA) salt.

The **3** acid was resolved as its (-)-ephedrine salt, obtained on treatment of **3** with either 1 or (better) $1/2$ equiv of the alkaloid. The (-)-**3** enantiomer gave a head crop salt, whose optical purity was determined by ³¹P NMR spectral examination. A product of 88% enantiomeric excess (ee) has been obtained after one recrystallization of the ephedrine salt from cyclohexane. Since further improvement in the optical purity of this salt resulted in a marked reduction in the yield, the stereochemical studies described below were performed with less than 100% ee material.

Optically active **3** presents a most useful reagent for the synthesis of chiral isomers of new complexes. In addition, it offers an entree into the study of the stereochemistry of ligand reactions,

Scheme I



if the OH group can be converted into a labile substituent replaceable by other species. For this purpose, therefore, the conversion of (\pm)-**3** into any of several sulfonate esters (**6a**) was tried. Unfortunately, only a pyro product (**6b**) could be isolated from these attempts, apparently due to further reaction of the desired ester immediately as it was formed. Also, a trimethylsilyl derivative (**6c**) was examined for possible utility, but is proved unexpectedly resistant to hydrolysis.

The stereochemical study that was successfully completed is summarized in Scheme I, which was developed with the use of racemic reagents. For the optically active material, the relative configuration and sign of rotation of each product is given in the scheme. Thus, (-)-**3** (69% ee) was converted directly into (+)- $[\text{Me}(\text{EtO})(\text{MeO})\text{P}]\text{Mo}(\text{CO})_5$ (**9**) by reaction with diazomethane. Then (-)-**3**, via its DCHA salt, $[\alpha]_D^{25} -5.75^\circ$ (75% ee), was converted as shown into (+)- $[\text{Me}(\text{EtO})(i\text{-Pr}_2\text{NCH}_2\text{CH}_2\text{O})\text{P}]\text{Mo}(\text{CO})_5$ (**7**), $[\alpha]_D^{25} +2.35^\circ$, which was quaternized to give the corresponding methiodide, (+)-**8**, $[\alpha]_D^{25} +1.67^\circ$ after crystallization. The final, key reaction shown in Scheme I, i.e., the methanolysis of (+)-**8**, produced nearly equal amounts of two major products: (-)-**9**, $[\alpha]_D^{25} -2.49^\circ$ (84% ee), and (-)-**3**, DCHA salt $[\alpha]_D^{25} -6.64^\circ$ (87% ee). In addition, a small amount (3%) of $[\text{Me}(\text{MeO})_2\text{P}]\text{Mo}(\text{CO})_5$ (**10**) was also formed in this reaction.

Discussion

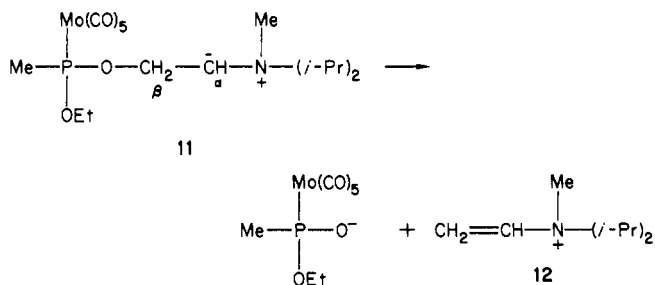
As summarized in Scheme I, the stepwise conversion of (-)-**3** to (+)-**7** to (+)-**8** occurs with overall retention of configuration at phosphorus, since no bond attached to the phosphorus atom is broken in this sequence. For the same reason, the conversion of (-)-**3** to (+)-**9** via diazomethane also occurs with retention of configuration. Therefore, the key step in this Walden cycle, the formation of (-)-**9** by the reaction of (+)-**8** with methoxide ion, must occur with inversion of configuration, presumably by a straightforward $\text{S}_{\text{N}}2$ displacement. This result is believed to be the first solvolytic displacement of a substituent on a complexed, optically active, chiral phosphorus ligand, although replacement of a ligand substituent by organometallic reagents (RMgX and RLi) on an analogous copper complex has been reported.⁶ The stereochemistry of these reactions, however, is still under investigation. In the closest known stereochemical report related to our study, an achiral phosphorus ligand was used, and the stereochemistry of the reaction (inversion) was assigned from an NMR analysis of the system.⁹ Our results are in agreement with this conclusion.

(4) Grayson, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1982**, *238*, 209. See also preceding papers in this series.
 (5) Kraihanzel, C. S.; Bartish, C. M. *J. Am. Chem. Soc.* **1972**, *94*, 3572.
 (6) (a) Chodkiewicz, W. *J. Organomet. Chem.* **1984**, *273*, C55. (b) Chodkiewicz, W.; Guillerme, D. *Tetrahedron Lett.* **1979**, 3573.
 (7) (a) Wroblewski, A. E.; Socol, S. M.; Okruszek, A.; Verkade, J. G. *Inorg. Chem.* **1980**, *19*, 3713. (b) Abicht, H.-P.; Spencer, J. T.; Verkade, J. G. *Ibid.* **1985**, *24*, 2132.
 (8) Dennenburg, R. J.; Darenbourg, D. J. *Inorg. Chem.* **1972**, *11*, 72.

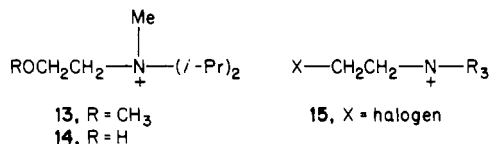
(9) Kraihanzel, C. S.; Bartish, C. M. *Phosphorus* **1974**, *4*, 271.

While not of primary relevance to the original goal of this investigation, the formation of **3** as a major solvolysis product of **8** was an interesting, unexpected result. Thus, when **3** was first obtained from the methanolysis of racemic **8**, we assumed that it had formed from a displacement reaction by hydroxide ion, which would be present if moisture had not been fully excluded, in spite of the anhydrous conditions that were used. This assumption was discounted, however, when the same product mixture was obtained from a second solvolysis, in which a much smaller volume of a more concentrated NaOMe/MeOH solution was used, with scrupulous attention given to the exclusion of moisture. The assumption was finally rejected on the basis of the (+)-**8** solvolysis results. Thus, if reaction of a hydroxide ion impurity with (+)-**8** had occurred, a (+)-**3** product undoubtedly should have been obtained by inversion of configuration, consistent with that observed from the reaction of methoxide ion to give (-)-**9**. We conclude, therefore, that both **3** and **9** are true products of the reaction of **8** with methoxide: **9** from the expected attack at phosphorus and **3** by an alternate mechanism.

We have considered two possible mechanisms that could account for the formation of (-)-**3** from (+)-**8** in this system: (1) attack by methoxide ion at the β-CH₂ carbon atom to directly displace the (-)-**3** anion or (2) attack by methoxide ion at the α-CH₂ hydrogen atom to form a nitrogen ylide (**11**), which could then generate the (-)-**3** anion by an elimination reaction:



By mechanism 1, a (β-methoxyethyl)ammonium ion (**13**) would be produced, while mechanism 2 would give the vinyl analogue **12**. To evaluate these possibilities, the water-soluble residue of the methanolysis reaction product was examined by ¹H NMR. Here, two quaternary ammonium species were observed, consistent with the assignment of a mixture of **12** and the (β-hydroxyethyl)ammonium ion **14**; no signal corresponding to the presence of any of **13** was detected. Compound **14**, which is the expected byproduct of the conversion of **8** to **9**, was separated from the mixture and identified by comparison with an authentic sample.



To preclude the possibility that **13** may have been formed, but immediately decomposed (e.g., by ylide formation and elimination to give **12**), authentic **13** was synthesized and subjected to the methanolysis reaction conditions. It was found to be completely stable and hence should have been observed in the reaction product had it been formed. From these results, we conclude that (-)-**3** is most likely formed via an elimination of the ylide intermediate (**11**), as indicated above. This mechanism corresponds to a reaction pathway for nitrogen ylides that was not considered in the list of possibilities that are given in an earlier review.¹⁰ However, that this mechanism is apparently generally applicable to nitrogen ylides that contain a potential leaving group as a β-substituent is shown by the fact that reaction of (β-haloethyl)trialkylammonium species (**15**) with alcoholic KOH is a preparative route to trialkylvinylammonium ions corresponding to **12**.¹¹

The fact that the (-)-**3** product (Scheme 1) was of greater optical purity (86% ee) than the starting material (75% ee) suggests that the (+)-**8**, as isolated, probably crystallized in >90% ee, since a loss in optical purity of (-)-**3** is generally obtained when the latter is isolated as its DCHA salt. Also, a control run has shown that the (-)-**9** product would have slightly racemized under the conditions of the experiment and hence would have been originally greater than the 84% ee calculated for the isolated product. Thus, the displacement reaction that yields (-)-**9** appears to be highly if not completely stereospecific.

The observed formation of a small amount of **10** from the methanolysis of (+)-**8** can be accounted for from two possible routes. The first requires the attack of a methoxide ion on the phosphorus atom of **8** with displacement of an ethoxide ion, to give [Me(MeO)(i-Pr₂MeN⁺CH₂CH₂O)P]Mo(CO)₅. Subsequent attack of methoxide on the phosphorus atom of this ester with displacement of the i-Pr₂MeN⁺CH₂CH₂O⁻ group would then give rise to **10**. The second route requires a simple displacement of an ethoxide ion from **9** by a methoxide ion. On the basis of a control run in which (-)-**9** (containing 2.0% **10**) was heated with an excess of sodium ethoxide for 1 h to give an absolute increase of only 0.6 mol % in **10** and ~12% racemization, it would appear that both of the above routes may be involved but that the former apparently predominates.

It should be noted that only the relative stereochemical relationships of these compounds are given in Scheme 1 and that the absolute configurations cannot be assigned at this time. Further studies of this and related systems are being pursued.

Experimental Section

General Data. Reactions of trivalent phosphorus compounds were all carried out under a dry nitrogen or argon atmosphere. The Mo(CO)₅L products were routinely handled in the atmosphere but were stored under a nitrogen atmosphere, protected from light. ³¹P NMR spectra were recorded on a Varian FT 80A or XL 200 spectrometer. A positive chemical shift value (δ) is taken downfield from 85% phosphoric acid as an external reference. ¹H NMR spectra were recorded on a Varian EM360A or EM 390 spectrometer. The NMR spectral analyses are reported as mol %, unless otherwise stated. IR spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. Optical rotations were recorded on a Perkin-Elmer 141 autopolarimeter. Organic solutions were all dried with anhydrous MgSO₄, unless otherwise stated, and routinely concentrated under reduced pressure.

(Methylphosphonous dichloride)pentacarbonylmolybdenum¹² (5). Molybdenum hexacarbonyl (57.8 g, 0.219 mol) and 20 mL of methylphosphonous dichloride (25.6 g, 0.219 mol)¹³ in 100 mL of dry toluene were heated with stirring for 5 h at 97 °C. After the mixture was allowed to stand overnight, 200 mL of petroleum ether (bp 30–60 °C) was added to precipitate the unreacted molybdenum hexacarbonyl. The mixture was filtered and concentrated, leaving 64 g of a dark red opaque oil, which was distilled to give 44 g (57%) of **5**, bp 67–73 °C (0.15–0.25 mm). The product crystallized on standing in the refrigerator to a waxy solid, which was recrystallized from cold (-20 °C) hexane to give crops of 15.9 g, mp 30–31 °C, and 16.8 g, mp 29–30 °C. The first crop was examined by NMR: ³¹P, δ 180.1 (benzene); ¹H, δ 2.70 (benzene or CCl₄).

(Ethyl hydrogen methylphosphonite)pentacarbonylmolybdenum (3). **Method 1.** A mixture of ethyl methylphosphinate¹⁴ (21.0 g, 0.19 mol) (**4**) and molybdenum hexacarbonyl (52.0 g, 0.19 mol) in 500 mL of dry methylcyclohexane was stirred and heated at 95 °C for 25 h. After the reaction was cooled to 25 °C, ³¹P NMR analysis of the clear supernatant reaction mixture showed a 25% conversion to **3** (δ 171). On the basis of earlier small scale runs, continued heating only resulted in a decrease in the percentage of this product. The precipitated solids were filtered through charcoal and Celite, and the filtrate was concentrated to yield 35 g of a dark oil. Adding 4.9 g (0.027 mol) of dicyclohexylamine (DCHA) to a solution of this oil in 80 mL of cyclohexane, allowing the mixture to stand overnight, and then concentrating and cooling the filtrate gave 3-DCHA: yield 14.5 g, mp 153–155 °C. After recrystalli-

(10) Musher, W. K. *Fortschr. Chem. Forsch.* **1970**, Vol. 14, p 296.

(11) Lucius, R. *Arch. Pharm. (Weinheim, Ger.)* **1907**, 245, 246; *Chem. Abstr.* **1908**, 2, 1553.

(12) This compound has been previously reported: Bartish, C. M.; Krahanzel, C. S. *Inorg. Chem.* **1973**, 12, 391. However, neither the details of the synthesis nor its physical properties were described.

(13) Methylphosphonous dichloride was available in our laboratory from in-house stores earlier manufactured by the U.S. Army. The compound is now commercially available from Strem Chemical Co., under the name methyl dichlorophosphine.

(14) Petrov, K. A.; Bilznyuk, N. K.; Studnev, Yu. N.; Kolomiets, A. F. *Zh. Obshch. Khim.* **1961**, 31, 179.

zation from 120 mL of toluene, 12 g (0.023 mol, 12%) of 3-DCHA was obtained; mp 154–156 °C. IR (KBr): 2975 (sh, CH₃); 2940 (s) and 2855 (CH₂); 1445 (s, CH₂); 2050, 1950 (s), 1900 (w, CO) 1265 (s, P–Me); 1005 cm⁻¹ (s, P–OR). ³¹P NMR (13% in CH₃OD): δ 146.5. Anal. Calcd for C₂₀H₃₀MoNO₇P: C, 45.72; H, 6.14. Found: C, 45.75; H, 6.04.

Method 2. A 95/5 mol % ethanol/water solution (160 mL) was deaerated with dry nitrogen and then added dropwise with swirling and cooling to a solution of **5** (44.5 g, 0.126 mol) in 80 mL of methylene chloride. Most of the solvent was then removed, and the residual solution was adjusted to pH 1 with aqueous base. The resulting mixture (two layers) was extracted with six 100-mL portions of cyclohexane. The latter were dried and then treated with 25 g (0.14 mol) of DCHA in 25 mL of cyclohexane. A crop of 38.4 g, mp 154–155 °C, of 3-DCHA was obtained after a few hours at room temperature. An additional 2.29 g, mp 151–153 °C, was obtained after concentrating and cooling the filtrate (total crude yield, 61.5%). The ³¹P NMR spectrum of the first crop in methanol/chloroform revealed a mixture of 93.7% 3-DCHA [δ 153.4 (*J*_{P–Mo} = 165 Hz)] and 6.3% [Me(OH)₂P]Mo(CO)₅-DCHA (δ 144.4). Recrystallization of an 11.0-g portion of this mixture from 150 mL of toluene gave 9.1 g of 3-DCHA, mp 155–156 °C, 99% pure from its ³¹P NMR spectrum.

Alternately, **5** has been solvolyzed without added methylene chloride with essentially identical results. Here, a solution of 6.5 g of **5** in 21 mL of 95/5 mol % EtOH/H₂O, observed (³¹P NMR) to be a mixture of 75% **3** [δ 169.1 (*J*_{P–Mo} = 175 Hz)], 19% [Me(OEt)₂P]Mo(CO)₅ [δ 182.9 (*J*_{P–Mo} = 179 Hz)], and 6% [Me(OH)₂P]Mo(CO)₅ (δ 156.4), was worked up as above to give 6.1 g (63%) of crude 3-DCHA salt, mp 154–155 °C, after recrystallization from toluene (83% recovery).

The 3-DCHA salt (2.55 g, 0.0484 mol) in 30 mL of methanol was cooled in an ice bath and then acidified to pH 1 with 1 N HCl. The methanol was removed, and the residue was shaken with 100 mL and then 50 mL of chloroform. These extracts were combined, dried, and concentrated. The residue was dissolved in 100 mL of ether, filtered to remove residual DCHA·HCl, and then redried and concentrated to give 1.38 g (0.040 mol, 83%) of **3** as a clear oil, which crystallized when stored at -40 °C; mp 40–41.5 °C. ³¹P NMR (C₆D₆): δ 178.3 (*J*_{P–Mo} = 176 Hz). ¹H NMR (C₆D₆): δ 0.97 (t, *J* = 7.0 Hz, CH₃CH₂), 1.22 (d, *J*_{P–H} = 3.9 Hz, CH₃P), ~3.25 (broad, s, OH), 3.50 (m, CH₂O). IR (thin film from melt): 3560, 3350 (br); 2990 (w), 2930 (vw), 2900 (vw), 2250 (w), 2070 (s), 1900 (vs); 1475, 1440, 1410, 1385 (w); 1290 (s), 1150 (w), 1090 (vw), 1025 (s), 940 (s), 875 (s), 820, 750, 725 (w); 705 (sh). A small sample sublimed at 35–40 °C (0.5–1.0 μm) had a melting point of 42.5–43 °C. Anal. Calcd for C₈H₉MoO₇P: C, 27.93; H, 2.64; neutralization equiv, 343. Found: C, 27.93; H, 2.68; neutralization equiv, 344.

Resolution of 3. The 3-DCHA salt (6.60 g, 12.6 mmol) was dissolved in 60 mL of methanol/water (4/1), acidified with 0.5 N HCl to pH 2, and then extracted with three 25-mL portions of chloroform. The extracts were dried and then concentrated to a dark blue oil. The latter, in 20 mL of cyclohexane, was warmed to dissolve 2.0 g (12.1 mmol) of added (-)-ephedrine hemihydrate [C₈H₉CH(OH)CH(CH₃)NHCH₃·0.5H₂O] (Fluka Chemical Corp). On standing at room temperature, the solution deposited 4.30 g (8.45 mmol, 67%) of ephedrine salt, mp 125–135 °C. A ³¹P NMR analysis of a chloroform solution of such a crop obtained from an earlier experiment had shown a diastereoisomeric mixture of salts in a 69/31 ratio (δ 157.3/δ 158.3). A 0.5-g sample of this head crop was successively recrystallized four times from cyclohexane (~25 mL each time); a little insoluble residue was filtered and discarded with each recrystallization. (Note: The compound is best if not unduly heated when exposed to air.) A final crop of 187 mg of (-)-eph(-)-**3** [(-)-eph = (-)-ephedrine] was thus obtained: 90% ee by ³¹P NMR; mp 136–137 °C; [α]_D²⁵ -23.25°, [α]_D⁵⁷⁸ -24.20° (c 1.68, methanol). A ³¹P NMR spectrum (CDCl₃, plus 2 drops of methanol) showed a 95/5 (δ 155.5/δ 156.2) diastereoisomer ratio, and no other phosphorus signal was observed. From this result, the specific rotation of 100% ee product is calculated to be [α]_D²⁵ -24.2°, if the specific rotation of (-)-eph-(±)-**3** is taken as -15.3°, calculated from the experimental value of [α]_D²⁵ -44.7° for (-)-eph-¹/₂H₂O (c 2.3) in methanol, containing 1 equiv of 0.1 N aqueous hydrochloric acid.

Alternately, the resolution of (±)-**3** was carried out by using only 0.5 equiv of (-)-ephedrine. Here, 12.8 g (0.0243 mol) of 3-DCHA (from method 2, above) was converted to **3** as described above, dissolved in 100 mL of cyclohexane, and treated with 2.12 g (0.122 mol) of (-)-eph-¹/₂H₂O with slight warming and stirring to give 5.13 g of a (-)-ephedrine salt: mp 132.5–133.5°; [α]_D²⁵ -22.0° (c 1.92, methanol); 92% pure, with a 90/10 isomer ratio (80% ee) by ³¹P NMR (δ 159.3/δ 160.3, respectively). The impurity (δ 145.5) is the (-)-ephedrine salt of [Me(OH)₂P]Mo(CO)₅, derived from the acid impurity that had not been completely removed from the 3-DCHA sample used in this resolution.

(-)-(Ethyl hydrogen methylphosphonite)pentacarbonylmolybdenum [(-)-3]. A 300-mg (0.59-mmol) sample of (-)-eph(-)-**3** (mp 137–138 °C, [α]_D²⁵ -23.7° (c 0.64, methanol), 93.2% ee by ³¹P NMR with no other phosphorus signals observed) was dissolved in 3 mL of methanol plus a few drops of water, treated with 1 N HCl to pH 1.5, and extracted with three 7-mL portions of chloroform.

The extracts were dried and concentrated to give (-)-**3**, yield 161 mg (80%) of a blue oil, too dark to allow its rotation to be recorded (see below). This oil was taken up in 3 mL of cyclohexane, and 85 mg (0.47 mmol) of DCHA was added. A crop of (-)-3-DCHA was obtained: yield 131 mg; mp 139–142 °C; [α]_D²⁵ -6.85° (c 1.93, methanol). Additional crops of 56 mg [mp 134–136 °C; [α]_D²⁵ -7.47° (c 1.41, methanol)] and 17 mg [[α]_D²⁵ -7.40° (c 0.770, methanol)] were collected after each filtrate was partially evaporated on standing. Since the higher melting racemic salt is apparently more insoluble in this system, the optical purity of the isolated product tends to improve after the first crop has been collected. The 204-mg total of (-)-3-DCHA collected corresponds to an 83% yield (247 mg, theory) from the blue oil [(-)-**3**], or 66% overall.

A weighted average of these three crops gives a value of [α]_D²⁵ -7.1° for their combined total, which corresponds to [α]_D²⁵ -7.6° for optically pure (-)-3-DCHA, if no fractionation of the 93.2% ee content of the original occurred during this procedure. In view of the greater solubility of the (-)-salt, however, it is possible that some fractionation in favor of the racemic salt may have occurred in the isolation. If so, the specific rotation of the optically pure product could be slightly more negative (perhaps by 0.1–0.2°) than -7.6°. However, [α]_D²⁵ -7.6 ± 0.1° for the 100% ee product is assigned on the basis of the results in hand.

An attempt to isolate and purify (-)-**3** was carried out, but with disappointing results. Thus, a molecular distillation of (-)-**3** obtained from its (-)-ephedrine salt (89% ee) resulted in a poor recovery of an oil, [α]_D²⁵ -2.24° (c 1.12, methanol), which could not be induced to crystallize.

(+)-[2-(Diisopropylamino)ethyl ethyl methylphosphonite]pentacarbonylmolybdenum (7). To a stirred, refluxing solution of 4.76 g (9.06 mmol) of (-)-3-DCHA [[α]_D²⁵ -5.75° (c 2.59, methanol), 75% ee] in 45 mL of acetone was added 1.50 g (9.16 mmol) of (diisopropylamino)ethyl chloride. The latter, bp 71 °C (15 mm), was obtained by treating its hydrochloride salt (Aldrich Chemical Co.) with base and extracting with ether. A white precipitate started to form in less than a minute. The reaction mixture was refluxed for 2 h. When a ³¹P NMR analysis of the acetone soluble portion of the reaction mixture indicated 9% unreacted starting material was still present, an additional 0.23 g (1.40 mmol) of (diisopropylamino)ethyl chloride was added. The mixture was then refluxed for 0.5 h, allowed to stand overnight, and filtered, and the precipitate was washed with three 8-mL portions of acetone. The filtrate and washings were combined and concentrated to give 5.17 g (4.27 g, theory) of a dark green oil. Analysis of this oil by ³¹P NMR revealed the following compounds: **7**, δ 182.9, 91%; **3**, δ 147.6, 5%; an unknown, δ 155.7, 4%. A portion (0.23 g) of the above oil was chromatographed on 4.67 g of alumina (Woelm, basic, activity III) with diethyl ether. A pale yellow oil (0.17 g) was recovered from the eluate; it had a ³¹P NMR purity of 99.5%. The remainder of the dark green product was then chromatographed on 84 g of alumina in the same manner. The resulting yellow oil (4.11 g) was degassed for 80 min at 0.15–0.030 mm to give 3.47 g (81.3%) of the desired **7**, [α]_D²⁵ +2.35° (c 6.30, methanol). A ¹H NMR analysis of this product revealed the presence of ~14% of two nonphosphorus impurities. Anal. Calcd for C₁₆H₂₆MoNO₇P: C, 40.78; H, 5.56; N, 2.97. Found: C, 42.27; H, 5.75; N, 2.77.

(+)-[2-(Diisopropylamino)ethyl ethyl methylphosphonite methiodide]pentacarbonylmolybdenum (8). A mixture of 3.40 g (7.21 mmol) of (+)-**7**, 20 mL of dry acetone, and 8 mL of methyl iodide was refluxed for 12.5 h and then concentrated to 4.50 g of a yellow solid. This solid was triturated with four 10-mL portions of diethyl ether and then with three 10-mL portions of hot benzene to give 3.41 g of a light brown solid. Recrystallization of this product from a benzene/acetone mixture gave two crops of crystals: first crop 1.83 g, mp 141–142 °C; second crop 0.31 g, mp 139–140 °C. These were combined, dissolved in acetone, filtered through Celite, and concentrated to give 2.09 g (47.3%) of the desired (+)-**8**, [α]_D²⁵ +1.67° (c 2.15, methanol). ³¹P NMR revealed **8** [δ 189.9, (*J*_{P–Mo} = 184 Hz)] in 97.4% yield, with minor impurities of 1.8% (δ 34.2) and 0.7% (δ 61.8), respectively. Anal. Calcd for C₁₇H₂₉IMoNO₇P: C, 33.30; H, 4.77; N, 2.28. Found: C, 32.93; H, 4.68; N, 2.31.

Methanolysis of (+)-8. To a solution of 2.06 g (3.36 mmol) of (+)-**8** prepared as described above in 4.0 mL of dry methanol was added 20.0 mL of a 0.74 M solution of sodium methoxide (from fresh sodium) in dry methanol. After the solution was heated at 70 °C for 1 h, its ³¹P NMR spectrum revealed a mixture of **9** (δ 186.7; 52%), **3** (δ 146.5; 45%), and **10** (δ 190.1; 3%). (Pending receipt of these results, the reaction had been heated an additional 0.5 h). It was then cooled, acidified with concentrated HCl to pH 1, and filtered and the filtrate concentrated. The

resulting residue was taken up in chloroform and washed with two 10-mL portions of water. The aqueous phase was set aside and later examined, as described below, while the chloroform solution was concentrated to give 1.7 g of a green oil. This oil was triturated with ether, and the ether solution was dried (sodium sulfate) and concentrated to give 1.23 g of a yellow oil. The latter, in hexane, was treated with 0.26 g (1.43 mmol) of DCHA to give 0.48 g of (-)-3-DCHA: mp 138–141 °C; $[\alpha]_{\text{D}}^{25}$ -6.64° (c 3.36, methanol); 87% ee. ³¹P NMR (methanol): δ 146.2 ($J_{\text{P-Mo}}$ = 162 Hz; 98.1%). ³¹P NMR also showed a trace of 9: δ 185.6; 1.9%. Anal. Calcd for C₂₀H₃₂MoNO₂P: C, 45.72; H, 6.14; N, 2.67. Found: C, 45.30; H, 5.97; N, 2.55.

The hexane filtrate from this (-)-3-DCHA salt was concentrated to a yellow oil (0.83 g), which was placed on an alumina column (Woelm, basic, activity grade III) and eluted with benzene. The benzene effluent was concentrated to give 0.67 g of a colorless oil, 97.6% pure by ³¹P NMR. This product was distilled in a micromolecular still at 0.24 mm and a bath temperature of 50–52 °C to give 0.41 g of (-)-9: $[\alpha]_{\text{D}}^{25}$ -2.49° (c 3.82, methanol); 84% ee from the 100% ee value for (+)-9 given below. ³¹P NMR (benzene-d₆): for 9, δ 187.1 ($J_{\text{P-Mo}}$ = 182 Hz, 98.0%); for 10, δ 190.2 (2.0%). The ¹H NMR analysis corroborated this result. Anal. Calcd for C₉H₁₁MoO₇P: C, 30.19; H, 3.10. Found: C, 30.21; H, 3.07.

The aqueous phase from the methanolysis reaction given above was taken to dryness and then triturated with a little chloroform to give a solution free of sodium chloride plus 1.30 g of an organic/inorganic salt residue. The chloroform solution was taken to dryness (0.25 g obtained) and redissolved in CD₃OD, and an ¹H NMR spectrum was recorded: δ 1.4 [(CH₃)₂C, m], 3.0 (two H₃CN⁺, s), 3.4 (H₂CN⁺, t), 4.0 (HCN⁺, coincident with H₂CO, m), 4.8 (OH, s), 5.8 (H₂C=C, m), 6.3 (-CH=C, m). The two singlets at δ 3.0 were separated by ~2 Hz; the one slightly more downfield represented 52% of the sum. A ¹H NMR spectrum of the organic/inorganic residue discussed above (1.30 g, containing sodium chloride) was almost identical with the above spectrum except for a reversal in the ratio of the H₃CN⁺ signals, accompanied by a similar decrease in the area under the vinyl portions. On the basis of the above spectra, the original aqueous phase appeared to contain a nearly equal mixture of 12 and 14 (plus sodium chloride), with 12 corresponding to the downfield H₃CN⁺ signal. The NMR solution from the chloroform-soluble residue described above was then taken to dryness, and after trituration with acetone, a crystalline solid was obtained: yield 0.07 g; mp 238–239 °C. The ¹H NMR spectrum of this product in D₂O revealed it to be 14 (by comparison to that of an authentic sample), with ~8% of 12 as an impurity. An authentic sample of 14, prepared by treating 2-(diisopropylamino)ethanol with an excess of methyl iodide in acetone, had a melting point of 239–240 °C. ¹H NMR (D₂O): δ 1.44 [(CH₃)₂C, d], 2.92 (H₃CN⁺, s), 3.46 (H₂CN⁺, t), 3.98 (HCN⁺, m), 4.05 (CH₂O, m), 4.75 (OH, s).

Stability of (-)-9 in Sodium Methoxide/Methanol Solution. A solution of 52.8 mg (0.147 mmol) of (-)-9 (from above, containing 2.0% 10) in 0.88 mL of 0.74 N sodium methoxide (from fresh sodium) in methanol was heated at 68 °C for 1 h. Analysis of the resulting solution by ³¹P NMR now revealed a mixture of 96.2% 9, 2.6% 10, and 1.2% of an unknown product (δ 21.0). The reaction mixture was treated with 0.054 mL of concentrated HCl. The sodium chloride that precipitated was filtered off, and the filtrate was concentrated. Since the residue still contain sodium chloride, it was taken up into methylene chloride, washed with water, and then reconcentrated to give 39.4 mg (75%) of a colorless oil, $[\alpha]_{\text{D}}^{25}$ -2.14° (c 3.60, methanol), down 14% from that of the original.

(+)-(Ethyl methyl methylphosphonite)pentacarbonylmolybdenum (9). A 2.0-g (3.93 mmol) sample of (-)-eph(-)-3, $[\alpha]_{\text{D}}^{25}$ -21.4° (c 1.25,

methanol), 69% ee, was dissolved in 18 mL of methanol and 2 mL of water, acidified with 1 N HCl to pH 1.0, and extracted with three 20-mL portions of chloroform. The latter were combined, dried, and concentrated to a blue residue that was dissolved in 15 mL of ether and added to a solution of diazomethane in ether. The latter had been distilled with about 35 mL of ether from the reaction of 2.9 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich Chemical Co.) with alcoholic KOH, according to the directions printed on the reagent bottle. After standing overnight, the ether solution was washed with 25 mL of water, dried, and evaporated to a brown oil, which was distilled in a micro apparatus at 0.10–0.075 mm (bath temperature, 48–62 °C) to give 1.3 g (3.62 mmol, 92%) of (+)-9, a yellow oil, $[\alpha]_{\text{D}}^{25}$ +2.04° (c 1.91, methanol). This product was redistilled to give 0.98 g of (+)-9 with only a trace of color, $[\alpha]_{\text{D}}^{25}$ +2.03° (c 5.66, methanol), presumably 69% ee, corresponding to that calculated for the (-)-3 starting material. The ³¹P NMR purity was 97% (δ 181.4, CDCl₃), and the ¹H NMR spectrum was in agreement with this assignment. From these results, the specific rotation of 100% ee (+)-9 is calculated to be +2.96°.

Diisopropyl(β -methoxyethyl)methylammonium (13) Iodide and Treatment with Sodium Methoxide. (Diisopropylamino)ethyl chloride (2.09 g, 0.0128 mol) in 5 mL of benzene was added dropwise with stirring and cooling (ice bath) to a freshly prepared (from sodium) solution of 0.235 mol of sodium methoxide in 10 mL of methanol and then left to stand at room temperature over the weekend. The precipitate was filtered and washed with 3 mL of benzene. The filtrate and wash were combined and concentrated to a solid/liquid residue, which was placed in a separatory funnel, treated with 4 mL of water, and extracted with two 12-mL portions of ether. The ether extracts were dried (K₂CO₃), filtered, and concentrated to give 1.27 g (62.2%) of 2-(diisopropylamino)ethyl methyl ether, 98.3% pure by ¹H NMR. This product (7.97 mmol) was dissolved in 10 mL of dry acetone, 38.8 mmol of methyl iodide was added, and the solution was refluxed for 9.5 h. The reaction mixture was then cooled in an ice bath, and 1.42 g of a white crystalline product was obtained. A second crop, obtained by concentrating the filtrate to dryness and recrystallizing the yellow residue from acetone/benzene, raised the total yield to 1.99 g (82.9%), mp 128–130 °C, after recrystallization. A ¹H NMR spectrum of the product was consistent for 13-I⁻ and showed no impurities.

This product (59.6 mg, 0.198 mmol) in 0.48 mL of dry methanol was mixed with 0.90 mL of a 0.96 N solution of sodium methoxide in methanol and then heated at 70 °C for 1.5 h. The solution was cooled, treated with 0.86 mL of 1 N HCl to a pH of ~1, and then concentrated to dryness. The resulting solid was triturated with CD₃OD, and the soluble portion was examined by ¹H NMR. Only the spectrum of the starting material was observed, and no unsaturated (vinyl) product was detected. The CD₃OD insoluble portion was dried and then dissolved in D₂O. The ¹H NMR spectrum of this (NaCl) solution revealed no proton-containing organic compounds.

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Registry No. 3, 101221-92-5; (-)-eph(-)-3, 101078-25-5; (-)-3-DCHA, 101078-26-6; 4, 16391-07-4; 5, 37549-13-6; (+)-7, 101078-27-7; (+)-8, 101144-79-0; (-)-9, 101078-28-8; (+)-9, 101078-29-9; 10, 101247-87-4; 13-I⁻, 101078-30-2; Mo(CO)₆, 13939-06-5; methylphosphonous dichloride, 676-83-5; ethyl methylphosphonous acid, 16391-07-4; 2-(diisopropylamino)ethyl ethyl methylphosphonite, 57856-11-8; 2-(diisopropylamino)ethyl ethyl methylphosphonite methiodide, 101078-31-3.