References and Notes

(1) Previous related papers on the biological uses of phosphazene polymers: H. R. Allcock, R. W. Allen, and J. P. O'Brien, *J. Am. Chem. Soc.*, **99**, 3984, 3987 (1977).

(2) Previous papers in the series: (a) H. R. Allcock, T. J. Fuller, K. Matsumura, and K. M. Smeltz, *Macromolecules*, **10**, 824 (1977); (b) H. R. Allcock, J. L. Schmutz, and K. M. Kosydar, *ibid.*, **11**, 179 (1978).

(3) Deceased 1974.

(4) Part of this work was taken from the Ph.D. Thesis of J. L. Schmutz, The Pennsylvania State University, 1976.

(5) J. P. Collman, C. M. Elliot, T. R. Halbert, and B. S. Tovrog, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 18 (1977).

(6) (a) J. P. Collman, R. R. Gagne, T. R. Halbert, J. C. Marchon, and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 7868 (1973); (b) J. P. Collman, R. R. Gagne, and C. A. Reed, *ibid.*, **96**, 2629 (1974); (c) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *ibid.*, **97**, 1427 (1975); (d) J. P. Collman, R. R. Gagne, and C. A. Reed, "Organo-Transition Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, p 329; (e) J. P. Collman, J. I. Brauman, and K. S. Suslick, *J. Am. Chem. Soc.*, **97**, 7185 (1975); (f) J. P. Collman and C. A. Reed, *ibid.*, **95**, 2048 (1973).

(7) (a) J. Almog, J. E. Baldwin, R. L. Dyer, and M. Peters, *J. Am. Chem. Soc.*, **97**, 226 (1975); (b) J. Almog, J. E. Baldwin, and J. Huff, *ibid.*, **97**, 227 (1975).

(8) (a) C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 5810 (1973); (b) *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2647 (1973); (c) W. S. Brinigar and C. K. Chang, *J. Am. Chem. Soc.*, **96**, 5595 (1974); (d) W. S. Brinigar, C. K. Chang, J. Geibel, and T. G. Traylor, *ibid.*, **96**, 5597 (1974); (e) C. K. Chang and T. G. Traylor, *Biochem. Biophys. Res. Commun.*, **62**, 719 (1975).

(9) O. Leal, D. A. Anderson, R. G. Bowman, F. Basolo, and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **97**, 5125 (1975).

(10) (a) J. H. Wang, *J. Am. Chem. Soc.*, **80**, 3168 (1958); (b) J. H. Wang, *Haematin Enzymes, Symp. Int. Union Biochem.*, **19**, 98 (1961).

(11) (a) E. Tsuchida, K. Honda, and H. Sata, *Biopolymers*, **13**, 2147 (1974); (b) E. Tsuchida, K. Honda, and E. Hasegawa, *Biochim. Biophys. Acta*, **393**, 483 (1975); (c) E. Tsuchida, E. Hasegawa, and K. Honda, *Biochem. Biophys. Res. Commun.*, **67**, 846 (1975); (d) E. Tsuchida, K. Honda, and H. Sata, *Inorg. Chem.*, **15**, 352 (1976).

(12) E. Bayer and G. Holzbach, *Angew. Chem., Int. Ed. Engl.*, **16**, 117 (1977).

(13) (a) A. H. Corwin and Z. Reyes, *J. Am. Chem. Soc.*, **78**, 2437 (1956); (b) A. H. Corwin and S. D. Bruck, *ibid.*, **80**, 4736 (1958).

(14) P. L. Anderson, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 5599 (1974).

(15) G. C. Wagner and R. J. Kassner, *J. Am. Chem. Soc.*, **96**, 5593 (1974).

(16) (a) J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.*, **95**, 5757 (1973); (b) J. Almog, J. E. Baldwin, R. C. Dyer, J. Huff, and C. J. Wilkerson, *ibid.*, **96**, 5600 (1974).

(17) H. R. Allcock, W. J. Cook, and D. P. Mack, *Inorg. Chem.*, **11**, 2584 (1972).

(18) (a) D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 4464 (1964); (b) D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc. A*, 1831 (1966).

(19) J. E. Falk, "Porphyrins and Metalloporphyrins", Elsevier, Amsterdam, 1964, p 81.

(20) J. O. Allen, W. H. Fuchsman, C. A. Beaudreau, and W. S. Caughey, *Biochemistry*, **7**, 624 (1968).

(21) M. J. Cowan, J. M. F. Drake, and R. J. P. Williams, *Discuss. Faraday. Soc.*, **27**, 217 (1959).

(22) C. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).

(23) G. Lang and W. Marshall, *Proc. Phys. Soc., London*, **87**, 3 (1966).

(24) T. S. Schwan, *J. Heterocycl. Chem.*, **4**, 633 (1967).

(25) J. Keilin, *Nature (London)*, **165**, 151 (1950).

(26) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).

Ligand Exchange in $TaX(\eta^4$-naphthalene$)(Me_2PC_2H_4PMe_2)_2$. The Pentagonal Bipyramid to Monocapped Trigonal Prism Traverse

J. O. Albright,[1a] **S. Datta,**[1a] **B. Dezube,**[1a] **J. K. Kouba,**[1a] **D. S. Marynick,**[1a]
S. S. Wreford,*[1b] **and Bruce M. Foxman***[1c]

Contribution from the Department of Chemistry, Harvard University,
Cambridge, Massachusetts 02138, and the Department of Chemistry, Brandeis University,
Waltham, Massachusetts 02154.

Received June 29, 1978

Abstract: Treatment of $TaCl_4(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with sodium naphthalene affords $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$, which is reduced by additional sodium naphthalene to an unisolated anion, $Na[Ta(\eta^4\text{-}C_{10}H_8)(dmpe)_2]$. Protonation or methylation of the anion gives $TaH(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ or $Ta(CH_3)(\eta^4\text{-}C_{10}H_8)(dmpe)_2$, respectively. Related procedures yield the analogous 1,3-cyclohexadiene adduct, $TaCl(\eta\text{-}C_6H_8)(dmpe)_2$. Exchange experiments suggest that the naphthalene unit and the bidentate phosphine are of similar lability, both being relatively inert. $TaH(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ is a poor hydrogenation catalyst. Crystals of the $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ compound are monoclinic, space group $P2_1/c$, with $a = 10.343$ (3) Å, $b = 10.281$ (3) Å, $c = 24.642$ (7) Å, $\beta = 97.39°$. Full-matrix least-squares refinement of positional and thermal parameters for all nonhydrogen atoms (including fixed H atom contributions) with 4019 data for which $F > 3.92\sigma(F)$ led to $R = 0.028$ and $R_w = 0.040$. The molecular structure of the complex may be considered to be an approximate pentagonal bipyramid, with Ta, 2P, Cl, and the midpoints of the η^4-olefin bonds forming the pentagonal plane (deviations $<\sim 0.2$ Å). The dihedral angle between the coordinated and uncoordinated portions of naphthalene is 43.0°. The naphthalene complexes undergo ^{31}P site exchange by a mechanism involving rotation of the diene unit. Formally, this corresponds to a pseudorotation exchanging axial and equatorial sites in the pentagonal bipyramid in a pairwise fashion. Activation parameters for the process in $Ta(CH_3)(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ are $\Delta H^{\ddagger} = 13.0 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = 1.0 \pm 0.9$ eu. These values are only approximate as they are based on the assumption that the rate of rotation of the diene over edges of the P_4 plane is the same for all edges.

Although seven-coordination is relatively rare for classical coordination compounds and for organometallic complexes of electron-rich transition metals, it is common for the electron-poor, early transition metals.[2] Since no regular polyhedron with seven vertices exists, a variety of structures are plausible. However, most (but not all) seven-coordinate complexes are derived by major or minor distortion from three idealized geometries—the monocapped octahedron (C_{3v}), the monocapped trigonal prism (C_{2v}), and the pentagonal bipyramid (D_{5h}).[2,3] The properties of seven-coordination (e.g., factors affecting structure, the relative energetics of the various structural types, and rearrangement mechanisms connecting the different geometries) may have consequences for the chemistry of the early transition metals. There is at least one explicit example of the stereochemistry of an octahedral isomerization reaction being controlled by the structure of a seven-coordinate intermediate.[4]

Earlier, in preliminary form, we reported the preparation, structure, and dynamics of $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), an approximate pen-

0002-7863/79/1501-0611$01.00/0

tagonal bipyramid.[5] The dynamic behavior of this compound was best explained by rotation of the 1,3-diene fragment, a mechanism which requires transit through an approximate monocapped trigonal prismatic geometry. Inasmuch as this represents one of the few examples of a fluxional seven-coordinate compound[6] with dynamics amenable to detailed analysis,[7] we report the details of the analysis and structural considerations. Further, the chemistry of these compounds is of interest, as they constitute members of the relatively rare class of η^4-arene complexes.[8]

Experimental Section

All manipulations were performed in vacuo or under an atmosphere of prepurified nitrogen. Methylene chloride and acetonitrile were purified by distillation from phosphorus pentoxide and calcium hydride, respectively; all other solvents were distilled from sodium benzophenone ketyl. 1-Dimethylphosphino-2-diethylphosphinoethane (dmdepe),[6l] $TaCl_2(dmpe)_2$,[9] $TaCl_4(dmpe)_2$,[9] and $MoCl_3\cdot 3THF$[10] were prepared by literature methods. 1-Octene, norbornadiene, and 1,3-cyclohexadiene were passed through an alumina column and distilled from sodium or phosphorus pentoxide prior to use. Sodium naphthalene was prepared by direct reaction and titrated immediately before use. All other materials were used as received from standard sources. ^1H NMR (100 MHz) and ^{31}P NMR (40.5 MHz), infrared, and mass spectra were obtained on Varian XL-100, Perkin-Elmer 457A, and AEI MS-9 spectrometers, respectively. ^{31}P NMR spin-tickling experiments were done as previously described.[7a] Line-shape calculations were performed on an IBM 360 computer using DNMR-3[11] modified locally and as described by Bushweller et al.[12] ^{31}P NMR chemical shifts are reported relative to external 85% phosphoric acid. Elemental analyses were performed by Alfred Bernhardt Microanalytische Laboratorium, West Germany.

TaCl(η^4-$C_{10}H_8$)(dmpe)$_2$ (3). To 14.3 g (23.0 mmol) of $TaCl_4(dmpe)_2$ dissolved in 150 mL of THF were added 25.0 g (195 mmol) of naphthalene and 68.8 mL of a 1.0 M solution of sodium naphthalene in THF. After stirring for 30 min, the solvent and excess naphthalene were removed in vacuo (70 °C, 1 μ). The red-brown residue was chromatographed on a silica column (2:1 THF/toluene eluent). The red fraction was evaporated to dryness and the residue recrystallized from toluene/hexane, affording 3.20 g (4.97 mmol, 21%) of **3** as red crystals: $^{31}P\{^1H\}$ NMR (toluene-d_8) ABCD pattern (−80 °C) δ_A −13.0, δ_B −14.2, δ_C −21.6, δ_D −25.5 ppm, (55 °C) (s) −18.6 ppm; mass spectrum *m/e* 644 $[^{12}C_{22}{}^1H_{40}{}^{35}Cl^{31}P_4{}^{181}Ta]^+$, 494 $[P - dmpe]^+$.

Anal. Calcd for $C_{22}H_{40}ClP_4Ta$: C, 40.67; H, 6.25. Found: C, 40.39; H, 6.24.

TaH(η^4-$C_{10}H_8$)(dmpe)$_2$ (5). **3** (387 mg, 0.601 mmol) dissolved in 40 mL of THF at 0 °C was treated with 2.3 mL of a 0.52 M solution of sodium naphthalene in THF. To the resulting dark brown solution was added 45 μL of cyclohexanol (1.20 mmol). Evaporation of the solvent and sublimation of the naphthalene (70 °C, 1 μ) left an orange residue. Recrystallization from toluene/hexane gave 252 mg (0.41 mmol, 68%) of **5** as orange crystals: $^{31}P\{^1H\}$ NMR (toluene-d_8) (−80 °C) $\delta_{A,B}$ −17.8, δ_C −23.9, δ_D −26.7 ppm, (20 °C) −20.8 (s) ppm; $^1H\{^{31}P\}$ NMR (toluene-d_8) (25 °C) τ 10.23 (s, 1 H), 9.03 (s, 12 H), 8.90 (br, 8 H), 8.81 (s, 12 H), 8.50 and 5.53 (A_2B_2, 4 H), 3.61 and 3.49 (A_2B_2, 4 H); mass spectrum *m/e* 610 $[^{12}C_{22}{}^1H_{41}{}^{31}P_4{}^{181}Ta]$, 460 $[P - dmpe]^+$.

Anal. Calcd for $C_{22}H_{41}P_4Ta$: C, 43.28; H, 6.77. Found: C, 43.01; H, 6.60.

Ta(CH$_3$)(η^4-$C_{10}H_8$)(dmpe)$_2$ (6). Similarly, 274 mg (0.425 mmol) of **3** was treated with 2 equiv of sodium naphthalene and 34 μL (0.42 mmol) of methyl fluorosulfonate. An analogous workup gave 166 mg (0.266 mmol, 62%) of **6**: $^1H\{^{31}P\}$ NMR (toluene-d_8) (40 °C) τ 11.58 (s, 3 H), 9.09 (s, 12 H), 8.97 (s, 12 H), 8.9 (br, 8 H), 8.49 and 6.06 (A_2B_2, 4 H), 3.42 and 3.54 (A_2B_2, 4 H); mass spectrum *m/e* 624 $[^{12}C_{23}{}^1H_{43}{}^{31}P_4{}^{181}Ta]^+$, 609 $[P - CH_3]^+$, 474 $[P - dmpe]^+$.

Anal. Calcd for $C_{23}H_{43}P_4Ta$: C, 44.24; H, 6.94. Found: C, 43.91; H, 6.80.

TaCl(η^4-C_6H_8)(dmpe)$_2$ (7). To 3.00 g (5.45 mmol) of $TaCl_2(dmpe)_2$ dissolved in 20 mL of THF were added 3.0 mL (31.5 mmol) of 1,3-cyclohexadiene and 35 mL of 1% Na/Hg. After stirring for 5 h the solution was decanted and centrifuged. Evaporation of the supernatant left a dark residue, which was extracted with 50 mL of hot hexane. The solids, which deposited on cooling the extract to −20 °C, were discarded. The supernatant was evaporated to dryness and the residue was dissolved in 15 mL of hexane. Cooling to −20 °C afforded 370 mg (0.62 mmol, 11%) of **7** as red crystals: $^{31}P\{^1H\}$ NMR (toluene-d_8) ABCD pattern (−80 °C) δ_A −15.5, δ_B −13.5, δ_C, δ_D −8.1 ppm, (20 °C) (s) −12.7 ppm; mass spectrum *m/e* 596.1249 $[P]^+$ (calcd for $[^{12}C_{18}{}^1H_{40}{}^{35}Cl^{31}P_4{}^{181}Ta]^+$, 596.1246), 446 $[P - dmpe]^+$; $^1H\{^{31}P\}$ NMR (toluene-d_8) (30 °C) τ 8.68 (s, 12 H), 8.48 (s, 12 H), 8.28 (br, m, 12 H), 8.16 and 6.24 (A_2B_2, 4 H).

The material was contaminated with an unidentified compound with a parent ion at *m/e* 592. Further crystallization did not improve the purity. Similar reactions with other dienes gave this unidentified product exclusively (on the basis of mass spectroscopy).

[MoI(η^4-C_7H_8)(dmpe)$_2$]I (8). $MoCl_3\cdot 3THF$ (3.45 g 8.25 mmol), 2.5 g (17 mmol) of dmpe, and 5.0 mL (50 mmol) of norbornadiene were combined with 200 g of 0.75% Na/Hg in 100 mL of THF and shaken for 3 h. The supernatant was decanted, filtered, and evaporated to dryness. The resulting brown residue was crystallized from ether, affording 0.94 g of a bright yellow solid, whose mass spectrum was consistent with the formulation $Mo(C_7H_8)(dmpe)_2$ (*m/e* 490 $[^{12}C_{19}{}^1H_{40}{}^{31}P_4{}^{98}Mo]^+$, 398 $[P - C_7H_8]^+$, 340 $[P - dmpe]^+$).

The yellow solid was dissolved in 20 mL of CH_2Cl_2 and treated at −78 °C with 501 mg (1.97 mmol) of I_2 in 15 mL of CH_2Cl_2. After warming to room temperature and evaporation of the solvent, the brown residue was washed with a little cold CH_2Cl_2/CH_3CN, affording 920 mg of **8** as pale orange crystals: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) AA′BB′ pattern δ_A 9.5, δ_B 29.6 ppm.

Anal. Calcd for $C_{19}H_{40}I_2MoP_4$: C, 30.74; H, 5.43. Found: C, 30.63; H, 5.45.

Exchange Reactions with 3. **3** (270 mg, 0.42 mmol), 276 mg (2.03 mmol) of naphthalene-d_8, and 3.0 mL of toluene were combined in a sealed tube. The tube was heated at 120 °C for 12 h, cooled, and opened. Evaporation of the volatile components and mass spectroscopic analysis of the residue indicated that **3** and TaCl(η^4-$C_{10}D_8$)(dmpe)$_2$ were present in the ratio 9:1.

Similarly, 352 mg (0.546 mmol) of **3** and 1.0 mL (5.0 mmol) of dmdepe were heated at 120 °C for 12 h. Mass spectroscopic analysis indicated **3** and TaCl(η^4-$C_{10}H_8$)(dmpe)(dmdepe) in the ratio 3:7 and a trace of TaCl(η^4-$C_{10}H_8$)(dmdepe)$_2$.

Hydrogenation of Octene with 5. In a representative experiment, 3.1 mL (39 mmol) of 1-octene and 49 mg (0.08 mmol) of **5** were heated at 93 °C for 24 h with 200 psi of hydrogen in a 50-mL Hoke bomb. GLC analysis (8 ft, 10% Carbowax 20M column) of the solution indicated a 0.084/1.000 (octane/octene) mixture, corresponding to 1.6 turnovers/h.

Collection and Reduction of Diffraction Data. Clear, orange prismatic crystals were grown by slow crystallization from toluene/hexane, mounted in capillary tubes, and sealed under nitrogen. Lauē photographs (Kodak No-Screen) of the crystal chosen for data collection (0.16 × 0.24 × 0.42 mm) indicated it to be of excellent quality. The crystal was transferred to a Super No. 455 goniometer and centered optically on a Syntex P2$_1$ diffractometer. The coordinates of 25 reflections recorded on a normal-beam, flat-film rotation photograph[13] were converted to diffractometer coordinates. Preliminary unit-cell parameters were established[14] from (1) the 2θ, ω, ϕ, and χ values obtained from an automatic centering routine, (2) "autoindexing", a procedure for generating real space vectors which are possible unit cell axes, and (3) least-squares refinement of cell and orientation parameters. Partial rotation photographs about the three-cell axes and rapid collection of a small data set ($2\theta < 18°$) indicated that the crystal was monoclinic, space group, $P2_1/c$. This was confirmed by inspection of the final data set. Most operations were carried out as described previously;[15] other operations are reported below. Details of the structure analysis, in outline form, are given in Table I. All operations and refinements were carried out using locally modified versions of the machine-language or FORTRAN diffractometer programs,[15] and the Syntex XTL structure determination system (24K Nova configuration).[16]

Intensity data were corrected for absorption by an empirical method. Several $0\bar{k}0$ reflections ($\chi = 73°$, Table IC) were measured at rotation intervals of 10° about the diffraction vector (from $\psi = 0$ to 350°). A set of normalized absorption curves, interpolated in ϕ, were derived and checked for consistency. There was little variation from curve to curve in (a) the positions of maxima and minima and (b) the ratio of maximum and minimum values.

Solution and Refinement. The analytical scattering factors of Cromer and Waber were used;[17a] real and imaginary components of

Table I. Data for the X-ray Diffraction Study of TaCl(η^4-$C_{10}H_8$)-($Me_2PC_2H_4PMe_2$)$_2$

A. Crystal Data at 23 (1) °C

crystal system:	monoclinic	$V = 2598.7$ Å^3
space group:	$P2_1/c$ [$C_{2h}{}^5$; no. 14]	$Z = 4$
$a =$	10.343 (3) Å	
$b =$	10.281 (3) Å	mol wt 644.9
$c =$	24.642 (7) Å	ρ (calcd) 1.648 g cm^{-3}
$\beta =$	97.39 (1)°	μ (calcd) 48.1 cm^{-1}

cell constant determination: 7 pairs of $\pm(khl)$ and refined 2θ, ω, ϕ, and ψ values in the range $45 < |2\theta| < 50°$ [λ(Mo K$\bar{\alpha}$ = 0.710 69 Å)]

B. Measurement of Intensity Data

radiation:	Mo Kα, highly oriented graphite monochromator
reflections measured:	$\pm h$, $-k$, $+l$ (to $2\theta = 50°$)
scan type; speed:	θ–2θ; variable, 1.95–4.88°/min
scan range:	from 0.7° below the Kα_1 peak to 0.9° above the Kα_2 peak
background measurement:	stationary, for one-quarter of scan time at each of scan limits
no. of reflections measured:	5305 total; 4614 in unique set
standard reflections:	800, 008, $0\bar{6}5$, measured after every 65 reflections; deviation $< \pm 3\sigma(I)$ for each

C. Treatment of Intensity Data[a]

absorption correction:	empirical; normalized transmission factors 0.639–1.000, based on 020, 040, 080, 0120 reflections
data reduction:	intensities, derived structure amplitudes, and estimated standard deivations as before[15]
statistical information:	$R_s = 0.012$ ($I > 1.96$ (I)); $R_{av} = 0.021$ ($kh0$ reflections)

D. Refinement,[b] with 4019 Data for Which $F > 3.92\sigma(F)$

weighting of reflections:	$w = [\sigma^2(\|F_o\|) + (\rho\|F_o\|)^2]^{-1}$; $\rho = 0.030$
Patterson solution:	Ta, $R = 0.354$
isotropic refinement, all nonhydrogen atoms:	$R = 0.048$; $R_w = 0.074$
anisotropic refinement, all nonhydrogen atoms:	$R = 0.036$; $R_w = 0.057$
anisotropic refinement, all atoms, extinction correction:	$R = 0.028$; $R_w = 0.040$
structure factor calculation, all 4614 data:	$R = 0.034$; $R_w = 0.042$
standard deviation of an observation of unit weight (SDU):	1.114
final difference map:	0.55 e/Å^3 near C13, C14; several peaks ~0.4 e/Å^3 near methyl carbon atoms; other peaks random and <0.34 e/Å^3

[a] $R_s = \Sigma\sigma(F_o)/\Sigma|F_o|$; $R_{av} = [(\Sigma||I| - |I_{av}||)/\Sigma|I|]$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o| - |F|]^2/\Sigma\omega|F_o|^2\}^{1/2}$. SDU = $\{\Sigma w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (= 4019) is the number of observations and n (= 253) is the number of parameters.

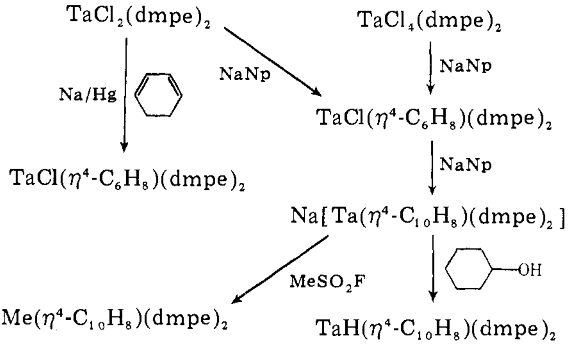
anomalous scattering were included in the calculations for Ta, P, and Cl.[17b] At the conclusion of anisotropic refinement of all nonhydrogen atoms, a difference Fourier synthesis revealed the positions of *all* hydrogen atoms. These were not used directly, but were used in the following manner to determine calculated positions for the hydrogen atoms. The program HPOSN[16] was used to generate "tetrahedral" positions for the methylene protons and idealized, in-plane positions for the naphthalene protons. The program METHYL[18] was used to generate positions for methyl H atoms at 10° intervals about the P–C bond axes. Calculated H atom positions were then selected, which were the "best fit" to a given set of three observed proton positions. The hydrogen atoms were included as fixed contributions to F_c (with C–H = 0.95 Å) in subsequent cycles of least-squares refinement. The calculation procedure above was repeated after each cycle of refinement. All data were corrected for secondary extinction by applying an empirical correction of the form $|F_o|\mathrm{cor} = |F_o|(1.0 + gI_o)$ where g (determined graphically) = 2.43×10^{-7}. At convergence [$(\Delta/\sigma)_{max} \leq 0.01$], a weighting scheme analysis revealed no systematic dependence of $\omega[|F_o| - |F_c|]^2$ on $|F_o|$, Miller indices, or sequence number. For several reflections with $\sin\theta/\lambda \leq 0.100$, the values of $\omega[|F_o| - |F_c|]^2$ were significantly higher; this may be due to primary extinction, neglect of anisotropy in the secondary extinction correction, and/or inadequacies in the empirical absorption correction. Table II lists the positional and anisotropic thermal parameters for all nonhydrogen atoms. Table III, available as supplementary material, lists positional and isotropic thermal parameters for hydrogen atoms.

Results and Discussion

Preparation of Compounds. As outlined in Scheme I, treatment of $TaCl_4(dmpe)_2$ (**1**) or $TaCl_2(dmpe)_2$ (**2**) with 3 or 1 equiv, respectively, of sodium naphthalene in the presence of excess naphthalene affords TaCl(η^4-$C_{10}H_8$)(dmpe)$_2$ (**3**). As previously reported, in the presence of 1 atm of CO, this reduction leads to $TaCl(CO)_2(dmpe)_2$.[9] However, in the presence of ethylene or other monoenes, only **3** is formed. Presumably, simple olefins do not compete effectively with naphthalene in trapping the Ta(I) intermediate formed on reduction, whereas CO does. Under these conditions, naphthalene is not displaced from **3** by CO. Treatment of **3** with an additional 2 equiv of sodium naphthalene gives a highly air-sensitive, dark brown solution, presumably containing Na[Ta(η^4-$C_{10}H_8$)(dmpe)$_2$] (**4**), isoelectronic with cis-octahedral $Na[Ta(CO)_2(dmpe)_2]$[9] and $Mo(CO)_2(dmpe)_2$.[19] Attempts to observe a Ta(0) intermediate by ESR monitoring during the reduction were unsuccessful. **4** was protonated by cyclohexanol, giving TaH(η^4-$C_{10}H_8$)(dmpe)$_2$ (**5**). Cyclohexanol generally gave better yields than other protonating agents, as **5** is inert to excess cyclohexanol, but not to strong acids, water, or primary alcohols. Similarly, treatment of **4** with 1 equiv of $MeOSO_2F$ gave TaMe(η^4-$C_{10}H_8$)(dmpe)$_2$ (**6**). Methyl iodide or bromide gave mixtures of **6** and TaI(η^4-$C_{10}H_8$)(dmpe)$_2$ or TaBr(η^4-$C_{10}H_8$)(dmpe)$_2$, respectively, as determined by mass spectroscopy. The latter products likely arise by one-electron oxidation of **4** and halogen abstraction by the resulting Ta(O) complex. Similar oxidations of $Mo(CO)_2(dmpe)_2$ by halocarbons have been shown to proceed through $[Mo(CO)_2(dmpe)_2]^+$.[20]

Since conjugated dienes are rapidly polymerized by sodium naphthalene,[21] other diene complexes were not accessible by this technique. Poor yields of TaCl(η-C_6H_8)(dmpe)$_2$ (**7**) could be obtained by sodium amalgam reduction of **2** in the presence of 1,3-cyclohexadiene (Scheme I). **7** could not be obtained in analytically pure form; it was contaminated by an unidentified product which was not removed by repeated crystallizations.

Scheme I



Np = naphthalene

Table II. Atomic Coordinates and Anisotropic Temperature Factors (Å^2) for TaCl(η^4-$C_{10}H_8$)(dmpe)$_2$^{a}

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	0.304 01 (2)	0.294 16 (2)	0.383 86 (1)	0.024 45 (12)	0.023 31 (13)	0.023 06 (13)	0.000 30 (7)	0.004 09 (8)	−0.002 75 (8)
P1	0.553 38 (13)	0.235 09 (14)	0.394 59 (6)	0.031 01 (68)	0.040 63 (75)	0.034 48 (73)	0.006 52 (56)	0.004 78 (55)	−0.003 30 (60)
P2	0.400 85 (13)	0.454 35 (14)	0.318 97 (6)	0.038 47 (69)	0.033 30 (70)	0.034 53 (73)	−0.002 39 (55)	0.007 51 (56)	0.003 74 (57)
P3	0.209 06 (13)	0.074 73 (13)	0.408 91 (6)	0.039 06 (70)	0.026 47 (66)	0.039 13 (76)	−0.002 68 (53)	0.006 86 (57)	−0.000 13 (56)
P4	0.078 67 (13)	0.292 91 (13)	0.322 13 (6)	0.032 09 (68)	0.034 72 (74)	0.039 14 (77)	−0.000 16 (52)	−0.002 64 (56)	−0.000 91 (59)
Cl	0.341 91 (13)	0.142 83 (13)	0.303 07 (5)	0.046 08 (69)	0.039 96 (71)	0.033 91 (67)	0.002 70 (56)	0.009 77 (54)	−0.010 48 (56)
C1	0.145 34 (44)	0.389 38 (49)	0.435 20 (20)	0.0278 (23)	0.0346 (26)	0.0315 (26)	0.0035 (20)	0.0079 (19)	−0.0051 (22)
C2	0.242 35 (52)	0.481 58 (48)	0.420 80 (21)	0.0515 (31)	0.0247 (25)	0.0330 (28)	0.0077 (22)	0.0096 (23)	−0.0039 (21)
C3	0.370 26 (48)	0.449 71 (50)	0.444 77 (21)	0.0382 (26)	0.0347 (27)	0.0316 (27)	−0.0068 (22)	0.0083 (21)	−0.0034 (22)
C4	0.379 13 (47)	0.333 44 (52)	0.477 25 (21)	0.0289 (24)	0.0400 (27)	0.0313 (27)	0.0029 (21)	−0.0002 (21)	−0.0034 (22)
C5	0.282 79 (50)	0.316 91 (46)	0.515 27 (21)	0.0389 (27)	0.0265 (25)	0.0324 (28)	0.0026 (20)	0.0063 (22)	−0.0075 (21)
C6	0.305 54 (59)	0.273 62 (57)	0.569 65 (23)	0.0522 (33)	0.0458 (34)	0.0320 (30)	0.0064 (25)	0.0031 (25)	−0.0011 (25)
C7	0.205 15 (68)	0.262 26 (68)	0.600 42 (25)	0.0842 (50)	0.0477 (36)	0.0335 (32)	−0.0051 (34)	0.0167 (32)	−0.0039 (29)
C8	0.078 40 (70)	0.296 49 (57)	0.578 95 (28)	0.0645 (41)	0.0490 (37)	0.0471 (37)	−0.0033 (28)	0.0298 (32)	−0.0059 (29)
C9	0.054 70 (53)	0.341 70 (54)	0.524 93 (24)	0.0438 (29)	0.0351 (28)	0.0475 (34)	0.0048 (23)	0.0179 (25)	−0.0061 (25)
C10	0.154 83 (48)	0.350 08 (49)	0.493 34 (21)	0.0392 (27)	0.0294 (26)	0.0322 (27)	0.0017 (21)	0.0066 (21)	−0.0050 (21)
C11	0.620 74 (58)	0.298 30 (59)	0.334 34 (27)	0.0378 (31)	0.0607 (40)	0.0509 (37)	0.0010 (25)	0.0154 (27)	0.0004 (29)
C12	0.579 95 (54)	0.441 56 (62)	0.325 33 (26)	0.0416 (30)	0.0522 (35)	0.0576 (38)	−0.0040 (26)	0.0150 (27)	0.0152 (30)
C13	0.064 35 (64)	0.038 83 (65)	0.359 63 (29)	0.0634 (40)	0.0479 (37)	0.0652 (45)	−0.0210 (31)	−0.0003 (33)	−0.0016 (32)
C14	−0.019 11 (56)	0.158 87 (69)	0.345 98 (32)	0.0330 (30)	0.0586 (40)	0.0850 (51)	−0.0079 (28)	−0.0099 (30)	0.0097 (38)
C15	0.671 84 (57)	0.304 64 (65)	0.448 61 (29)	0.0294 (29)	0.0795 (49)	0.0585 (42)	0.0029 (27)	−0.0027 (27)	−0.0141 (34)
C16	0.610 86 (60)	0.066 00 (62)	0.397 11 (27)	0.0579 (37)	0.0486 (35)	0.0542 (38)	0.0202 (29)	0.0982 (30)	0.0013 (30)
C17	0.358 07 (65)	0.448 55 (68)	0.244 60 (25)	0.0724 (42)	0.0619 (41)	0.0389 (34)	−0.0122 (33)	0.0128 (30)	0.0088 (30)
C18	0.383 19 (64)	0.629 68 (57)	0.327 14 (29)	0.0693 (41)	0.0305 (30)	0.0700 (44)	−0.0072 (28)	0.0127 (33)	0.0035 (30)
C19	0.297 57 (70)	−0.078 36 (65)	0.403 28 (36)	0.0763 (48)	0.0389 (36)	0.1001 (58)	0.0042 (31)	0.0391 (43)	0.0903 (36)
C20	0.149 24 (66)	0.041 26 (63)	0.473 54 (27)	0.0719 (41)	0.0462 (35)	0.0523 (38)	−0.0064 (31)	0.0284 (32)	0.0008 (29)
C21	−0.033 93 (58)	0.431 39 (64)	0.317 86 (29)	0.0430 (32)	0.0558 (39)	0.0699 (45)	0.0141 (28)	−0.0072 (30)	0.0028 (33)
C22	0.064 39 (64)	0.257 17 (83)	0.248 29 (29)	0.0534 (38)	0.0788 (45)	0.0477 (38)	0.0005 (36)	−0.0112 (30)	−0.0178 (36)

^{a}Standard deviations in the least significant digit appear in parentheses in this and subsequent tables. The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2b^*c^*U_{23}kl)]$.

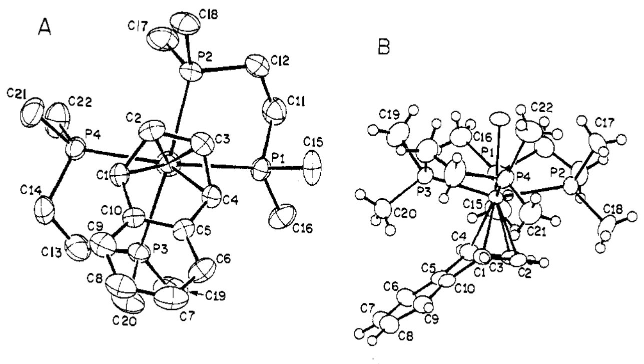


Figure 1. Complementary views of TaCl(η^4-$C_{10}H_8$)(dmpe)$_2$, (A) viewed along the Ta-Cl vector and (B) oriented to show the crowded environment of the coordinated naphthalene moiety.

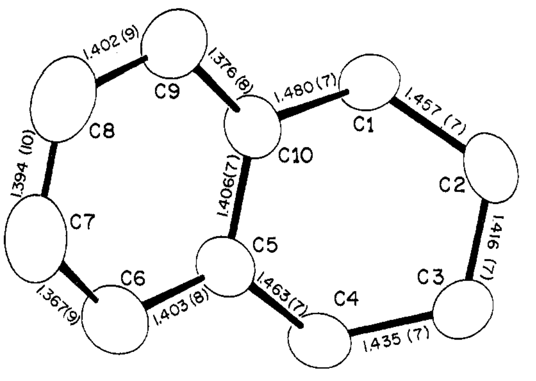


Figure 2. Bond lengths in the η^4-naphthalene unit.

Correct high-resolution mass spectral, ^{31}P, and ^{1}H NMR data were observed, however. Analogous preparations using norbornadiene, 1,5-cyclooctadiene, and other dienes led exclusively to the unidentified product.

The isoelectronic Mo(II) norbornadiene complex, [MoI(η-C_7H_8)(dmpe)$_2$]I (**8**), was prepared as in eq 1.

$$\begin{array}{c} \mathrm{MoCl_3\cdot 3THF + dmpe + norbornadiene} \\ \big\downarrow \mathrm{Na/Hg} \\ \mathrm{Mo(\eta\text{-}C_7H_8)(dmpe)_2} \xrightarrow[\mathrm{I_2}]{} [\mathrm{MoI(\eta\text{-}C_7H_8)(dmpe)_2}]\mathrm{I} \end{array} \quad (1)$$

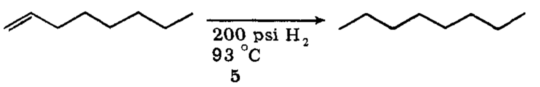
Attempts to exchange the naphthalene in **3** with other dienes were not successful but, rather, led to degradation. Subsequently, mass spectroscopic monitoring of exchange reactions of **3** with naphthalene-d_8 and dmdepe suggested that the bidentate phosphine and naphthalene units were of similar lability (eq 2 and 3).

$$\underset{1:5}{\mathbf{3} + \mathrm{C_{10}D_8}} \xrightarrow{\Delta} \underset{9:1}{\mathbf{3} + \mathrm{TaCl(\eta^4\text{-}C_{10}D_8)(dmpe)_2}} \quad (2)$$

$$\begin{array}{lr} \underset{1:9}{\mathbf{3} + \mathrm{dmdepe}} \xrightarrow{\Delta} \mathbf{3} & 3: \\ \qquad + & \\ \qquad \mathrm{TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)(dmdepe)} & 7: \\ \qquad + & \\ \qquad \mathrm{TaCl(\eta^4\text{-}C_{10}H_8(dmdepe)_2} & \mathrm{trace} \end{array} \quad (3)$$

The exchanges indicated in eq 2 and 3 were accompanied by substantial decomposition.

5 catalyzed the hydrogenation of 1-octene as indicated in eq 4. The conditions required and rate (1.6 turnovers/h) render



(4)

5 an unexceptional hydrogenation catalyst. The hydrogenation of benzene or D_2/C_6H_6 exchange is not catalyzed by **5** as it is, in the former case, by other η^4-arene complexes[8] or, in the latter instance, by TaH$_5$(dmpe)$_2$.[22] The poor activity is likely an effect of the stability of the η^4-naphthalene-Ta bond.

Treatment of **3** with 1 equiv of anydrous HCl resulted in hydrogen evolution and formation of oxidized tantalum

Table IV. Selected Bond Lengths, Bond Angles, and Least-Squares Planes[a]

A. Bond Lengths

Ta-Cl	2.596 (1)	P1-C11	1.838 (7)
Ta-P1	2.630 (1)	P2-C12	1.844 (6)
Ta-P2	2.585 (1)	P3-C13	1.840 (7)
Ta-P3	2.567 (1)	P4-C14	1.850 (7)
Ta-P4	2.614 (1)	P1-C15	1.835 (7)
Ta-C1	2.405 (5)	P1-C16	1.836 (7)
Ta-C2	2.258 (5)	P2-C17	1.834 (6)
Ta-C3	2.240 (5)	P2-C18	1.825 (6)
Ta-C4	2.367 (5)	P3-C19	1.839 (7)
Ta-Cent 1	2.216 (7)	P3-C20	1.814 (7)
Ta-Cent 2	2.190 (7)	P4-C21	1.843 (7)
C11-C12	1.540 (9)	P4-C22	1.844 (7)
C13-C14	1.519 (10)		

B. Bond Angles

Cl-Ta-P1	72.29 (4)	C1-C2-C3	112.6 (4)
P1-Ta-Cent 2	78.74 (19)	C2-C3-C4	114.5 (5)
Cent 1-Ta-Cent 2	53.80 (27)	C3-C4-C5	117.0 (5)
Cent 1-Ta-P4	79.20 (19)	C4-C5-C10	114.3 (5)
P4-Ta-Cl	76.23 (4)	C5-C10-C1	112.4 (4)
P1-Ta-P2	75.90 (4)	C10-C1-C2	116.8 (4)
P3-Ta-P4	78.21 (4)	C5-C6-C7	120.7 (6)
P1-Ta-P4	147.87 (4)	C6-C7-C8	120.8 (6)
P2-Ta-P3	154.04 (4)	C7-C8-C9	119.0 (6)
Ta-P1-C15	122.5 (2)	C8-C9-C10	120.4 (5)
Ta-P1-C16	122.1 (2)	C9-C10-C5	120.5 (5)
Ta-P2-C17	120.6 (2)	C10-C5-C6	118.6 (5)
Ta-P2-C18	120.6 (2)		
Ta-P3-C19	121.8 (3)	Ta-P1-C11	107.8 (2)
Ta-P3-C20	124.2 (2)	Ta-P2-C12	111.5 (2)
Ta-P4-C21	122.8 (2)	Ta-P3-C13	108.8 (2)
Ta-P4-C22	121.9 (2)	Ta-P4-C14	107.6 (2)

C. Least-Squares Planes[b]

plane no. 1, equation:

$$0.2282X - 0.05444Y - 0.8072Z + 10.7333 = 0$$

atoms in plane: C1, C2, C3, C4

distances:	C1	−0.002 (5)	C3	−0.005 (5)
	C2	0.005 (5)	C4	0.003 (5)

plane no. 2, equation:

$$-0.1200X - 0.9454Y - 0.3031Z + 7.0497 = 0$$

atoms in plane: C1, C4, C5, C6, C7, C8, C9, C10

distances:	C1	0.027 (5)	C7	0.027 (7)
	C4	−0.015 (5)	C8	0.002 (6)
	C5	0.002 (5)	C9	−0.028 (6)
	C6	0.008 (10)	C10	−0.012 (5)

plane no. 3, equation:

$$0.2971X + 0.8063Y - 0.5115Z + 1.7836 = 0$$

atoms in plane: Ta, P1, P4, Cl, Cent 1, Cent 2

distances:	Ta	−0.0031 (2)	Cl	−0.055 (1)
	P1	0.129 (2)	Cent 1	0.237 (7)
	P4	0.124 (2)	Cent 2	−0.015 (7)

[a] Cent 1 is the midpoint of the C1-C2 vector; Cent 2 is the midpoint of the C3-C4 vector. [b] Orthogonal coordinates X, Y, Z used in these calculations were derived as described in B. M. Foxman and H. Mazurek, *Inorg. Chem.*, in press.

products. **5** could be recovered unchanged after stirring with MeLi, PhLi, or $NaBH_4$ or after refluxing (THF, 12 h) with $K[B(\textit{sec}\text{-}Bu)_3H]$.

Structure Description. The molecular structure of **3** is shown in Figure 1. Tantalum resides in an approximate pentagonal bipyramidal environment where the ligated 1,3-diene portion of naphthalene, Cl, P1, and P4 form the equatorial ligand set and P2 and P3 are the apical ligands. Selected bond lengths, angles, and least-squares planes are listed in Table IV and Figure 2.

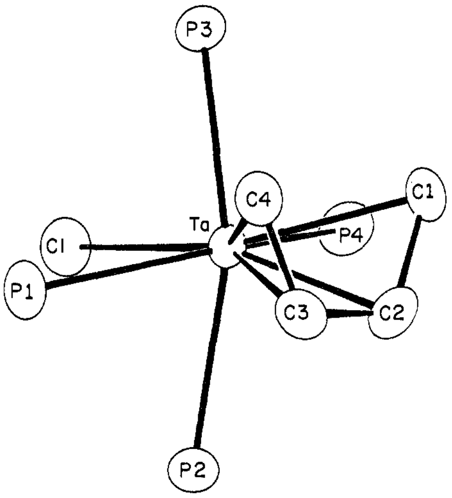


Figure 3. Inner coordination sphere of $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$, emphasizing the idealized D_{5h} symmetry and the near planarity of atoms Ta, P1, P4, Cl, and midpoints of the C1-C2, C3-C4 bonds.

The inner coordination sphere about tantalum, depicted in Figure 3, shows minor deviations from the pentagonal plane defined by the midpoints of the Cl-C2 and C3-C4 vectors and the remaining ligands indicated in the figure, the maximum deviation being 0.24 Å (Table IV). The equatorial ligand-Ta-equatorial ligand angles are near the 72° expected for a pentagonal bipyramid, excepting that subtended by the chelating diene, 53.8°. The bite angle of the 1,3-diene is somewhat smaller than those for more typical olefin complexes, e.g., 61.6° for a substituted η^4-cyclohexadiene-$Fe(CO)_3$ complex[23] and 59.7° for $IrH(\eta\text{-}C_4H_6)[P(i\text{-}C_3H_7)_3]_2$,[24] a consequence of the relatively long Ta-carbon bonds (>2.24 Å). The apical phosphorus atoms are tipped 17.6 (P2) and 15.0° (P3) from the normals to the equatorial plane, a result of the small bite angle required by the dmpe ligand. The bite angles of the dmpe ligands, 75.9 and 78.2°, fall within the range observed for all other dmpe complexes, 75.3-85.4° (Table V), and are similar to those values reported for other Ta-dmpe complexes. The Ta-equatorial P and axial P distances are substantially different; the equatorial bond lengths are ca. 0.05 Å longer than the apical distances. The conformations of the dmpe chelate rings are similar to other dmpe complexes,[25] and the internal P-C-C and C-P-C angles are normal.

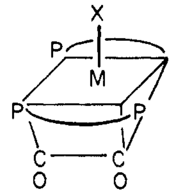
The naphthalene ligand, depicted in Figure 2, contains a "fixed" butadiene group bound to tantalum. The angle between the planes defined by the four carbon atoms of the complexed diene and uncomplexed benzene ring is 43.0°. Other structurally characterized η^4-arene complexes have similar dihedral angles—47.9° for $(\eta\text{-}C_5H_5)Rh[\eta^4\text{-}C_6(CF_3)_6]$,[27] 37.4° for the bis(iron tricarbonyl) complex of 3,α-dimethylstyrene,[28] 42.8° for $Ru(\eta\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$,[29] 42.0° for $Rh(C_9H_7F_6O_2)(\eta^4\text{-}C_6(CF_3)_6)$,[30] and 43.0° for $Fe(CO)_3(\eta^4\text{-}C_6Me_4(CF_3)_2)$.[31] The C2-Ta and C3-Ta bonds are more than 0.1 Å shorter than the C1-Ta and C4-Ta distances, a pattern previously established for $Fe(CO)_3$(1,3-diene) complexes.[23] The C2-C3 distance, 1.416 (7) Å, is shorter than the C1-C2 (1.457 (7) Å) and C3-C4 (1.435 (7) Å) distances; however, the differences are relatively small on a statistical basis, and follow the patterns established for Fe-diene complexes.[23] The structural parameters found for the complexed diene portion of the arene suggest that the π-accepting interaction is substantial,[23,31,32] a hypothesis consistent with the substitutional inertness of the Ta-naphthalene unit (vide supra). The C-C distances in the uncoordinated benzene fragment are normal.[33] The two C-C bonds connecting the diene and aromatic portions of the naphthalene ligand (C1-C10 = 1.480 (7), C4-C5 = 1.463 (7) Å) are elongated to the point of a typical $C(sp^2)$-$C(sp^2)$ linkage, 1.465 Å.[34] The C-C-C angles in the complexed portion of the naphthalene are all significantly smaller than 120° (Table IV).

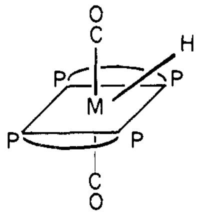
Table V. Comparative Structural Data for dmpe–Metal Complexes

compd	bite angle, deg	M–P distance, Å
$[(\eta\text{-}C_5H_5)_2Ta(dmpe)\text{-}Cl^{25}\cdot CH_3CN$	77.21 (4)	2.535^b
$TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$	78.21 (4)	2.585 (1) 2.630 (1)
	75.90 (4)	2.614 (1) 2.567 (1)
$TaH(CO)_2(dmpe)_2{}^{6f,a}$	75.8	2.497 2.530
$\{Ta[H_2Al(OC_2H_4OCH_3)_2]\text{-}(dmpe)_2\}_2{}^{26}$	76.8^b	2.51^b
$RuH(\sigma\text{-}C_{10}H_7)(dmpe)_2{}^{35}$	82.5 (1)	2.333 (3) 2.303 (3)
	85.4 (1)	2.280 (3) 2.301 (3)
$OsH(\sigma\text{-}C_{10}H_7)(dmpe)_2{}^{35}$	82.4 (2)	2.325 (6) 2.397 (5)
	84.9 (2)	2.285 (5) 2.301 (5)
$[Ru(dmpe)_2]_2{}^{36,c}$	85.0^d	2.321^d 2.262^d
	85.1^d	2.302^d 2.309^d
$[Mo(\eta\text{-}C_6H_3(CH_3)_3)\text{-}(dmpe)]_2(N_2)^{37}$	79.4 (1)	2.402^b
$WI_2(CO)_3(dmpe)^{38}$	75.3^e	2.506^e 2.569^e

[a] Because of extensive disorder, these values are probably of low accuracy.[6f] [b] Average values. [c] This compound is not a simple adduct; one of the dmpe methyl groups is metalated. [d] Averaged over two crystallographically independent molecules. [e] Averaged over five crystallographically independent molecules.

Compounds of the general formula $MX(CO)_2$(bidentate phosphine)$_2$ (M = Mo(II), W(II), Ta(I)) have monocapped trigonal prismatic structures when X is halogen, alkyl, or pseudohalogen and monocapped octahedral structures for X = H.[9] For example, $[Mo(diars)_2(CO)_2Cl]I_3$ (diars = *o*-phenylenebis(dimethylarsine)),[39] $TaX(CO)_2(dmpe)_2$ ($X \neq H$),[9] and $MoX(CO)_2(dmpe)_2{}^+$ ($X \neq H$)[61,19] have capped trigonal prismatic structures on the basis of crystallographic and spectroscopic evidence, respectively. However, $TaH(CO)_2(dmpe)_2$[6f] and $MH(CO)_2(L\text{-}L)_2{}^+$ (M = Cr,[40] Mo,[7a,19] W;[40,41] L-L = bidentate group V donor) have monocapped octahedral structures on the basis of crystallographic and spectroscopic data, respectively. **3** is structurally related to $TaCl(CO)_2(dmpe)_2$ by rotation of the naphthalene unit about the Ta–Cl vector; rotation by ca. 45° produces a capped trigonal prism analogous to the carbonyl complex (see Figure 1). Inasmuch as **3** is isoelectronic with $TaCl(CO)_2(dmpe)_2$, the pentagonal bipyramidal geometry of **3** must be a consequence of the replacement of the two carbonyl groups by the 1,3-diene ligand. This conformation is favored on electronic grounds as it allows overlap of the highest valence π^* level of the butadiene unit (i.e., ψ_4) with the filled d orbital directed at the edges of the P_4 plane (a δ interaction).[42] The barrier to rotation of the diene (vide infra) arises from breaking of the δ overlap as well as steric effects.





Some estimate of the steric interactions which might arise during a rotation of the naphthalene ring may be deduced from inspection of nonbonded contacts and the "edge-on" view of the molecule in Figure 1. Nonbonded contacts less than 3.4 Å are Cl-C21, C2-C18, and C5-C20, each 3.26 Å; and C4-C15 and C10-C20, each 3.21 Å. Clearly, during a rotation, these important interactions may become more severe, and other interactions may arise to C15, C18, C20, and C21.

Dynamics. At low temperatures **3, 5,** and **6** exhibit ABCD ^{31}P NMR spectra, consistent with the lack of symmetry found for **3** in the solid state. The cyclohexadiene adduct, **7**, has a similar spectrum. These data, together with the ^1H NMR evidence presented below, imply that **5, 6,** and **7** have approximate pentagonal bipyramidal structures, closely related to that of **3**. In each case, warming collapses the ^{31}P NMR resonances to a single line, establishing a process which equilibrates phosphorus environments (e.g., Figure 4).

The temperature-dependent ^1H NMR spectra for **3** are similar to those for **5, 6,** and **7**; **3** is discussed as a representative example. In the low-temperature limit (Figure 5, −50 °C), each dmpe methyl resonance is distinct. The uncomplexed portion of the naphthalene ring occurs at low field and is well separated from the protons associated with the diene group bound to tantalum. Two of the latter protons resonate at τ 6.6 and 7.5;[43] the remaining two are obscured by the phosphine methyl and methylene groups. At 70 °C, the dmpe methyl resonances coalesce to two equally intense signals, which do not average below the decomposition point. Hence, the process equilibrating phosphorus environments creates two equally weighted, chemically inequivalent methyl group environments. Similar inequivalence is apparent in the dmpe methyl resonances of monocapped, trigonal prismatic $MX(CO)_2(dmpe)_2{}^n$ (M = Mo, n = 1+;[61,19] M = Ta, n = 0;[61] X = halogen). In these cases, the methyl groups directed toward the capping halogen (the phosphorus ligands occupy the capped quadrilateral face sites) are resolved from those directed toward the symmetry-related carbonyl sites. By analogy, the two methyl resonances in the high-temperature limiting spectrum of **3** are those groups (exchanging among themselves) directed toward Cl and those (also exchanging) directed toward the naphthalene fragment. That these sets do not mix requires that naphthalene and CO retain their positions relative to the P1-P2-P3-P4 plane and eliminates any "arm-off, arm-on" mechanism involving the bidentate phosphine, as rapid rotation about the P-C and C-C bonds in an intermediate containing a monodentate dmpe ligand would equilibrate the methyl sets. Further, at 70 °C (Figure 5), the resonances of the unbound naphthalene ring remain distinct from those of the complexed diene fragment, although an effective mirror plane has been created within both portions (as shown by averaging of the protons attached to C2 and C3[43] and collapse of the signals of the protons attached to C6-C9 to an AA′BB′ pattern). This observation eliminates any process involving complete dissociation of naphthalene (as does the preservation of J_{PCH} evident in ^{31}P coupled spectra at 70 °C) or any mechanism involving migration of Ta from one ring to the other.

The simplest explanation for the temperature-dependent ^1H and ^{31}P NMR spectra is rotation of the diene fragment about the Ta–Cl vector, as indicated in Scheme II. By symmetry, k_1 and k_2 need not be equal. This mechanism requires structures A and B as intermediates or transition states. Both are approximate monocapped trigonal prisms, structurally analogous to $TaCl(CO)_2(dmpe)_2$.[9] Either A or B could be equally well represented by the ortho-quinoidal resonance form C, a distorted pentagonal bipyramid. However, this possibility is mitigated by the observation of identical spectral details for **7**, as is the operation of 1,2 or 1,3 shifts.[44]

It should be noted that an "arm-off, arm-on" mechanism involving naphthalene (i.e., rupture of one Ta–olefin bond and

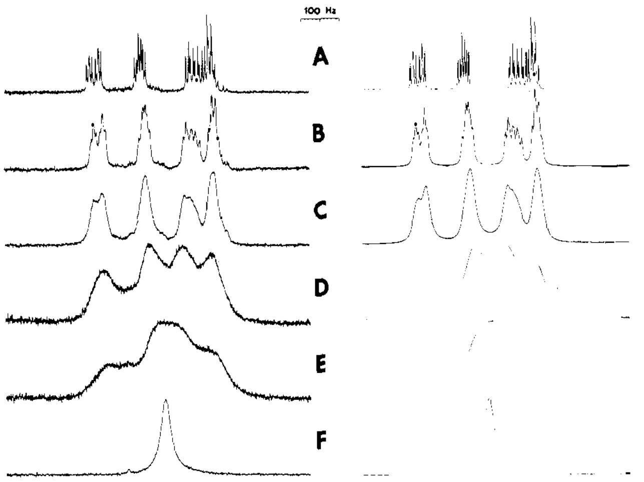
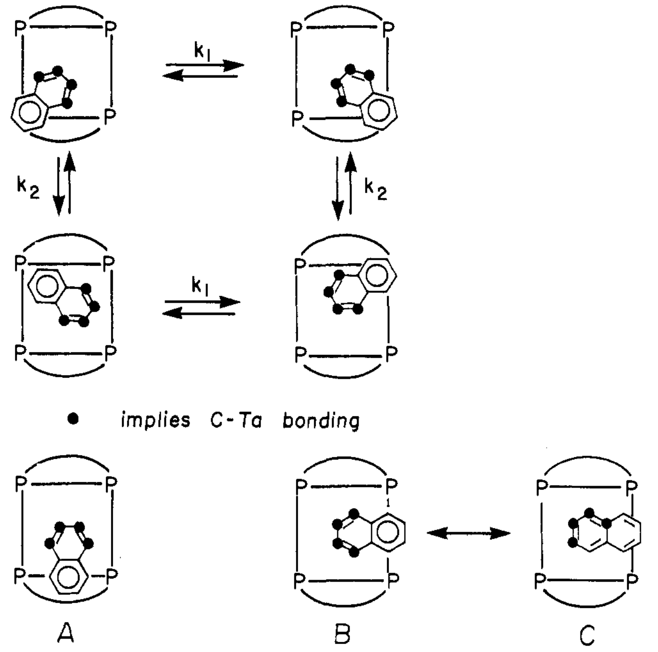


Figure 4. Calculated and observed ^{31}P NMR spectra (toluene-d_8/THF) of $Ta(CH_3)(\eta^4\text{-}C_{10}H_8)(dmpe)_2$: A, −60 °C, $k = 0\ s^{-1}$; B, −29 °C, $k = 16\ s^{-1}$; C, −18 °C, $k = 52\ s^{-1}$; F, 28 °C, $k = 3000\ s^{-1}$. Ground-state spectral parameters are given in the text.

Scheme II



rotation about the other) is not rigorously eliminated by the data. But this possibility is unlikely as the diene is constrained to the cis,cis configuration. Further, it is inconsistent with the inertness of the Ta-naphthalene bond to substitution reactions or with the magnitude of the activation parameters (vide infra).

Line-shape calculations were performed on **6** because the ground-state ^{31}P NMR spectrum could be analyzed, approximately, in first order. The relative signs of J_{PP} were determined by spin tickling experiments in conjunction with energy level calculations. The final parameters were refined by iterative procedures:[45] P_A δ −9.9, P_B −12.2, P_C −19.1, P_D −25.1, $J_{P_AP_B} = \pm 15.59$, $J_{P_AP_C} = \mp 21.47$, $J_{P_AP_D} = \mp 15.71$, $J_{P_BP_C} = \pm 23.96$, $J_{P_BP_D} = \mp 47.69$, $J_{P_CP_D} = \pm 12.49$ Hz. The temperature dependence of the chemical shifts was measured and fitted to a straight line over the slow exchange region; values used in the intermediate and fast exchange regions were extrapolated (those quoted above are at −60 °C). Since chemical shifts could not be unambiguously assigned to particular phosphorus sites, initial calculations were performed with $k_1 = k_2$ for all possible assignments consistent with the exchange vectors implied by Scheme II. Only the scheme in eq 5 gave results in close agreement with the experimental

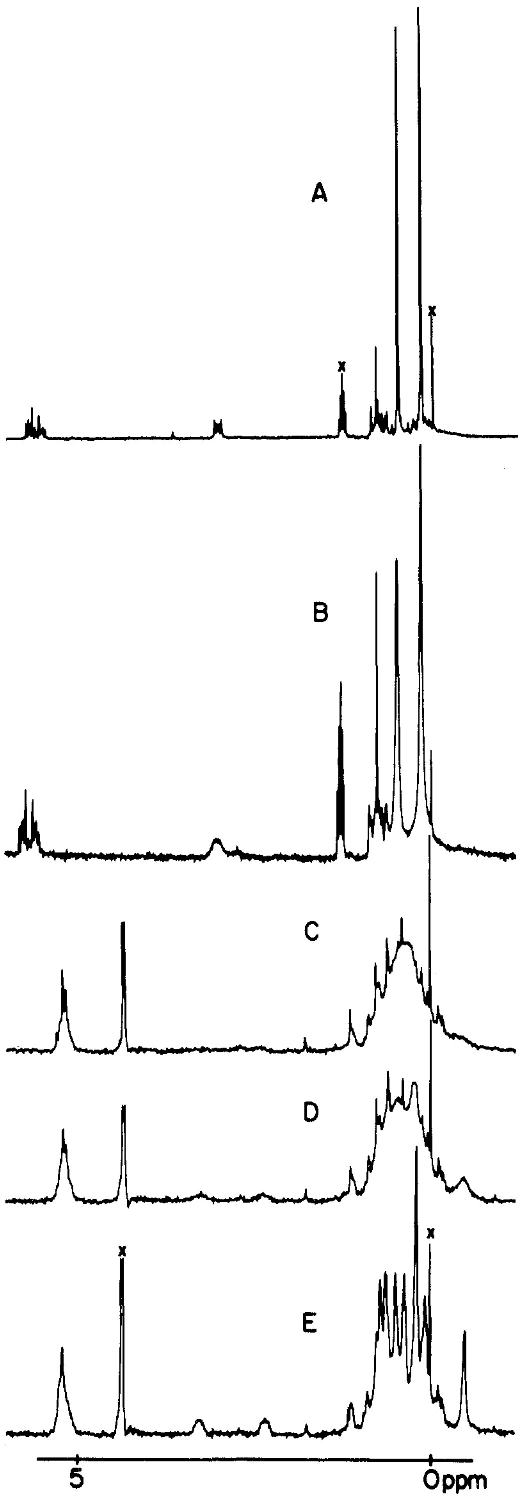


Figure 5. $^1H\{^{31}P\}$ NMR spectra of $TaCl(\eta^4\text{-}naphthalene)(dmpe)_2$ in toluene-d_8 (A, B) and CD_2Cl_2 (C, D, E) at 70 (A), 30 (B), −10 (C), −30 (D), and −50 °C (E).

$$\begin{tikzcd}(P_A)(P_B)(P_C)(P_D) \arrow[rr, shift left, "\;"] \arrow[dr, leftrightarrow] & & (P_AP_C)(P_BP_D) \arrow[ll, shift left] \arrow[dl, leftrightarrow] \\ & (P_AP_D)(P_BP_C) & \end{tikzcd} \qquad (5)$$

spectra (Figure 4). Since the mechanism in Scheme II averages cis phosphorus nuclei, eq 5 requires that the pairs P_A-P_C, P_B-P_D, P_A-P_D, and P_B-P_C be cis and, therefore, that P_A-P_B and P_C-P_D be trans. This is consistent with the relative signs

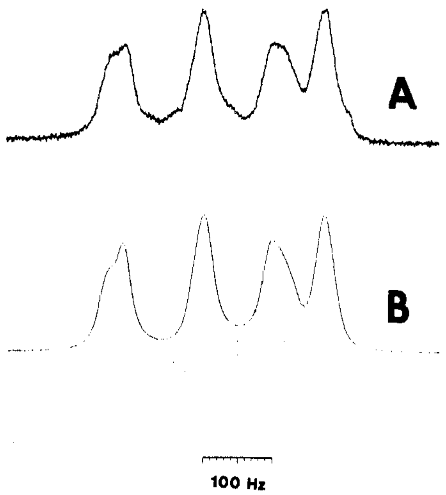


Figure 6. Observed (A) ^{31}P NMR spectrum of $Ta(CH_3)(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ at −12 °C and that calculated (B) using the four-configuration model described in the text with $k_1 = 95\ s^{-1}$ and $k_2 = 35\ s^{-1}$.

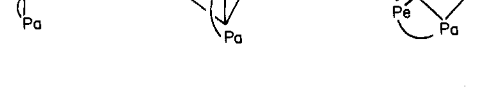
of the coupling constants; $J_{P_AP_B}$ and $J_{P_CP_D}$ are opposite in sign to $J_{P_AP_C}$, $J_{P_AP_D}$, $J_{P_BP_C}$, and $J_{P_BP_D}$. Cis ^{31}P couplings are generally opposite in sign to trans couplings.[61,46]

Activation parameters obtained from an Eyring plot of the rate data are $\Delta H^{\ddagger} = 13.0 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = 1.0 \pm 0.9$ eu.[47] The small value of $\Delta S^{\ddagger}$ is consistent with a nondissociative mechanism.[61] However, these activation parameters are of limited accuracy as they are derived from the exchange scheme in eq 5 and, consequently, are based on the assumption that $k_1 = k_2$. This assumption is almost certainly invalid. Careful inspection of the spectra in Figure 4 reveals small deviations from the calculated spectra in the slow exchange region, where differences in k_1 and k_2 would be most apparent. The spectrum at −12 °C was simulated using the four-configuration model in eq 6. Good agreement between calculated and observed spectra was only obtained when k_1 was substantially larger than k_2. The best fit was with $k_1 = 95\ s^{-1}$ and $k_2 = 35\ s^{-1}$, as indicated in Figure 6. The spectral differences are too small to accurately determine k_1/k_2 over a sufficient temperature interval to determine individual activation parameters. The data does establish, however, that $k_1 \neq k_2$ and, therefore, supports the mechanism proposed in Scheme II.

$$\begin{array}{ccc} (P_A)(P_B)(P_C)(P_D) & \underset{k_1}{\rightleftarrows} & (P_AP_C)(P_BP_D) \\ \upharpoonleft\!\downharpoonright k_2 & & \upharpoonleft\!\downharpoonright k_2 \\ (P_AP_D)(P_BP_C) & \underset{k_1}{\leftrightarrows} & (P_AP_B)(P_CP_D) \end{array} \qquad (6)$$

The isoelectronic molybdenum–norbornadiene complex **8** exhibits an AA′BB′ ^{31}P NMR spectrum over the temperature range −70 to 80 °C. An AA′BB′ spectrum is consistent with a pentagonal bipyramidal structure analogous to **3** with naphthalene replaced by the more symmetrically bound norbornadiene. The lack of ^{31}P exchange, however, suggests that **8** may have a different structure. ^1H NMR spectra were too poorly resolved to distinguish between possible geometries.

Rotation of the naphthalene unit as indicated in Scheme II corresponds to rotation of two adjacent equatorial sites about one of the C_2 axes of an idealized pentagonal bipyramid.



Formally, the process is a pseudorotation exchanging two axial with two equatorial sites in a pairwise fashion by passage through a monocapped trigonal prism. The mechanism preserves the C_2 axis common to the idealized geometries and is the least motion coordinate connecting the idealized D_{5h} and C_{2v} ML_7 geometries.[61] This mechanism has previously been suggested as a probable path connecting these geometries[3d,48] and has been proposed to explain the ^{31}P site exchange observed for $[MoH(C_2H_4)_2(diphos)_2][BF_4]$.[7b]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-75-19177 and CHE-76-05582) for support of this research. We are also grateful to Professor T. Albright for communication of results prior to publication.

Supplementary Material Available: Hydrogen atom positions (Table III) and calculated structure factor amplitudes (Table VI) (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Harvard University; (b) Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1; (c) Brandeis University.

(2) A recent review mentions 161 crystal structures: M. G. B. Drew, *Prog. Inorg. Chem.*, **23**, 67 (1977).

(3) (a) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967); (b) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974); (c) J. K. Kouba and S. S. Wreford, *Inorg. Chem.*, **15**, 1463 (1976); (d) R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *ibid.*, **16**, 511 (1977).

(4) S. Datta, T. J. McNeese, and S. S. Wreford, *Inorg. Chem.*, **16**, 2661 (1977).

(5) 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).

(6) (a) 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 and M. E. Tully, *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) L. D. Brown, S. Datta, J. K. Kouba, L. K. Smith, and S. S. Wreford, *Inorg. Chem.*, **17**, 729 (1978); (m) E. L. Muetterties, J. F. Kirner, W. J. Evans, P. L. Watson, S. Abdel-Meguid, I. Tavanaiepour, and V. W. Day, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 1056 (1978).

(7) Other examples: (a) S. Datta, B. Dezube, J. K. Kouba, and S. S. Wreford, *J. Am. Chem. Soc.*, **100**, 4404 (1978); (b) J. W. Byrne, J. R. M. Krees, J. A. Osborn, L. Ricard, and R. E. Weiss, *J. Chem. Soc., Chem. Commun.*, 662 (1977).

(8) For example, see J. W. Johnson and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 7395 (1977), and references cited therein.

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

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

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

(12) 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).

(13) E. J. Brooker and E. W. Nuffield, *Acta Crystallogr.*, **20**, 496 (1966).

(14) "Syntex P2₁ Operations Manual", Syntex Analytical Instruments, Cupertino, Calif., 1973; "Syntex P2₁ FORTRAN Operations Manual", Cupertino, Calif., 1975.

(15) B. M. Foxman, *Inorg. Chem.*, in press.

(16) "Syntex XTL Operations Manual", 2nd ed., Syntex Analytical Instruments, Cupertino, Calif., 1976.

(17) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99–101; (b) pp 148–150.

(18) B. M. Foxman, "METHYL, a Program for Calculating Methyl Hydrogen Atom Positions", 1977.

(19) (a) J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Less-Common Met.*, **36**, 207 (1974); (b) J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Chem. Soc., Dalton Trans.*, 589 (1974).

(20) J. A. Connor, personal communication.

(21) G. E. Coates and K. Wade, "Organometallic Compounds", Vol. I, "The Main Group Elements", 3rd ed., Methuen, London, 1969, p 56.

(22) (a) F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 5823 (1973); (b) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).

(23) F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Am. Chem. Soc.*, **95**, 4522 (1973).

(24) G. D. Piero, G. Perego, and M. Cesari, *Gazz. Chim. Ital.*, **105**, 529 (1975).

(25) B. M. Foxman, T. J. McNeese, and S. S. Wreford, *Inorg. Chem.*, **17**, 2311 (1978).

(26) T. J. McNeese, S. S. Wreford and B. M. Foxman, *J. Chem. Soc., Chem.*

Commun., 500 (1978).
(27) M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, **292**, 61 (1966).
(28) F. H. Herbstein and M. G. Reisner, *J. Chem. Soc., Chem. Commun.*, 1077 (1972).
(29) (a) G. Huttner, S. Lange, and E. O. Fischer, *Angew Chem., Int. Ed. Engl.*, **10**, 556 (1971); (b) G. Huttner and S. Lange, *Acta Crystallogr., Sect. B*, **28**, 2049 (1972).
(30) D. M. Bartex, J. A. Evans, R. D. W. Kemmitt and D. R. Russell, *Chem. Commun.*, 331 (1971).
(31) A. Bond, M. Bottrill, M. Green, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2372 (1977).
(32) (a) M. L. H. Green, "Organometallic Compounds", Vol. II, Chapman and Hall, London, 1972, p 72; (b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley-Interscience, New York, N.Y., 1972, p 731.
(33) R. E. Davis and R. Pettit, *J. Am. Chem. Soc.*, **92**, 716 (1970).
(34) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **8**, 1941 (1969), and references cited therein.
(35) W. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971).
(36) F. A. Cotton, D. L. Hunter, and B. A. Frenz, *Inorg. Chim. Acta*, **15**, 155 (1975).
(37) R. A. Forder and K. Prout, *Acta Crystallogr., Sect. B*, **30**, 2778 (1974).
(38) M. G. B. Drew and C. J. Rix, *J. Organomet. Chem.*, **102**, 467 (1975).
(39) M. G. B. Drew and J. C. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2664 (1973).
(40) B. D. Dombeck and R. J. Angelici, *Inorg. Chem.*, **15**, 2397 (1976).
(41) A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, **14**, 2526 (1975).
(42) T. Albright, R. Hoffman, Y.-C, Tse, and T. D'OHavio; submitted for publication.
(43) By comparison with $Fe(CO)_3(\eta^4\text{-}C_{10}H_8)$, these resonances may be assigned to protons bound to C2 and C3: (a) T. A. Manuel, *Inorg. Chem.*, **3**, 1794 (1964); (b) H. Gunther, R. Wenzl, and H. Klose, *Chem. Commun.*, 605 (1970).
(44) $(\eta\text{-}C_6H_6)Rh[C_6(CO_2Me)_6]$, an η^4-arene complex, exchanges carboxymethyl sites by 1,2 shifts. The barrier is substantial ($\Delta G^{\ddagger} \simeq 20$ kcal/mol): J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, **92**, 720 (1970).
(45) LAOCN-4.
(46) (a) F. B. Oglive, R. J. Clark, and J. G. Verkade, *Inorg. Chem.*, **8**, 2346 (1969); (b) R. D. Bertrand, F. B. Oglive, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 1908 (1970); (c) R. M. Lynden-Bell, J. F. Nixon, J. Roberts, and J. R. Swain, *Inorg. Nucl. Chem. Lett.*, **7**, 1187 (1971).
(47) From an unweighted least-squres fit of 11 points in the temperature range −35 to 28 °C. The error limits are the standard errors from the least-squares fit.
(48) E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, N.Y., 1975, p 28.

A Study of the Stereochemistry at Iron of Electrophilic Cleavage of the Iron–Carbon σ Bond in Methyl(η^5-1-methyl-3-phenylcyclopentadienyl)carbonyl(triphenylphosphine)iron(II)

Thomas G. Attig,[1a,b] Raymond G. Teller,[1c] Su-Miau Wu,[1c] Robert Bau,[1c] and Andrew Wojcicki*[1b]

Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210, and University of Southern California, University Park, Los Angeles, California 90007. *Received August 28, 1978*

Abstract: The stereochemistry at iron of electrophilic cleavage, with insertion or elimination, of the Fe–CH_3 σ bond in the diastereomers (used as enantiomeric pairs) of the "pseudotetrahedral" $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (**2**) was investigated by ^1H NMR spectroscopy and X-ray crystallography. The insertion of SO_2 in **2** to yield the corresponding S-sulfinate, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3$ (**3**), is essentially stereoselective (>95% stereospecificity) in CH_2Cl_2 solution, and highly (79%) stereospecific in neat SO_2. Eliminative cleavage of **2** by a deficiency of each of HI, I_2, and HgI_2 to afford the iodo complex, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (**4**), proceeds with variable stereospecificity (0–67%). The stereospecificity of this cleavage by a given electrophile is unequal for the two diastereomers of **2** (0–38 and 38–67%), and higher with I_2 (38–67%) than with HI and HgI_2 (0–47%). Unreacted **2** undergoes epimerization during the reaction to an extent (20–42%) which appears to be independent of the diastereomer employed. To elucidate the stereochemistry of these eliminative cleavage reactions crystal structure determinations were carried out of one diastereomer each of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]C(O)CH_3$ (**1**) and **4**. The structural results, taken in conjunction with the known stereochemistry of the photochemical decarbonylation of acyl(η^5-cyclopentadienyl)iron complexes, show that the cleavage of **2** by the iodine-containing electrophiles (EI) proceeds with net retention of configuration at iron. A mechanism is proposed which involves attack of the electrophile at the iron center to generate an ionic intermediate, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3](CH_3)E^+I^-$ (**5**), containing a square pyramidal cation. Reductive elimination of CH_3E followed by coordination of iodide or, alternatively, nucleophilic attack of iodide at the ligated CH_3 (when E = I) lead to product **4**. These individual steps are discussed in the context of the observed net retention of configuration at iron and the previously reported stereochemical results at α carbon of such cleavage processes. A possible fluxional behavior of **5** and its relationship to partial epimerization of unreacted **2** are also considered. Crystallographic details follow. Crystals of the iodide complex (**4a**) are monoclinic, space group $P2_1/n$, with $a = 9.773$ (7) Å, $b = 15.635$ (8) Å, $c = 17.235$ (8) Å, $\beta = 92.43$ (4)°, $V = 2631$ (6) Å^3, $Z = 4$. The structure, refined to an R value of 0.078 for 2541 reflections, consists of a racemic mixture of molecules having *RS* and *SR* configurations. The acetyl complex (**1b**) crystallizes as a benzene solvate in the triclinic space group $P\bar{1}$, with $a = 15.359$ (4) Å, $b = 9.072$ (3) Å, $c = 14.112$ (4) Å, $\alpha = 86.22$ (3)°, $\beta = 119.64$ (2)°, $\gamma = 109.38$ (2)°, $V = 1601$ (2) Å^3, $Z = 2$. Final R factor = 0.081 for 2370 reflections. Crystals of the acetyl complex are also racemic, and contain equal numbers of each member of the enantiomeric pair (*RR*/*SS*).

Introduction

Cleavage of transition metal–carbon σ bonds, either insertive or eliminative, is a reaction of great importance in catalysis and stoichiometric synthesis, as well as in the identification of organometallic compounds.[2–6] This reaction is often promoted by electrophilic reagents which vary considerably in nature and include, inter alia, protic acids, halogens, covalent oxides, and metal salts. Although the literature abounds in examples of such electrophilic cleavage, relatively little is known about mechanism. A very recent review[7] considers this subject in some detail.

0002-7863/79/1501-0619$01.00/0