References and Notes

(1) F. J. Kristine, D. R. Gard, and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 994 (1976).
(2) F. J. Kristine and R. E. Shepherd, *J. Am. Chem. Soc.*, **99**, 6562 (1977).
(3) (a) H. J. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967); (b) H. J. Schugar, A. P. Hubbard, F. C. Anson, and H. B. Gray, *ibid.*, **91**, 71 (1969).
(4) H. J. Schugar, G. R. Rossman, J. Thibeault, and H. B. Gray, *Chem. Phys. Lett.*, **6**, 26 (1970); L. Lohr, *Coord. Chem. Rev.*, **8**, 241 (1972); D. L. Dexter, *Phys. Rev.*, **126**, 1962 (1962).
(5) R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, **8**, 1470 (1969).
(6) G. McLendon, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, **15**, 2306 (1976).
(7) S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
(8) J. K. Hurst and R. H. Lane, *J. Am. Chem. Soc.*, **95**, 1703 (1973).
(9) J. K. Hurst, *J. Am. Chem. Soc.*, **98**, 4001 (1976).
(10) J. Jwo and A. Haim, *J. Am. Chem. Soc.*, **98**, 1172 (1976); D. Gaswick and A. Haim, *ibid.*, **96**, 7845 (1974).
(11) V. Durante and P. C. Ford, *J. Am. Chem. Soc.*, **97**, 6898 (1975); D. Piering and J. M. Malin, *ibid.*, **98**, 6045 (1976).
(12) J. K. Farr and R. H. Lane, *J. Chem. Soc., Chem. Commun.*, 153 (1977).
(13) (a) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, pp. 285–286; (b) *ibid.*, p 99.
(14) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).
(15) H. Fischer, G. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).
(16) J. Nelson and R. E. Shepherd, *Inorg. Chem.*, **17**, 1030 (1978).
(17) W. R. Schiedt, R. Countryman, and J. L. Hoard, *J. Am. Chem. Soc.*, **93**, 3878, 3867 (1971).
(18) J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965).
(19) D. W. Margerum, G. R. Cayley, D. C. Weaterburn, and G. P. Pagenkopf, Vol. IIA, A. E. Martell, Ed., ACS Monograph No. 174, American Chemical Society, Washington, D.C., 1978.
(20) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).
(21) J. D. Ellis, G. A. K. Thompson, and A. G. Sykes, *Inorg. Chem.*, **15**, 3172 (1976).
(22) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 537 (1973).
(23) J. H. Espenson and R. J. Christensen, *J. Am. Chem. Soc.*, **91**, 7311 (1969).
(24) K. Shaw and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 6622 (1968).
(25) A. Rabinonovitch, *Trans. Faraday Soc.*, **33**, 1225 (1937); S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941, p 516.
(26) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975).
(27) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).
(28) W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Englewood Cliffs, N.J., 1952, p 369.
(29) A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1961, p 144.
(30) M. Goldberg and I. Pecht, *Biochemistry*, **15**, 4197 (1976).
(31) S. Wherland, R. A. Holwerda, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 5260 (1975).
(32) S. H. Koenig and R. D. Brown, *Ann. N.Y. Acad. Sci.*, **222**, 752 (1973).
(33) A. Finazzi-Argo, G. Rotillio, L. Avigliano, P. Guerrieri, V. Boffi, and B. Mondovi, *Biochemistry*, **9**, 2009 (1970).
(34) N. Boden, M. C. Holmes, and P. F. Knowles, *Biochem. Biophys. Res. Commun.*, **57**, 845 (1974).
(35) P. Rosen and I. Pecht, *Biochemistry*, **15**, 775 (1976).
(36) J. V. McArdle, K. Yocom, and H. B. Gray, *J. Am. Chem. Soc.*, **99**, 4141 (1977); P. M. Wood, *Biochim. Biophys. Acta*, **357**, 370 (1974).
(37) F. K. Kristine and R. E. Shepherd, *Inorg. Chem.*, submitted for publication.
(38) (a) K. Wuthrich, *Helv. Chim. Acta*, **48**, 779 (1965); (b) C. R. Johnson and R. E. Shepherd, *Bioinorg. Chem.*, **8**, 115 (1978).

Dynamics of Monocapped Octahedral [MoH(CO)₂(bidentate phosphine)₂]⁺

S. Datta, B. Dezube, J. K. Kouba, and S. S. Wreford*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received December 14, 1977

Abstract: The compounds $[MoH(CO)_2(P-P)_2]^+$ (P–P = $R_2PC_2H_4ER_2'$: R = R' = Me, E = P-dmpe; R = R' = Ph, E = P-diphos; R = Me, R' = Et, E = P-dmdepe; R = Me, R' = Ph, E = P-dmdPhpe, R = R' = Me, E = As-dmpdmae; R = R' = Ph, E = As-arphos; R = Ph, R' = Me. E = As-dPhpdmae) have a monocapped octahedral structure (*trans*-MoP₄(CO)₂ octahedron with hydride capping a PP(CO) face). Two NMR-differentiable exchange permutations exist for derivatives with symmetric phosphines, corresponding to pairwise and nonpairwise exchange of chelate ends. ¹H NMR line shapes for P–P = dmpe fit neither (similar to those for TaH(CO)₂(dmpe)₂), suggesting a mixed mechanism. Spectra for P–P = diphos agree well with those calculated for pairwise exchange, $\Delta H^{\ddagger}$ = 18.7 ± 0.2 kcal/mol, $\Delta S^{\ddagger}$ = 1.1 ± 0.6 eu. This corresponds to rotation of H about the CO–Mo–CO axis and constitutes detection of the monocapped octahedron ⇌ pentagonal bipyramid interconversion. The related process in which H migrates between faces above and below the P₄ plane has been detected in $[MoH(^{13}CO)_2(diphos)_2]^+$. *cis*-Mo(CO)₂(P–P)₂ (P–P = dmdPhpe, dmpdmae, and dPhpdmae) is nearly isomerically pure, i.e., of the three possible isomers (C_2, C_2, and C_1), one C_2 isomer is predominant. Protonation at low temperature affords the hydride with "labels" mutually trans. Following first-order, reversible kinetics, this isomer converts to one with labels mutually cis; the activation parameters for this nonpairwise process are (P–P = dmdPhpe) $\Delta H^{\ddagger}$ = 18.0 ± 0.4 kcal/mol, $\Delta S^{\ddagger}$ = −4.2 ± 1.5 eu. The similarity of $\Delta H^{\ddagger}$ for the nonpairwise process to that for pairwise exchange suggests a nondissociative mechanism for the former. Moreover, similar stereochemical behavior was observed for all unsymmetric derivatives. Oxidation of C_2-*cis*-Mo(CO)₂-(dmdPhpe)₂ affords *trans*-$[Mo^I(CO)_2(dmdPhpe)_2]^+$. The Mo(I) cation is formed stereospecifically as the isomer with -PPh₂ groups mutually cis. This observation is consistent with the cis–trans isomerization which occurs on oxidation proceeding by a trigonal twist mechanism.

Seven-coordinate complexes generally exist as one of three commonly found geometries—the monocapped trigonal prism, the monocapped octahedron, and the pentagonal bipyramid.[1] The barriers to interconversion between idealized forms are thought to be small on both theoretical[1c,2] and empirical grounds. Intramolecular exchange in ML₇ complexes appears to be too rapid for measurement by NMR techniques; no report of quenched exchange has appeared.[3] However, limiting NMR spectra for systems having inequivalent or chelating ligands have been obtained for a number of compounds.[4] In general, the mechanisms for ligand exchange are poorly understood, with the exceptions of TaX(η⁴-naphthalene)(dmpe)₂[41] and

[MoH(C₂H₄)₂(diphos)₂][BF₄]⁴ⁿ (dmpe = 1,2-bis(dimethylphosphino)ethane, diphos = 1,2-bis(diphenylphosphino)ethane), which have been proposed to exchange phosphorus sites by a pseudorotation analogous to the Berry mechanism in five coordination.

TaH(CO)₂(dmpe)₂,[5,6] first prepared by Tebbe,[5] has been assigned an approximate monocapped octahedral structure on the basis of x-ray results.[4f] As such, this compound constitutes one of the few examples of the monocapped octahedral geometry with sufficient NMR handles for detailed mechanistic studies of site exchange. Reportedly, phosphorus exchange, as shown by ¹H and ³¹P NMR, occurs at temperatures greater than −10 °C. Two NMR-differentiable permutational sets (excluding the identity) exist under the C_s symmetry constraint, corresponding to pairwise and nonpairwise exchange of chelate ends.[4f] The original study noted that the
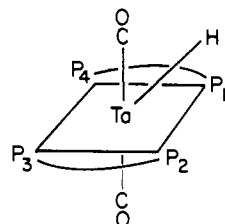
pairwise exchange (14)(23)

non-pairwise exchange (14)

change of chelate ends.[4f] The original study noted that the experimental spectra did not adequately fit those calculated for either set or a 1/1 mixture, although agreement was best for the nonpairwise set.[4f]

In the course of other investigations on the isoelectronic [MoH(CO)₂(bidentate phosphine)₂]⁺, we noted similar behavior for [MoH(CO)₂(dmpe)₂][SO₃F]. We felt that the most obvious explanation was a mixed mechanism, unequally weighted. Since computation of spectra for a spin system of this size, with the assumption of competing exchange permutations having unequal rate constants, was beyond the practical limits of the programs available to us, our attention was directed to more classical kinetic methods, using unsymmetric bidentate phosphines to lower the symmetry and reduce the problem to one of isomer exchange. Further, this work has led us to some observations regarding the stereochemical course of protonation and oxidation of *cis*-Mo(CO)₂(bidentate phosphine)₂.

Experimental Section

Solvents were purified by distillation from sodium benzophenone ketyl except for methylene chloride, which was distilled from phosphorus pentoxide. 1-Dimethylphosphino-2-diphenylphosphinoethane (dmdPhpe),[7] [MoH(CO)₂(dmpe)₂][SO₃F],[8] *cis*-Mo(CO)₂(dmdepe)₂[41] (dmdepe = 1-dimethylphosphino-2-diethylphosphinoethane), *trans*-Mo(N₂)₂(diphos)₂[9] (diphos = 1,2-bis(diphenylphosphino)ethane), and [MoH(CO)₂(diphos)₂][SO₃F][6b] were prepared by literature methods.

Manipulations were performed in vacuo or under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ¹H, 40.5-MHz ³¹P, and 25.2-MHz ¹³C NMR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, and AEI-MS9 spectrometers, respectively. ³¹P NMR chemical shifts are relative to external 85% H₃PO₄. Elemental analyses were by Alfred Bernhardt Microanalytisches Laboratorium.

1-Dimethylphosphino-2-dimethylarsinoethane (dmpdmae). Dimethylvinylphosphorus sulfide[7] (10.0 g, 83.3 mmol) and 2 g of potassium *tert*-butoxide were combined in a 100-mL Hoke bomb. The vessel was attached to a vacuum manifold, evacuated, and cooled to −196 °C. THF (20 mL) and 8.83 g (83.3 mmol) of dimethylarsine[10] were distilled into the bomb, which was then sealed and allowed to warm; noticeable heat evolution occurred near room temperature. After heating at 110 °C overnight, the bomb was cooled and the contents decanted and filtered. Evaporation of the filtrate left a white, crystalline solid which was dissolved in 100 mL of CH₂Cl₂ and treated with 50 mL of oxygen-free water. After separation of the organic

phase, the aqueous phase was washed with 2 × 25 mL of CH₂Cl₂. The pooled organic extracts were dried (MgSO₄) and evaporated to dryness. The colorless residue was identified as (CH₃)₂P(S)-C₂H₄As(CH₃)₂ by mass spectral analysis (*m/e* 226 [¹²C₆¹H₁₆⁷⁵As³¹P³²S]⁺, 211 [P − CH₃]⁺). The solid was dissolved in 100 mL of dioxane, treated with 3.19 g of LiAlH₄, and refluxed for 18 h. After dropwise addition of water until hydrogen evolution ceased, the mixture was diluted with ether (100 mL) and filtered. Distillation of the filtrate afforded 10.0 g (51.4 mmol, 62%) of dmpdmae: bp 28 °C (0.1 mm); mass spectrum *m/e* 194 [¹²C₆¹H₁₆⁷⁵As³¹P]⁺, 179 [P − CH₃]⁺; ³¹P NMR (benzene-d_6) −51.7 ppm (s); ¹H NMR (benzene-d_6) δ 1.25 (m, 4 H), 0.75 (d, J_{PH} = 2.9 Hz, 6 H), 0.71 (d, J_{PH} = 0.4 Hz, 6 H).

Anal. Calcd for C₆H₁₆AsP: C, 37.13; H, 8.30. Found: C, 37.24; H, 8.40.

1-Diphenylphosphino-2-dimethylarsinoethane (dPhpdmae). Diphenylvinylphosphine[11] (16.0 g, 75.5 mmol) and 2 g of potassium *tert*-butoxide were combined in a 100-mL Hoke bomb. The bomb was cooled to −196 °C and evacuated, and 7.1 g (75.5 mmol) of dimethylarsine[10] and 20 mL of THF were distilled into the vessel. The bomb was sealed, warmed to room temperature, and heated at 140 °C overnight. After cooling, the contents was rinsed out of the bomb with additional THF, filtered, and fractionally distilled. The product (14.0 g, 44.0 mmol, 58%) was collected at 142 °C (0.05 mm) as a colorless liquid: mass spectrum *m/e* 318 [¹²C₁₆¹H₂₀⁷⁵As³¹P]⁺, 303 [P − CH₃]⁺; ³¹P{¹H} NMR (benzene-d_6) 15.5 ppm (s); ¹H{³¹P} NMR (toluene-d_8) δ 7.2 (m, 10 H), 2.1 and 1.4 (A₂B₂, 4 H), 0.7 (s, 6 H).

Anal. Calcd for C₁₆H₂₀AsP: C, 60.39; H, 6.34. Found: C, 60.38; H, 6.45.

***cis*-Mo(CO)₂(dmdPhpe)₂.** dmdPhpe (4.00 g, 14.60 mmol) and 1.85 g of Mo(CO)₆ (7.0 mmol) were charged to a 50-mL Hoke bomb and heated for 60 h with occasional venting of evolved CO. The bomb was cooled and opened, and the contents was extracted with 4 × 20 mL of CH₂Cl₂. The combined extracts were evaporated to dryness. The yellow residue was washed with 5 × 10 mL of hexane and recrystallized from benzene–heptane, affording 3.14 g (4.48 mmol, 64%) of the product as small yellow crystals: mass spectrum *m/e* 702 [¹²C₃₄¹H₄₀⁹⁸Mo¹⁶O₂³¹P₄]⁺, 674 [P − CO]⁺; IR (CH₂Cl₂ solution) ν_{CO} 1841 (s), 1775 cm⁻¹ (s).

Anal. Calcd for C₃₄H₄₀MoO₂P₄: C, 58.29; H, 5.76. Found: C, 58.17; H, 5.74.

***cis*-Mo(CO)₂(arphos)₂ (arphos = 1-Diphenylphosphino-2-diphenylarsinoethane).** MoCl₃(THF)₃ (1.14 g, 2.73 mmol), 2.45 g of arphos (5.50 mmol), and 20 mL of 1% Na/Hg were added to 20 mL of THF. The mixture was stirred for 4 h while CO was bubbled through it. The solution was then decanted, centrifuged, and evaporated to dryness. The residue was washed with 2 × 10 mL of acetone and extracted with 2 × 25 mL of boiling acetone and 2 × 30 mL of boiling 2/1 acetone–THF. Evaporation of the combined extracts left a yellow solid, which was recrystallized from acetone–THF, affording 450 mg (0.44 mmol, 16%) of the product: mass spectrum *m/e* 1038 [¹²C₅₄¹H₄₈⁷⁵As₂⁹⁸Mo¹⁶O₂³¹P₂]⁺, 1010 [P − CO]⁺; ³¹P{¹H} NMR (CH₂Cl₂) −71.2 (s, C₂ isomer), −51.6 and −74.9 (d, J_{AB} = 20 Hz, C₁ isomer); IR (THF solution) ν_{CO} 1860 (s), 1794 cm⁻¹ (s).

Anal. Calcd for C₅₄H₄₈As₂MoO₂P₂: C, 62.56; H, 4.67. Found: C, 63.16; H, 4.67.

[MoH(CO)₂(dPhpdmae)₂][SO₃F]. dPhpdmae (5.0 g, 15.7 mmol) and 2.07 g (7.85 mmol) of Mo(CO)₆ were heated in a 50-mL Hoke bomb for 48 h at 210 °C with occasional venting of evolved CO. After cooling, the bomb was opened and rinsed with THF until the washings were colorless. The combined extracts were filtered through a Celite pad and evaporated, leaving 2.4 g of an oily residue. The residue was dissolved in THF–ether and treated with 102 mg (1.02 mmol) of HSO₃F. The resulting precipitate was collected by filtration, washed with ether, and dried in vacuo, affording 850 mg of a colorless solid, identified as [MoH(CO)₂(dPhpdmae)₂][SO₃F] on the basis of spectral data and its conversion to Mo(CO)₂(dPhpdmae)₂ (vide infra): IR (THF solution) ν_{CO} 1876 cm⁻¹ (s); ¹H{³¹P} NMR (acetone-d_6) δ 7.4 (m, 20 H), 3.0 and 2.4 (A₂B₂, 8 H), 1.8 (s, 12 H), −4.8 (s, 1 H); ¹H NMR (acetone-d_6) δ −4.8 (t, J_{PH} = 66.0 Hz, 1 H); ³¹P{¹H} NMR (CD₂Cl₂) −88.5 ppm (s).

***cis*-Mo(CO)₂(dPhpdmae)₂.** The hydride was suspended in 20 mL of THF and treated with 1.0 mL of a 1 M solution of potassium in *tert*-butyl alcohol. After the solution was stirred for 20 min, the solvent was removed in vacuo and the residue extracted with 2 × 25 mL of hot 1/1 hexane–benzene. The combined extracts were refluxed

overnight, filtered, and evaporated to dryness. Crystallization from hexane–THF afforded 480 mg (0.61 mmol, 8%) of the product: mass spectrum m/e 790 $[^{12}C_{34}{}^{1}H_{40}{}^{75}As_2{}^{98}Mo^{16}O_2{}^{31}P_2]^+$, 762 $[P - CO]^+$; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) −76.0 ppm (s); $^1H\{^{31}P\}$ NMR (CD_2Cl_2) δ 9.0 and 8.3 (m, 20 H), 0.7 (s, 6 H), 0.4 (s, 6 H); IR (THF solution) ν_{CO} 1857 (s), 1793 cm^{-1} (s).

Anal. Calcd for $C_{34}H_{40}As_2MoO_2P_2$: C, 51.79; H, 5.11. Found: C, 51.69; H, 5.09.

[MoH(CO)₂(dmdPhpe)₂][SO₃F]. *cis*-Mo(CO)₂(dmdPhpe)₂ (4.88 g, 6.98 mmol) was dissolved in ca. 100 mL of THF and treated with 0.50 mL (8.70 mmol) of HSO₃F. The white precipitate was collected by filtration, washed with 2 × 5 mL of THF, and dried in vacuo: 4.97 g (6.21 mmol. 89%); IR (CH₂Cl₂ solution) ν_{CO} 1870 cm^{-1} (s); ^1H NMR (CD_2Cl_2) δ 7.5 (m, 20 H), 1.83 (m, 12 H), −4.94 (tt, J_{P_AH} = 8.4, J_{P_BH} = 68 Hz, 1 H) (C_s isomer, C_1 isomer unresolved).

Anal. Calcd for $C_{34}H_{41}FMoO_5P_4S$: C, 51.01; H, 5.16. Found: C, 50.82, H, 5.34.

Hydrides of the other Mo dicarbonyl complexes were prepared analogously or by treating a CH₂Cl₂ solution of the dicarbonyl with excess 50% HBF₄. Treatment of methylene chloride solutions with HSO₃F did not give the hydrides in acceptable yields, but led to unidentified products.

***cis*-Mo(CO)₂(dmpdmae)₂.** Mo(CO)₆ (1.20 g) and 1.80 g of dmpdmae were charged to a 50-mL Hoke bomb and heated at 210 °C for 40 h with occasional venting of the evolved CO. The bomb was cooled and opened, and the contents was extracted with THF until the extracts were colorless. The combined extracts were evaporated to dryness and chromatographed on a 2 × 10 cm silica column (10% THF in hexane eluent). The yellow band was collected and evaporated, and the oily residue was recrystallized from hexane. The resulting crystalline solid was contaminated with a yellow oil. Decantation of the oil left the product, which was recrystallized again from hexane–THF. After drying in vacuo, 240 mg (0.44 mmol, 10%) of pale yellow crystals was obtained: m/e 542 $[^{12}C_{14}{}^{1}H_{32}{}^{75}As_2\-{}^{98}Mo^{16}O_2{}^{31}P_2]^+$, 514 $[P - CO]^+$, 486 $[P - 2CO]^+$; IR (THF solution) ν_{CO} 1858 (s), 1796 cm^{-1} (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) −97.0 (s) (C_2 isomer) and −78.4 (d) and −99.5 ppm (d) (J_{AB} = 24 Hz, C_1 isomer); $^1H\{^{31}P\}$ NMR (CD_2Cl_2) δ 1.64 (s, PCH₃, 3 H), 1.83 (s, PCH₃, 3 H), 1.94 (s, AsCH₃, 3 H), 2.13 (s, AsCH₃, 3 H).

Anal. Calcd for $C_{14}H_{32}As_2MoO_2P_2$: C, 31.13; H, 5.97. Found: C, 31.34; H, 5.83.

[MoH(¹³CO)₂(diphos)₂][SO₃F]. Mo(N₂)₂(diphos)₂ (1.218 g, 1.29 mmol) and 40 mL of THF were placed in a 150-mL cylindrical Pyrex vessel equipped with a stopcock and magnetic stir bar. The tube was cooled to −196 °C, evacuated, and charged with 3.21 mmol of 90% ¹³CO with the aid of a Töppler pump. The mixture was heated for 10 h at 90 °C with vigorous stirring, then cooled and vented. The solution was passed through a 10-cm Florisil column (THF eluent). The resulting yellow solution was concentrated and treated with 1.30 mmol of HSO₃F. Evaporation of the solvent gave a red oil which, on trituration with ether, afforded 832 mg (0.88 mmol, 68%) of a light pink solid, IR (THF solution) $\nu_{¹³CO}$ 1839 cm^{-1} (s).

[MoH(¹³CO)₂(dmpe)₂][SO₃F]. MoCl₃(THF)₃¹² (10.6 g, 25.3 mmol) and 7.65 g (51.0 mmol) of dmpe¹³ in 125 mL of THF were shaken with 90 mL of 0.75% Na/Hg at 0 °C for 3 h under 20 psi N₂. The brown solution was decanted, centrifuged, and evaporated to dryness. The resulting semisolid was washed with 2 × 25 mL of ether at −20 °C, affording a yellow powder with an IR spectrum consistent with *trans*-Mo(N₂)(dmpe)₂ (ν_{NN} (THF solution) 1980 cm^{-1} (s)). This solid (760 mg, 1.68 mmol) was treated with 3.80 mmol of 90% ¹³CO as described above. A similar workup afforded 560 mg (1.01 mmol, 60%) of the product: IR (THF solution) $\nu_{¹³CO}$ 1823 cm^{-1} (s); ¹³C NMR (acetone-d_6, 30 °C) 207 ppm (triplet of triplet of doublets, J_{CP_A} = 10.0, J_{CP_B} = 8.8, J_{CH} = 4.4 Hz).

***trans*-[Mo(CO)₂(dmdPhpe)₂][BF₄].** *cis*-Mo(CO)₂(dmdPhpe)₂ (221 mg, 0.31 mmol) in 50 mL of THF was treated with 70 mg (0.35 mmol) of AgBF₄. The red-brown precipitate was collected by filtration, washed with 2 × 5 mL of THF, and then extracted with 2 × 5 mL of CH₂Cl. Slow addition of 50 mL of THF to the orange extracts gave small yellow crystals of the product: 170 mg (0.22 mmol, 70%); IR (CH₂Cl₂ solution) ν_{CO} 1870 cm^{-1} (s); 9.5-GHz ESR (CH₂Cl₂ solution) g = 2.088, A_{31P} = 26 G.

Anal. Calcd for $C_{34}H_{40}BF_4MoO_2P_4$: C, 51.79; H, 5.37. Found: C, 51.38; H, 5.12.

Reduction of *trans*-[Mo(CO)₂(dmdPhpe)₂][BF₄]. *trans*-[Mo(CO)₂(dmdPhpe)₂][BF₄] (113 mg, 0.14 mmol) was suspended in 10

mL of THF at −20 °C and treated with 0.14 mmol of a freshly prepared solution of sodium naphthalene in THF. The resulting orange solution exhibited a single ν_{CO} at 1812 cm^{-1} consistent with *trans*-Mo(CO)₂(dmdPhpe)₂: $^{31}P\{^1H\}$ NMR (THF-d_8) −42.9 and −72.5 ppm (AA′BB′ spectrum). On refluxing or prolonged standing the trans isomer was converted to a material whose IR, mass, and ³¹P NMR spectra were identical with those of an authentic sample of *cis*-Mo(CO)₂(dmdPhpe)₂.

NMR monitoring experiments in THF-d_8 were performed analogously in a 12-mm tube fitted with a rubber septum.

³¹P NMR Kinetic Experiments. A weighed sample of the appropriate dicarbonyl complex and 1.5 mL of CD₂Cl₂ were charged to a 12-mm tube. The tube was fitted with a rubber septum and cooled to ca. −78 °C. HBF₄ (50%, 100 μL) was added via a syringe and the tube shaken until the solution was colorless, indicating complete conversion to the cationic hydride. The sample was inserted into the precooled probe and spectra accumulated at timed intervals. Samples were sufficiently concentrated that negligible reaction occurred during acquisition of spectra.

Infrared Monitoring of Low-Temperature Protonations. A flask containing a CH₂Cl₂ solution of *cis*-Mo(CO)₂(dmdPhpe)₂ was fitted with a rubber septum pierced by two hypodermic needles. One needle was connected to a nitrogen inlet and the other via narrow-bore Tygon tubing to a 1-mm path IR cell equipped with AgCl windows. The outlet port of the cell was similarly connected to a vented flask. The cell was enclosed by Styrofoam cups, cut to allow passage of the IR beam and insertion of a thermometer and a Tygon tube for admission of cold nitrogen (cooled by passage through a copper coil immersed in liquid nitrogen). After the system was flushed, the cell was cooled to −80 °C and the CH₂Cl₂ solution immersed in a dry ice bath. Following addition of excess 50% HBF₄ and shaking to complete protonation, the solution was pressed through the cell with nitrogen pressure. The first 50 mL was discarded, then spectra were recorded while gradually raising the cell temperature.

Line Shape Calculations. Line shape calculations were performed on IBM 360 and PDP 11 computers, using Kleier and Binsch's DNMR-3¹⁴ as modified by Bushweller et al.¹⁵

Results

Assuming that electronic and steric requirements of R and R′ in R₂PC₂H₄PR₂′ are similar, *cis*-Mo(CO)₂-(R₂PC₂H₄PR₂′)₂ should exist as three isomers (neglecting enantiomers of the C_1 form). Protonation, which has been shown to afford the cationic hydride with trans carbonyls,⁸ should result in the three isomers (neglecting enantiomers of the C_1 form) indicated in Scheme I. Since pairwise exchange equilibrates the C_s isomers without affecting the C_1 isomer, whereas nonpairwise exchange mixes all three, the rate constants for different exchange paths are, in principle, separable by solving a triangular kinetic scheme. Such an approach requires that a ligand can be found which gives all three isomeric hydrides and that they can be generated in a nonequilibrium distribution.

Isomerization of [MoH(CO)₂(dmdPhpe)₂]⁺. Treatment of Mo(CO)₆ with dmdPhpe at 200 °C affords *cis*-Mo(CO)₂-(dmdPhpe)₂. The ³¹P NMR spectrum in Figure 1 shows a single AA′BB′ pattern. Hence, only one of the two possible C_2 isomers is present; none of the C_1 isomer is detectable. Steric considerations would suggest that the observed isomer is the one with the bulky -PPh₂ ends of the chelate mutually trans and the carbonyls trans to the relatively poor π-accepting PMe₂ groups.¹⁶

Protonation of *cis*-Mo(CO)₂(dmdPhpe)₂ with HSO₃F in THF or HBF₄ in CH₂Cl₂ gives [HMo(CO)₂(dmdPhpe)₂]⁺, assigned a monocapped octahedral structure analogous to TaH(CO)₂(dmpe)₂,⁴ᶠ [MoH(CO)₂(dmpe)₂]⁺,⁸,¹⁷ [MoH(CO)₂(diphos)₂]⁺,⁸ and Cr¹⁹ and W⁸ᵃ,¹⁸,¹⁹ congeners. The ³¹P NMR shows a single AA′BB′ spectrum superimposed on an ABCD pattern (Figure 1). Assignment of multiplets to ABCD or AA′BB′ groups was confirmed by spin-tickling experiments at −70 °C.²⁰ Thus, the hydride exists as an equilibrium mixture of the C_1 isomer and *one* of the two possible

Scheme I
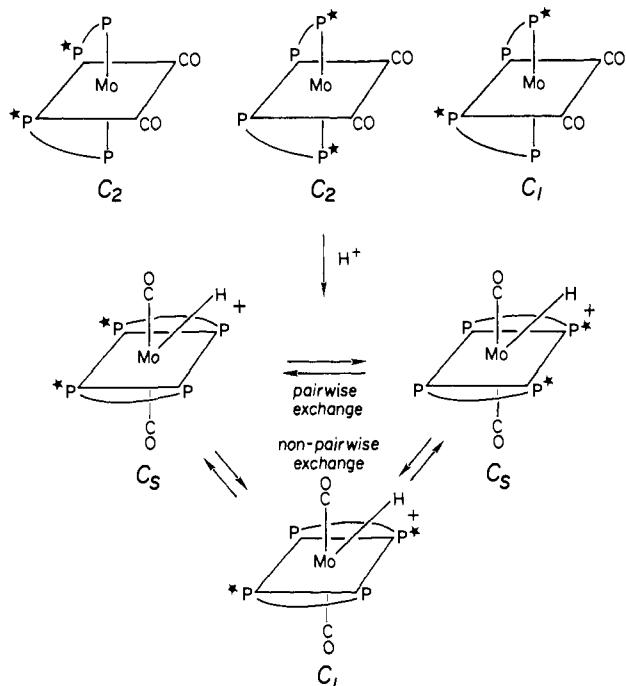
Scheme II
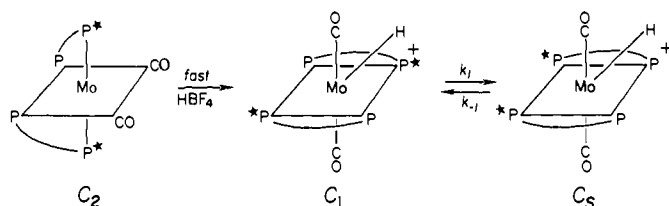
C_s isomers (Scheme I). We cannot confidently differentiate between the possible C_s isomers on the basis of spectral data, although we note that the complex with the hydride capping the PMe₂-CO-PMe₂ face is, presumably, the least crowded.

Protonation of *cis*-Mo(CO)₂(dmdPhpe)₂ at temperatures below −30 °C results in a nonequilibrium isomer distribution, the C_1 hydride being the major product with one C_s isomer present in small amounts. Subsequent warming results in diminution of the resonances assigned to the C_1 isomer and growth of those attributable to the more stable C_s form (Figure 1). That is, protonation of isomerically pure C_2-*cis*-Mo-(CO)₂(dmdPhpe)₂ gives C_1-[MoH(CO)₂(dmdPhpe)₂]⁺ as the kinetic product, which equilibrates to the thermodynamic ratio of C_1 and C_s isomers, as shown in Scheme II. Monitoring the protonation by IR at −50 °C revealed only one carbonyl band attributable to the initially formed hydride, which was superimposable with that for the C_1, C_s equilibrium mixture.[21] These observations confirm that the species giving rise to the ABCD ³¹P NMR spectrum is indeed the C_1 isomer and not an intermediate with cis carbonyls. Further, decoupling experiments have established that the kinetic product has one -PPh₂ with a large J_{PH} (ca. 60 Hz) and one with a small J_{PH} (ca. 10 Hz) (similarly for the -PMe₂ chelate ends), as anticipated for the structure in Scheme II.[22]

Integration of the ³¹P NMR spectra after low-temperature protonation allows measurement of the C_1 and C_s isomer concentrations during the approach to equilibrium. A plot of ln $[K(C_1)_t − (C_s)_t/K(C_1)_0 − (C_s)_0]$ vs. time is linear with zero intercept (Figure 2), consistent with reversible, first-order kinetics. Rates are independent of Mo concentration (Table
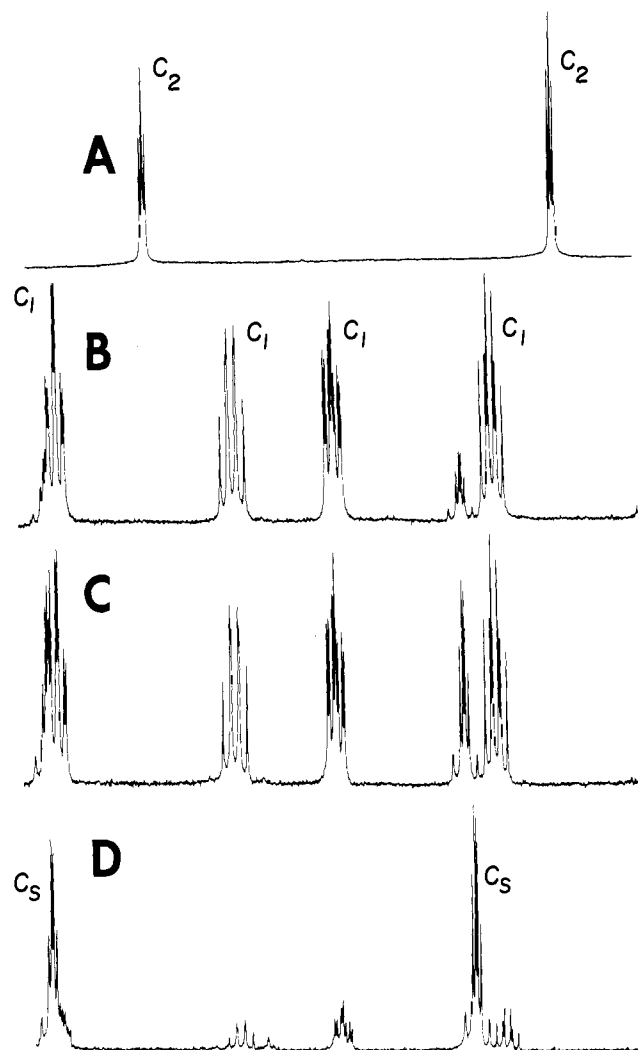
Figure 1. ³¹P{¹H} NMR spectra of (A) *cis*-Mo(CO)₂(dmdPhpe)₂ in CD₂Cl₂, (B) after addition of 50% aqueous HBF₄ at ca. −70 °C and warming to −30 °C, (C) at t = 10 min, (D) at equilibrium. The ABCD spectrum of the C_1 intermediate and the AA'BB' spectrum of the C_s isomer are indicated. The spectral parameters follow: C_1 isomer −28.6 (P_A), −48.4 (P_B), −60.8 (P_C), −82.8 ppm (P_D), $|J_{AB}|$ = 30.0, $|J_{AC}|$ = 39.1, $|J_{AD}|$ = 38.0, $|J_{BC}|$ = 42.5, $|J_{BD}|$ = 10.9, $|J_{CD}|$ = 36.9 Hz; C_s isomer −33.2 ($P_{A,A'}$), −84.1 ($P_{B,B'}$), $|J_{AA'} + J_{BB'}|$ = 40.5, $|J_{AA'} − J_{BB'}|$ = 37.2, $|J_{AB} + J_{AB'}|$ = 10.0, $|J_{AB} − J_{AB'}|$ = 69.2 Hz.

I), as expected. Variation of the acid concentration is not practical as the HBF₄ from the protonating agent (50% aqueous HBF₄) is partitioned between the methylene chloride and aqueous phases. Because of the slow approach to equilibrium over the temperature range investigated, the equilibrium constants (Table II) required for evaluation of k_1 and k_{-1} were measured at 0-60 °C and extrapolated to the temperatures used for kinetic runs. An Eyring plot gave the activation parameters which are collected with the equilibrium thermodynamic data in Table III.

The C_1 to C_s isomerization corresponds to nonpairwise exchange of chelate ends in the symmetrically substituted systems. Pairwise exchange is equivalent to equilibration between the two possible C_s isomers. Inasmuch as only one C_s isomer is present in this system, the rates for the pairwise process cannot be evaluated.

Phosphorus Exchange in [MoH(CO)₂(symmetric, bidentate phosphine)₂]⁺. The hydride resonance of [MoH(CO)₂(diphos)₂]⁺ appears as a triplet of triplets (Figure 3). On warming, the spectrum approaches the binomial quintet required by rapid ³¹P site exchange. The high-temperature limit cannot
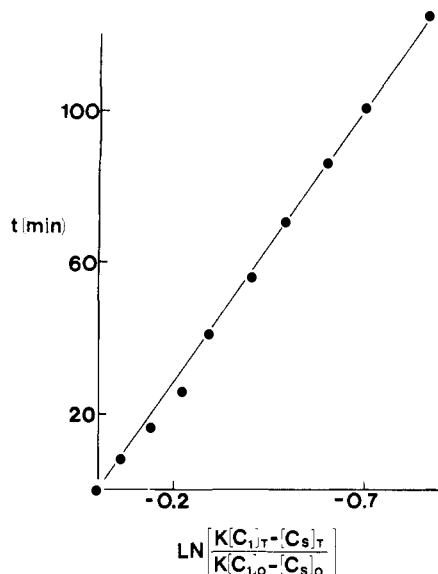
Figure 2. Plot of kinetic data for the C_1 to C_s isomerization of [MoH(CO)$_2$(dmdPhpe)$_2$][BF$_4$] in CD$_2$Cl$_2$ at -25 °C.

Table I. Rate Constants for C_1 to C_s Isomerization of [MoH(CO)$_2$-(dmdPhpe)$_2$]$^+$

Temp, °C	$10^5 k_1$, s^{-1} [a]	$10^5 k_{-1}$, s^{-1} [a]	K^d
-15^c	34.6 ± 2.5	13.9 ± 1.0	2.49
-20^c	18.0 ± 1.4	7.03 ± 0.53	2.55
-20^b	17.9 ± 1.2	7.01 ± 0.48	2.55
-25^c	8.11 ± 0.54	3.11 ± 0.21	2.61
-30^c	3.79 ± 0.28	1.42 ± 0.10	2.67

[a] Error limits are the standard errors from the least-squares fits. [b] 200 mg of Mo complex/2.0 mL of CH$_2$Cl$_2$. [c] 300 mg of Mo complex/1.5 mL of CH$_2$Cl$_2$. [d] Equilibrium values used for separation of k_1 and k_{-1}, evaluated from the thermodynamic parameters in Table III as discussed in the text.

Table II. Equilibrium Constants for C_1 and C_s Isomers of [MoH(CO)$_2$(dmdPhpe)$_2$][SO$_3$F] [a]

Temp, °C	K^b	Temp, °C	K^b
60	1.98	20	2.10
50	1.96	10	2.28
40	2.04	0	2.38
30	2.09		

[a] Measured in CH$_2$Cl$_2$ solution. [b] Accuracy is estimated to be 5%.

Table III. Activation and Equilibrium Thermodynamic Parameters [a] for Interconversion of C_1 and C_s Isomers of [MoH(CO)$_2$(dmdPhpe)$_2$]$^+$

	$C_1 \rightarrow C_s$
$\Delta H^{\ddagger}$	18.0 ± 0.4 kcal/mol
$\Delta S^{\ddagger}$	-4.2 ± 1.5 eu
	$C_s \rightarrow C_1$
$\Delta H^{\ddagger}$	18.5 ± 0.4 kcal/mol
$\Delta S^{\ddagger}$	-3.7 ± 1.4 eu
	$C_1 \rightleftarrows C_s$
ΔH	-0.58 ± 0.08 kcal/mol [b]
ΔS	-0.44 ± 0.26 eu [b]

[a] Error limits are standard errors from least-squares fits. [b] Evaluated from the equilibrium data in Table II.

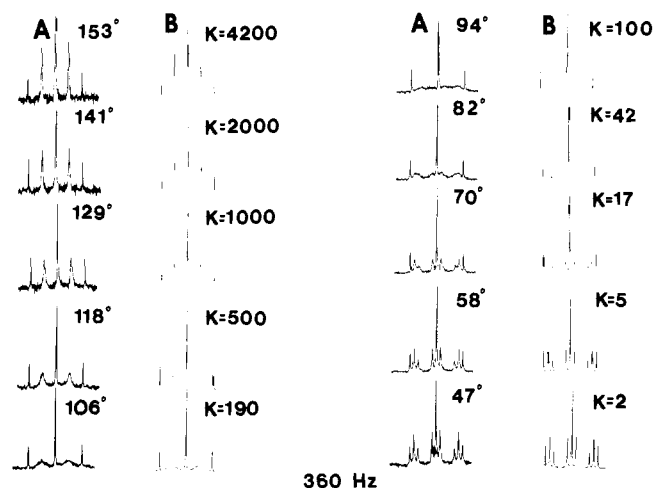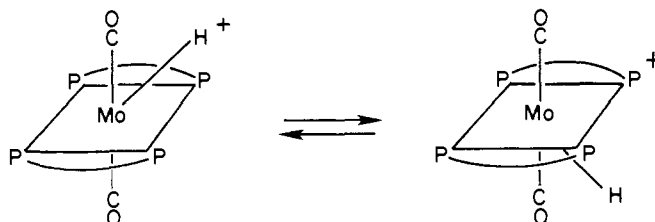**Figure 3.** (A) ^{1}H NMR spectra of [MoH(CO)$_2$(diphos)$_2$]$^+$ in 1,2-dichloroethane-d_4. (B) Spectra computed for pairwise exchange. Rate constants are in s^{-1}.

be reached because of sample decomposition. The experimental spectra are in excellent agreement with those calculated for pairwise exchange, although a small fraction of nonpairwise exchange cannot be eliminated because of the similarity of the line shapes (e.g., Figure 4). Further, the asymmetry and broadening of the outer lines reported for TaH(CO)$_2$(dmpe)$_2$ and attributed to a non-mutual-exchange process[4f] is not present. An Eyring plot of the rate data gave the activation parameters: $\Delta H^{\ddagger} = 18.7 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = 1.1 \pm 0.6$ eu.

In contrast, spectra for [MoH(CO)$_2$(dmpe)$_2$]$^+$ do not agree exactly with those calculated for either the pairwise or nonpairwise permutation (Figure 4), although agreement is best for the nonpairwise path, as with TaH(CO)$_2$(dmpe)$_2$.[4f] Attempts to fit the data with an equally weighted mixture were also unsuccessful. These spectra are very similar to those reported for TaH(CO)$_2$(dmpe)$_2$,[4f] except that the asymmetry discussed above is not significant.

^{13}C Exchange in [MoH(^{13}CO)$_2$(diphos)$_2$]$^+$. Since the neutral dicarbonyls are accessible by carbonylation of the corresponding dinitrogen complexes,[23] high degrees of ^{13}C enrichment in the dicarbonyl hydrides are easily accomplished. ^{13}C{^{1}H} NMR spectra of [MoH(^{13}CO)$_2$(diphos)$_2$]$^+$ show a

binomial quintet at elevated temperatures (Figure 5), implying effective D_{2h} symmetry. As the permutational set responsible for the pairwise ^{31}P exchange observed in this compound creates only effective C_{2v} symmetry, an additional process must be occurring which equilibrates ^{13}C sites. This requires migration of the hydride between faces above and below the P$_4$ plane. At lower temperatures, the spectrum approaches a triplet of triplets; i.e., ^{31}P exchange is quenched, but ^{13}C sites are still equilibrating. At -80 °C (the lower limit of our

spectrometer), the resonances are severely broadened (Figure 5), while the solvent resonance is unaffected. As the low-temperature limit cannot be reached, the chemical shift difference between the carbonyl sites cannot be evaluated. Consequently, the relative energetics of this process are not elucidated. These observations, however, are consistent with the process occurring.
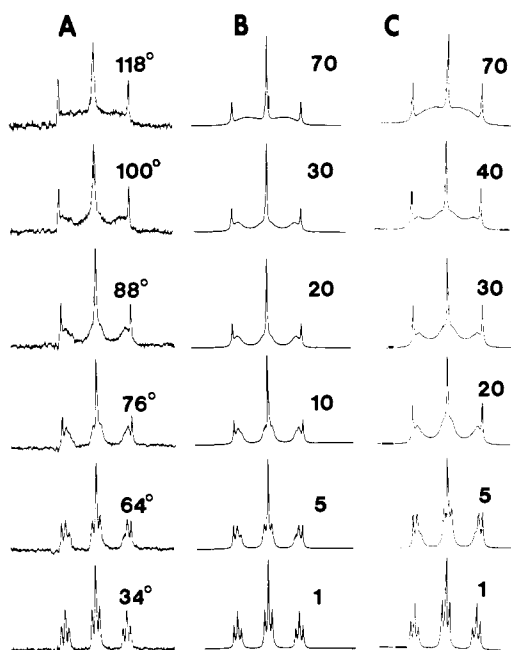
Figure 4. (A) ^{1}H NMR spectra of [MoH(CO)₂(dmpe)₂][SO₃F] in Me₂SO-d_6. (B) Spectra computed for pairwise exchange. (C) Spectra computed for nonpairwise exchange. Rate constants are in s⁻¹.

Spectra for [MoH(^{13}CO)₂(dmpe)₂]⁺ are qualitatively similar. Less broadening is observed at −80 °C, implying a lower coalescence temperature.

Stereochemistry of Protonation and Oxidation of *cis*-Mo(CO)₂(unsymmetric, bidentate phosphine)₂. In an attempt to find an unsymmetric system which would give both of the C_s isomers and the C_1 isomer of the hydride, thereby allowing determination of rates for pairwise and nonpairwise exchange for the same compound, we prepared *cis*-Mo(CO)₂-(R₂PC₂H₄AsR₂′)₂ (R = R′ = Ph, arphos; R = R′ = Me, dmpdmae; R = Ph, R′ = Me, dPhpdmae). As indicated in Table IV, the neutral dicarbonyls proved to be nearly isomerically pure, predominantly one of the two possible C_2 isomers. Excepting the arphos derivative, protonation afforded the C_1 hydride in good isomeric purity, a minor component being one of the C_s isomers. In no case could both C_s isomers be detected. At equilibrium the C_s isomer was markedly favored. As for [MoH(CO)₂(dmdPhpe)₂]⁺, we cannot confidently decide which C_s isomer is favored. However, since J_{PH} is similar in all cases (Table IV), the same C_s isomer is present for each compound.[24] The arphos derivative proved too insoluble for low-temperature protonation experiments. Similar attempts with *cis*-Mo(CO)₂(dmdepe)₂ gave a mixture of isomers with substantially overlapping ^{31}P NMR resonances. Confident isomer assignments or adequate concentration estimates could not be made.

In summary, in each case examined, the stereochemistry of protonation was the same as found for the dmdPhpe system and illustrated in Scheme II.

Oxidation of C_2-*cis*-Mo(CO)₂(dmdPhpe)₂ with silver ion affords *trans*-[Mo^I(CO)₂(dmdPhpe)₂]⁺, analogously to chemical or electrochemical oxidation of *cis*-Mo(CO)₂-(dmpe)₂[17] and *cis*-Mo(CO)₂(diphos)₂.[25] Treatment of the Mo(I) cation with 1 equiv of sodium naphthalene in THF gives the metastable *trans*-Mo(CO)₂(dmdPhpe)₂, which undergoes slow thermal isomerization to the cis isomer. Similar behavior has been observed on electrochemical reduction of [Mo^I(CO)₂(diphos)₂]⁺.[25b,26] Reduction of *trans*-[Mo^I-(CO)₂(dmdPhpe)₂]⁺ at −30 °C while monitoring by ^{31}P NMR gave a species having a single AA′BB′ spectrum; i.e., the initially formed *trans*-Mo(CO)₂(dmdPhpe)₂ is isomeri-
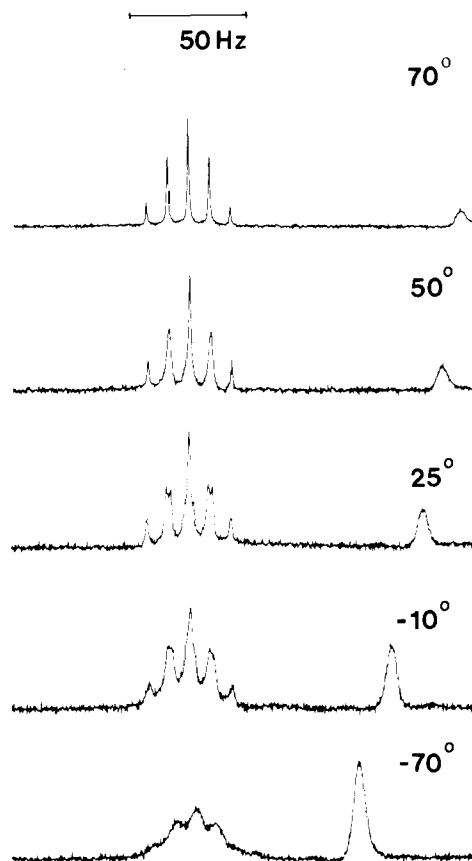
Figure 5. ^{13}C{^{1}H} NMR spectra of 90% enriched [MoH(^{13}CO)₂(diphos)₂][SO₃F] in acetone-d_6. The featureless resonance moving to lower field with decreasing temperature is the acetone-d_6 carbonyl carbon.

Table IV. Isomer Distributions for *cis*-Mo(CO)₂(R₂PC₂H₄AsR₂′) and [MoH(CO)₂(R₂PC₂H₄AsR₂′)₂]⁺

Ligand	*cis*-Mo(CO)₂(R₂PC₂H₄AsR₂′)₂ % C_2	% C_2	% C_1
arphos[a]	80	0	20
dmpdmae[a]	91	0	9
dPhpdmae[a]	100	0	0

Ligand	[MoH(CO)₂(R₂PC₂H₄AsR₂′)₂]⁺ % C_s	% C_s	% C_1
arphos[b]	c	c	c
dmpdmae[a]	88 (J_{PH} = 67.4 Hz)[d]	0[d]	12[d]
	15[e]	0[e]	85[e]
dPhpdmae[a]	97 (J_{PH} = 71.6 Hz)[d]	0[d]	3[d]
	8[e]	0[e]	92[e]
	100 (J_{PH} = 66.0 Hz)[d]	0[d]	0[d]

[a] Measured in CD₂Cl₂. [b] Measured in acetone-d_6. [c] Low-temperature protonation was not possible because of poor solubility. [d] Ratios are quoted at equilibrium at 30 °C. [e] Isomer distribution is the kinetic one, i.e., measured immediately after protonation at temperatures below −30 °C.

cally pure. Treatment of this metastable trans isomer with HBF₄ gave a single AA′BB′ spectrum identical with that observed for the C_s isomer of [MoH(CO)₂(dmdPhpe)₂]⁺. Moreover, deprotonation of the C_1, C_s [MoH(CO)₂-(dmdPhpe)₂]⁺ equilibrium mixture with potassium *tert*-butoxide gave *trans*-Mo(CO)₂(dmdPhpe)₂; the predominant isomer (i.e., the one derived by deprotonation of the C_s isomer) had an AA′BB′ ^{31}P NMR spectrum identical with that observed for the trans isomer derived by reduction of the Mo(I) cation. These observations are consistent only with the *trans*-

Scheme III
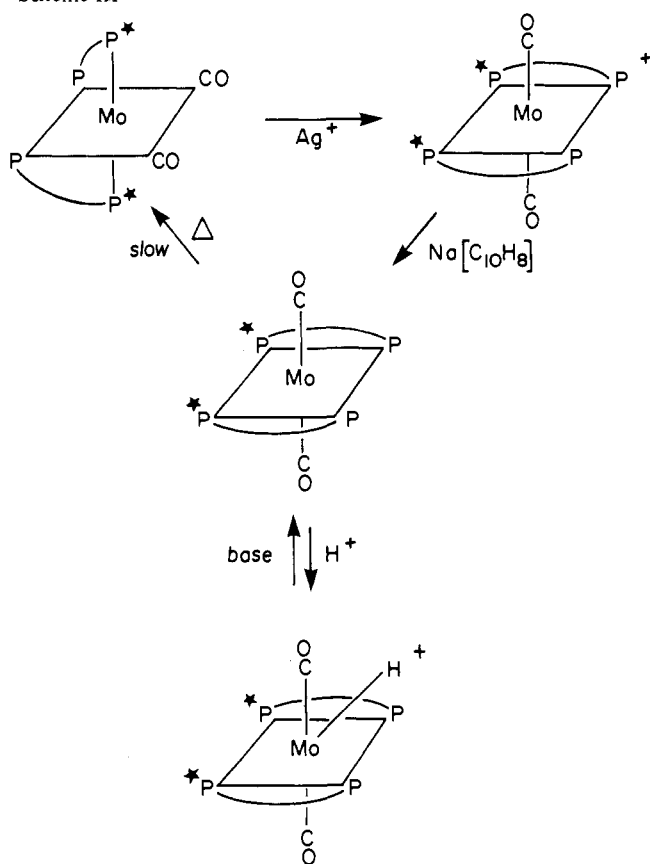
Mo(CO)$_2$(dmdPhpe)$_2$, formed by sodium naphthalene reduction, being the isomer with "labeled" ends of the phosphine mutually cis. Assuming that isomerization does not occur during reduction, these data imply that [Mo^I(CO)$_2$-(dmdPhpe)$_2$]$^+$ has the same arrangement of phosphorus ligands. That is, oxidation is stereospecific as indicated in Scheme III.

Discussion

Pairwise Exchange. Mechanistically, the pairwise exchange observed for [MoH(CO)$_2$(diphos)$_2$]$^+$ [27] is most simply accounted for by migration of the capping hydride about the upper faces of the octahedron.[28] This process requires the
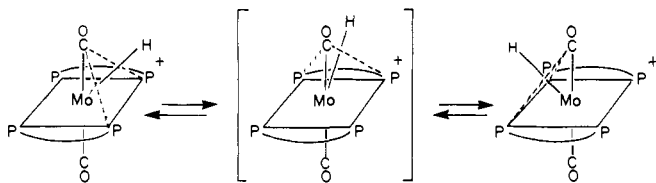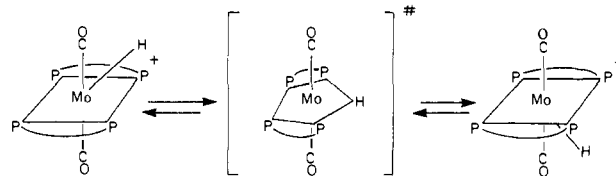

undetected intermediate with the hydride capping the face containing the phosphine backbone and a transition state with H located on a CO-P edge, i.e., an approximate pentagonal bipyramid. In terms of the idealized seven-coordinate geometries, this process represents the cycle monocapped octahedron $\rightleftarrows$ pentagonal bipyramid.[16,29] It should be noted that the structural results for TaH(CO)$_2$(dmpe)$_2$ indicate that the carbonyl groups are not collinear with tantalum.[4f] Rather, one carbonyl is bent away from the face containing the hydride. If the structures of the molybdenum complexes are similar, migration of the hydride about the upper faces of the octahedron, as in the proposed mechanism for pairwise exchange, must be coupled with precession of the Mo-CO vector.

The ground-state geometry of [MoH(C$_2$H$_4$)$_2$(diphos)$_2$]$^+$

is equivalent to the transition state proposed for pairwise ^{31}P exchange in [MoH(CO)$_2$(diphos)$_2$]$^+$, i.e., the hydride resides on a C$_2$H$_4$-P edge of a *trans*-Mo(C$_2$H$_4$)$_2$P$_4$ octahedron.[4n]

The ^{13}C exchange observed for [MoH([13]CO)$_2$(diphos)$_2$]$^+$ is consistent with the mechanistically related migration of the hydride between adjacent upper and lower faces. This process represents the monocapped octahedron $\rightleftarrows$ pentagonal bipyramid cycle[16,29] as well. Unpublished x-ray results for isoelectronic [WH(N$_2$)$_2$(diphos)$_2$]$^+$ indicate an approximate pen-

tagonal bipyramidal structure, derived by placing the hydride on an edge of the P$_4$ plane of a *trans*-Mo(N$_2$)$_2$P$_4$ octahedron.[30] Thus, the ground state of [WH(N$_2$)$_2$(diphos)$_2$]$^+$ is structurally equivalent to the proposed transition state for ^{13}C site exchange in [MoH([13]CO)$_2$(diphos)$_2$]$^+$.

Nonpairwise Exchange. While it is not possible to unambiguously identify the mechanism responsible for nonpairwise exchange, the available data suggest that it does not involve a dissociative or "arm-off, arm-on" mechanism. Since rates of dissociation of phosphines are generally sterically controlled,[31] nonpairwise exchange would be anticipated to be predominant for the diphos derivative (ligand cone angle = 125°)[31] if an "arm-on, arm-off" mechanism were involved. However, exclusive pairwise exchange is found, as discussed above.

We feel that the simplest explanation for the failure of the ^{1}H NMR spectra of [MoH(CO)$_2$(dmpe)$_2$]$^+$ to agree well with those calculated for the two possible exchange paths is the existence of a mixed mechanism. Inspection of the spectra implies that the nonpairwise fraction is predominant for this compound, despite the decreased phosphine bulk (ligand cone angle = 107°).[31] This suggestion is supported by the direct observation of the nonpairwise process for [MoH(CO)$_2$-(dmdPhpe)$_2$]$^+$. Although pairwise exchange may occur for the latter compound, it could not be observed because of the lack of a detectable concentration of the third possible isomer (C_s). We were unable to find an unsymmetric phosphine which gave all three isomers with sufficiently different ^{31}P NMR chemical shifts for accurate concentration estimates (Table IV).

Further, since the pairwise process cannot be dissociative, the similarity of $\Delta H^{\ddagger}$ for pairwise and nonpairwise exchange in [MoH(CO)$_2$(diphos)$_2$]$^+$ and [MoH(CO)$_2$(dmdPhpe)$_2$]$^+$, respectively, would not be anticipated if one process involved P-Mo bond breaking. Finally, we point out that the nonpairwise exchange of chelate ends observed for the isoelectronic, monocapped trigonal prismatic MX(CO)$_2$(unsymmetric, bidentate phosphine)$_2$^{n} (M = Mo, n = 1+; M = Ta, n = 0; X = halogen) has been suggested to result from a polytopal process rather than an "arm-off, arm-on" mechanism on the basis of steric effects on $\Delta G^{\ddagger}$.[4m]

Cis-Trans Isomerization in [Mo^I(CO)$_2$(dmdPhpe)$_2$]$^+$. The oxidation of *cis*-Mo(CO)$_2$(bidentate phosphine)$_2$ to the paramagnetic, 17-electron Mo^I(CO)$_2$(bidentate phosphine)$_2$ complexes is known to be accompanied by rapid, irreversible cis to trans isomerization;[17,25] i.e., although the thermodynamically stable form of the Mo(0) species has cis carbonyls,[8b] the stable form of the Mo(I) complex has a trans arrangement. As outlined in the Results section, oxidation of the dmdPhpe derivative shows that the cis to trans isomerization is accompanied by a stereospecific rearrangement of phosphorus ligands. Moreover, since the product, *trans*-[Mo^I(CO)$_2$-(dmdPhpe)$_2$]$^+$, has the bulky -PPh$_2$ ends of the chelates mu-

Scheme IV
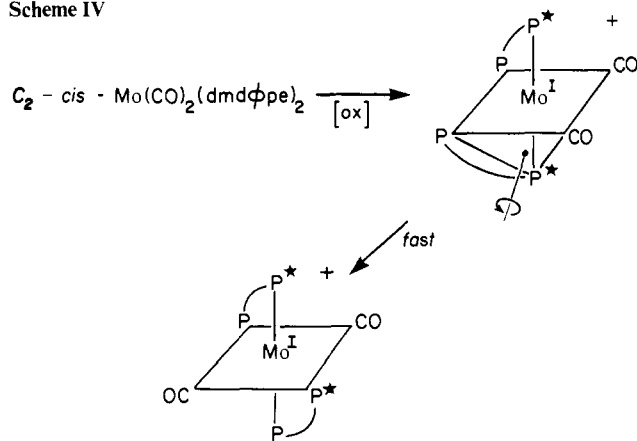
tually cis, it is likely less stable than the isomer with bulky ends trans. That is, the observed product is the kinetic one. This observation is inconsistent with the cis to trans isomerization occurring by an "arm-off, arm-on" mechanism, as the isomer with mutually trans $-PPh_2$ groups or a mixture would be anticipated. The observed stereochemistry is consistent with cis to trans isomerization occurring by a trigonal twist[32] of the PP(CO) face as indicated in Scheme IV. This mechanism leads only to the observed product, providing that the cis to trans carbonyl isomerization, which occurs on oxidation, is irreversible.

The origin of the stereospecificity observed for protonation of cis-$Mo(CO)_2$(unsymmetric, bidentate phosphine)$_2$ (i.e., C_2 neutral dicarbonyl $\rightarrow$ C_1 cationic hydride) is obscure. However, we note that although one-electron oxidation and protonation are both accompanied by a cis to trans isomerization with respect to the carbonyl ligands, the stereochemistry with respect to the "labeled" ends of the chelate is the opposite. In the former case, the $-PPh_2$ groups are mutually cis; in the latter they are mutually trans.

References and Notes

(1) (a) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967); (b) J. K. Kouba and S. S. Wreford, *Inorg. Chem.*, **15**, 1463 (1976); (c) R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *ibid.*, **16**, 511 (1977); (d) M. G. B. Drew, *Prog. Inorg. Chem.*, **23**, 67 (1977).

(2) (a) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); (b) D. Britton, *ibid.*, **41**, 1632 (1963); (c) T. A. Claxton and G. C. Benson, *ibid.*, **44**, 157 (1966); (d) H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, **7**, 488 (1968).

(3) (a) E. L. Muetterties and K. J. Packer, *J. Am. Chem. Soc.*, **86**, 293 (1964); (b) R. J. Gillespie and J. W. Quail, *Can. J. Chem.*, **42**, 2671 (1964).

(4) B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc. A*, 1668 (1969); (b) M. Elder, J. G. Evans, and W. A. Graham, *J. Am. Chem. Soc.*, **91**, 1245 (1969); (c) J. J. Howe and T. J. Pinnavia, *ibid.*, **92**, 7342 (1970); (d) R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc. A*, 994 (1971); (e) A. P. Ginsburg, S. C. Abrahams, and P. B. Jamieson, *J. Am. Chem. Soc.*, **95**, 4749 (1973); (f) P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, **13**, 1025 (1974); (g) T. J. Pinnavaia, J. J. Howe, and R. G. Teets, *ibid.*, **13**, 1074 (1974); (h) R. R. Schrock and P. Meakin, *J. Am. Chem. Soc.*, **96**, 5289 (1974); (i) J. Chatt and J. R. Dilworth, *J. Chem. Soc., Chem. Commun.*, 508 (1974); (j) K. Henrick and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, 2500 (1974); (k) W. R. Cullen and L. M. Mihichuk, *Can. J. Chem.*, **54**, 2548 (1976); (l) J. O. Albright, L. D. Brown, S. Datta, J. K. Kouba, S. S. Wreford, and B. M. Foxman, *J. Am. Chem. Soc.*, **99**, 5518 (1977); (m) L. D. Brown, S. Datta, J. K. Kouba, L. K. Smith, and S. S. Wreford, *Inorg. Chem.*, **17**, 729 (1978); (n) J. W. Byrne, J. R. M. Kress, J. A. Osborn, L. Ricard, and R. E. Weiss, *J. Chem. Soc., Chem. Commun.*, in press.

(5) F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 5823 (1973).

(6) S. Datta and S. S. Wreford, *Inorg. Chem.*, **16**, 1134 (1977).

(7) R. B. King, J. C. Cloyd, Jr., and P. K. Hendrick, *J. Am. Chem. Soc.*, **95**, 5083 (1973).

(8) (a) J. A. Connor, P. I. Riley, and C. J. Rix, *J. Chem. Soc., Dalton Trans.*, 1317 (1977); (b) S. Datta, T. J. McNeese, and S. S. Wreford, *Inorg. Chem.*, **16**, 2661 (1977).

(9) (a) J. Chatt and A. G. Wedd, *J. Organomet. Chem.*, **27**, C15 (1971); (b) T. A. George and C. D. Seibold, *ibid.*, C13 (1971).

(10) R. D. Feltham and W. Silverthorn, *Inorg. Synth.*, **10**, 159 (1967).

(11) R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, **93**, 4158 (1971).

(12) M. W. Anker, J. Chatt, G. J. Leigh, and A. G. Weld, *J. Chem. Soc., Dalton Trans.*, 2639 (1975).

(13) S. A. Butter and J. Chatt, *Inorg. Synth.*, **15**, 185 (1974).

(14) D. A. Kleier and G. Binsch, *J. Magn. Reson.*, **3**, 146 (1970).

(15) C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunelle, H. S. Bilofsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc.*, **97**, 65 (1975).

(16) Compare ν_{CO} 1766 and 1834 for dmpe, 1783 and 1850 for diphos, and 1778 and 1844 cm^{-1} for dmdPhpe, measured in CH_2Cl_2 with an accuracy of 1.0 cm^{-1}.

(17) J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Less-Common Met.*, **36**, 207 (1974).

(18) A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, **14**, 2526 (1975).

(19) B. D. Dombeck and R. J. Angelici, *Inorg. Chem.*, **15**, 2397 (1976).

(20) Isomer exchange is sufficiently slow at this temperature that saturation spin transfer effects may be neglected. Homonuclear ^{31}P spin tickling was performed while ^1H broad band decoupling. Selective irradiation of the appropriate transitions was accomplished by using a gated Southwest Technical Products frequency synthesizer with stability better than 0.1 Hz. The frequency was modulated at ca. 5 kHz. The first upper side band was used for irradiation; variation of the frequency was accomplished by changing the modulation frequency.

(21) The ν_{CO} of the C_1 and C_s isomers of $[MoH(CO)_2(dmdPhpe)_2]^+$ were not resolved.

(22) That the C_1 isomer is a species protonated over the backbone of the bidentate phosphine, i.e., i, is, we believe, implausible since protonation of

i
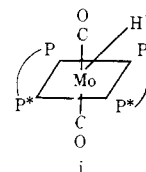
cis-$Mo(CO)_2(dmpe)_2$, cis-$Mo(CO)_2(diphos)_2$, or cis-$Ta(CO)_2(dmpe)_2^-$ gives the analogous hydrides directly (no intermediates). It is not obvious why an intermediate related to that above would be found only with unsymmetric ligands. Further, a recent paper lists 17 hydrides of the type $MH(CO)_2(bidentate\ ligand)_2$ (ref 8a); in each case only one isomer is observed. Each unsymmetric derivative examined in this paper (except $MoH(CO)_2(dPhpdmae)_2^+$) exists as an equilibrium mixture of two isomers. The original claim that additional lines in the ^{31}P NMR spectrum of $TaH(CO)_2(dmpe)_2$ may be due to an isomeric species (ref 4f) is incorrect as samples prepared by the method of ref 6 do not show additional lines after repeated recrystallization. It seems likely, therefore, that the derivatives above with unsymmetric phosphines are positional isomers with respect to the chelate labels.

A suggestion that $CrH(CO)_2(Ph_2PCH_2PPh_2)_2^+$ might be a pure isomer of the type above on the basis of the multiplicity of the ^1H NMR resonance of the P–CH_2–P group is unsupported as both possible isomers are AA′-BB′XY spin systems; small changes in J_{PH} can perturb these resonances, which are not properly analyzed by first-order procedures.

Finally, we note that deprotonation of the C_1 isomer of MoH-$(CO)_2(dmdPhpe)_2^+$ (Me_2SO-d_6/THF) with potassium *tert*-butoxide at -30 °C results in an AA′BB′ ^{31}P NMR spectrum with different parameters (δ_A -37.4, δ_B -78.6 ppm) than those for ii, which are known from the oxida-

ii   iii
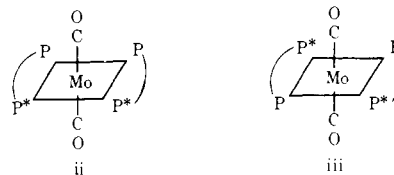
tion–reduction cycle experiments described below. Therefore, deprotonation produces iii, which supports the isomer assignments in the text.

(23) (a) M. Aresta, *Gazz. Chim. Ital.*, **102**, 781 (1972); (b) M. Hidai, K. Tominari, and Y. Uchida, *J. Am. Chem. Soc.*, **94**, 110 (1972); (c) T. A. George and C. D. Seibold, *Inorg. Nucl. Chem. Lett.*, **8**, 465 (1972); (d) D. J. Darensbourg, *ibid.*, **8**, 529 (1972); (e) L. K. Holden, A. H. Mawby, D. C. Smith, and R. Whyman, *J. Organomet. Chem.*, **55**, 343 (1973); (f) T. A. George and C. D. Seibold, *Inorg. Chem.*, **12**, 2548 (1973).

(24) Compare $J_{P_AH} = 70.8$, $J_{P_BH} = 14.04$ Hz for $[MoH(CO)_2(diphos)_2]^+$ and $J_{P_AH} = 68.2$, $J_{P_BH} = 8.6$ Hz for $[MoH(CO)_2(dmpe)_2]^+$: ref 8b.

(25) (a) P. F. Crossing and M. R. Snow, *J. Chem. Soc. A*, 610 (1971); (b) A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, **13**, 1617 (1974).

(26) C. M. Elson, *Inorg. Chem.*, **15**, 469 (1976).

(27) The observation that ^1H NMR line shapes for $[MoH(CO)_2(diphos)_2]^+$ were, qualitatively, in accord with the pairwise exchange set was first made by Professor J. A. Osborn and Dr. J. W. Byrne.

(28) An alternate mechanism for the pairwise ^{31}P equilibration is one involving a formyl intermediate:
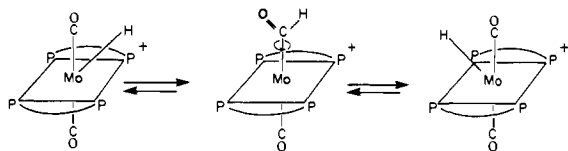
Metal formyls have been isolated [(a) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973); (b) S. R. Winter, G. W. Cornett, and E. A.

Thompson, *J. Organomet. Chem.*, **133**, 339 (1977); (c) C. P. Casey and S. M. Neuman, *J. Am. Chem. Soc.*, **98**, 5395 (1976)] and implicated in Fischer–Tropsch processes [(d) G. A. Mills and F. W. Seffgen, *Catal. Rev.*, **8**, 159 (1973)]. However, this mechanism does not account for the observed ^{13}C exchange.

(29) (a) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974); (b) E. L. Muetterties, *Tetrahedron*, **30**, 1595 (1974).

(30) G. A. Heath and R. Mason, personal communication quoted in G. A. Heath, J. Chatt, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074 (1974).

(31) See C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977), and references cited therein.

(32) (a) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943); (b) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958); (c) R. C. Fay, *Inorg. Chem.*, **3**, 348 (1964).

Cavities in Macrobicyclic Ligands and Complexation Selectivity.[1] Crystal Structures of Two Cryptates, |Na+ ⊂ 221|·SCN− and |K+ ⊂ 221|·SCN−[2]

François Mathieu, Bernard Metz, Dino Moras, and Raymond Weiss*

Contribution from the Laboratoire de Cristallochimie, Institut Le Bel, 67070 Strasbourg-Cédex, France. Received December 29, 1977

Abstract: The crystal structures of two alkali metal ion cryptates, |Na+ ⊂ 221|·SCN− (I) and |K+ ⊂ 221|·SCN− (II), where |221| is 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, have been determined. The crystals of I are monoclinic, $a = 13.258 (5)$, $b = 12.906 (5)$, $c = 12.645 (5)$ Å, and $\beta = 94.77 (3)°$, space group $P2_1/c$. The structure was refined to an R_1 factor of 0.046 on 2590 independent nonzero reflections. The crystals of II are monoclinic, $a = 7.957 (3)$, $b = 15.488 (5)$, $c = 18.503 (5)$ Å, and $\beta = 103.16 (3)°$, space group $P2_1/c$. The structure has been refined to an R_1 factor of 0.042 on 3077 independent nonzero reflections. In both compounds, the alkali cation is held inside the molecular cavity of the bicyclic ligand by ion-dipole interactions. In the potassium cryptate, the metallic ion also interacts with the thiocyanate anion. The selectivity of complexation is discussed in terms of structural parameters. The three-dimensional structures show that an enthalpic preselection is made by the ligand and an important entropic effect does the final selection.

It was proposed many years ago that ring chelates could be designed to select for metal ions on the basis of a compatibility between the cavity size of the ligand and the cation size.[3] This expectation has been fulfilled in the last 10 years for the alkali and alkaline-earth metal cations.[4] Many natural and synthetic ligands presenting high selectivities among these cations are now known and their properties are well documented.[5]

The most stable complexes known to date with the alkali and alkaline-earth metal cations are obtained with macrobicyclic ligands.[6] Such ligands form inclusion complexes (cryptates) in which the metal cation is contained in a three-dimensional intramolecular cavity.[7] Some of these bicyclic ligands display also very high selectivities for one alkali or alkaline-earth metal cation. For instance, ligand |221| displays a peak selectivity for Na+. Its cavity size as evaluated on molecular models is ca. 1.1 Å, thus very close to the size of Na+. However, the thermodynamic quantities ΔG, ΔH, and ΔS involved in the complexation process in water show that the preference of ligand |221| for Na+ over K+ is of entropic origin.[6c] Thus the cavity radius–cation radius effect evaluated with molecular models does not give an accurate picture of the conformational parameters involved in the selectivity of complexation. In order to obtain a deeper insight into these parameters (equilibrium cavity, adaptability, and steric deformation of the ligand) we have studied the crystal and molecular structures of alkali metal cryptates with the bicyclic diazapolyether ligands presenting a peak selectivity for one cation. We report here the results obtained with the sodium and potassium salts: |Na+ ⊂ 221|·(SCN)− (I) and |K+ ⊂ 221|·(SCN)− (II) (see Figure 1).

Experimental Section

X-Ray Data Collection. Crystals were obtained by slow evaporation at room temperature of a methanol–butanol solution containing the metal thiocyanate and the ligand in a 1:1 mole ratio. Preliminary precession photographs showed monoclinic 2/*m* Laue symmetry. Systematic absences of $h0l, l = 2n + 1, 0k0, k = 2n + 1$, identified the space group as $P2_1/c$ for both compounds. Subsequently, crystals were sealed in Lindemann glass capillaries and optically aligned on a PC2200-controlled Philips PW1100 diffractometer. Unit cell constants were determined from a least-squares analysis of the θ, χ, and ϕ angles of 19 reflections centered automatically, using graphite monochromated Cu Kα radiation. Relevant crystal data are given in Table I.

The diffraction data were collected at room temperature (20 ± 1°C). The takeoff angle was 4°. The intensities of three standard reflections were measured after intervals of 90 min. They varied less than 1.25% for I and 4.04% for II. These values are obtained using the expression

$$\left[\frac{\sum_{1}^{n} (\chi_n - \bar{\chi})^2}{n - 1} \frac{100}{\bar{\chi}} \right]^{1/2}$$

where χ_n and $\bar{\chi}$ are the number of counts of the *n*th measurement and the mean number of counts, respectively. The intensity data for the two compounds were reduced to relative squared amplitudes $(F_o)^2$ by application of standard Lorentz and polarization factors. Extinction and absorption effects were neglected for both data set.

Both structures were solved by direct methods. The structure factors were first put on an absolute scale by calculating the statistical distribution of the E values for all the reflections. This resulted in 510 reflections with E values greater than 1.5 for I (408 for II). The most consistent set of signs for these reflections was calculated using the