

This article was downloaded by:

On: 30 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

CRYSTAL AND MOLECULAR STRUCTURE OF BIS(CIS-2-METHOXY-4,6-DIMETHYL-1,3,2-DIOXAPHOSPHORINANE)TETRA-CARBONYLMOLYBDENUM(0)-A COMPLEX CONTAINING A THERMODYNAMICALLY UNSTABLE LIGAND ISOMER

R. A. Jacobson^a; B. A. Karcher^a; R. A. Montag^a; S. M. Socol^a; L. J. Vande Griend^a; J. G. Verkade^a

^a Contribution from Gilman Hall and Ames Laboratory of the DOE, Iowa State University, Ames, Iowa

To cite this Article Jacobson, R. A. , Karcher, B. A. , Montag, R. A. , Socol, S. M. , Griend, L. J. Vande and Verkade, J. G.(1981) 'CRYSTAL AND MOLECULAR STRUCTURE OF BIS(CIS-2-METHOXY-4,6-DIMETHYL-1,3,2-DIOXAPHOSPHORINANE)TETRA-CARBONYLMOLYBDENUM(0)-A COMPLEX CONTAINING A THERMODYNAMICALLY UNSTABLE LIGAND ISOMER', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 11: 1, 27 – 32

To link to this Article: DOI: 10.1080/03086648108077400

URL: <http://dx.doi.org/10.1080/03086648108077400>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CRYSTAL AND MOLECULAR STRUCTURE OF BIS(CIS-2-METHOXY-4,6-DIMETHYL-1,3,2-DIOXA- PHOSPHORINANE)TETRA-CARBONYL- MOLYBDENUM(0)-A COMPLEX CONTAINING A THERMODYNAMICALLY UNSTABLE LIGAND ISOMER

R. A. JACOBSON, B. A. KARCHER, R. A. MONTAG, S. M. SOCOL,
L. J. VANDE GRIEND and J. G. VERKADE

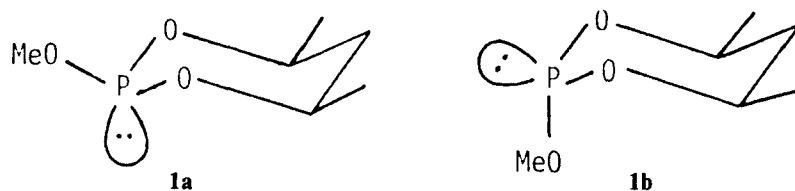
*Contribution from Gilman Hall and Ames Laboratory of the DOE, Iowa State
University, Ames, Iowa 50011*

(Received October 20, 1980; in final form January 12, 1981)

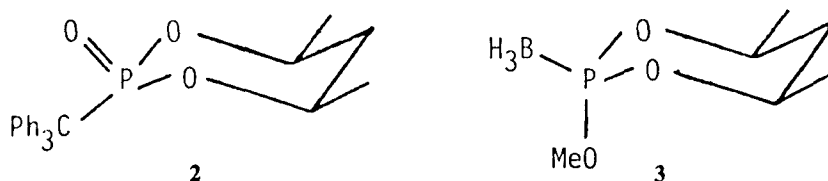
The crystal and molecular structure of the title complex determined by x-ray diffraction techniques demonstrates that the thermodynamically unstable form of the phosphorinane ligand (i.e., phosphorus lone pair axial) coordinates to the metal with retention of configuration at phosphorus. It is noted that the CH_3O group of both ligands adopts a conformation such that the $\text{P}(\text{OC})_3$ moiety in each ligand possesses a spatial arrangement similar to that of the $\text{P}(\text{OCH}_3)_3$ ligand in complexes whose structures have been determined (Ref. 16).

INTRODUCTION

The stereochemistry shown for the ligand **1a** of the title complex was strongly



suggested by the molecular structure of the Michaelis-Arbuzov product (**2**) of **1a** with



Ph_3CCl .¹ Further support for the stereochemistry of **1a** was derived from the molecular structure of the borane adduct (**3**) of **1a**.² Subsequently it was found from studies of the B—H stretching frequencies of the BH_3 adducts of **1a** and **1b**,³ ^1JPH spin-spin couplings of protonated **1a** and **1b**,⁴ and $^1\text{JPSe}$ spin-spin couplings of the selenide derivatives these phosphite esters⁵ that **1a** is more Lewis basic than **1b** in

solution. The difference in Lewis basicity was attributed to differential endocyclic oxygen and phosphorus lone pair orbital repulsion effects arising from the isomeric phosphorus stereochemistries in **1a** and **1b**.⁶ Recently the greater basicity of **1a** was demonstrated to persist in the gas phase where the phosphorus lone pair adiabatic ionization energy of **1a** (192 kcal/mole) is lower than that of **1b** (200 kcal/mole) and the phosphorus proton affinity of **1a** (227.5 kcal/mole) is greater than that of **1b** (224.9 kcal/mole).⁷ Isomer **1a** readily isomerizes to **1b** in the presence of acid or on warming. Moreover **1b** is formed in an equilibrium transesterification reaction of the parent diol with P(OMe)₃.⁸ Thus **1a** is thermodynamically less stable than **1b**.

Coordination of these ligands to transition metals readily takes place.^{9–11} In the case of *cis*-(**1a**)₂Mo(CO)₄ and *cis*-(**1b**)₂Mo(CO)₄, the lower CO stretching frequencies of the former suggested that coordination of the phosphorus ligands occurred with retention of the phosphorus configuration.⁹ This is now confirmed by the determination of the molecular structure of *cis*-(**1a**)₂Mo(CO)₄ in which the thermodynamically unstable form **1** is preserved in the complex.

EXPERIMENTAL

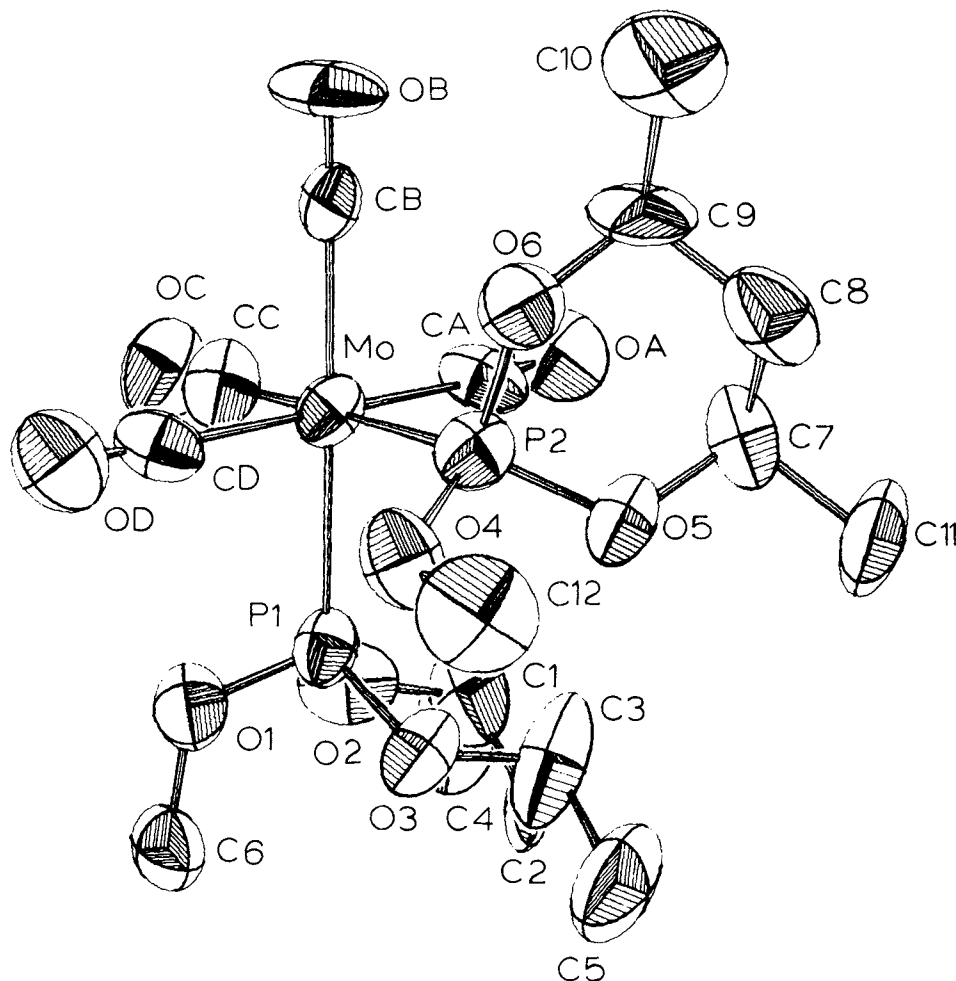
The title complex was prepared from pure **1a**¹² by the method described previously.⁹ A crystal grown by slow evaporation of a pentane solution in a nitrogen atmosphere was mounted in a 0.3 mm Lindemann capillary and sealed. The crystal was found to be monoclinic with $a = 12.220(3)$, $b = 9.963(2)$, $c = 20.150(6)$ Å and $\beta = 103.01(3)^\circ$ with four molecules of Mo(CO)₄(**1a**)₂ per unit cell. A density of 1.48 g/cc was computed based on a cell volume of 2390.1(1) Å³. Systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$) indicated space group P2_{1/c}. Axial photographs confirmed the monoclinic symmetry.

Using an automated four-circle diffractometer, built in the Ames Laboratory, equipped with a scintillation counter and interfaced to a PDP-15 computer, data were collected at room temperature with graphite monochromated Mo K α radiation ($\lambda = 0.70954$ Å) employing a procedure described previously.¹³ Four octants were examined within a sphere of $2\theta < 50^\circ$ yielding 4890 measured intensities. There was no significant crystal decomposition as judged by repeated measurements of three standard reflections. Corrections for Lorentz-polarization effects and averaging of equivalent data yielded 2057 observed reflecting [$F_o \geq 3\sigma(F_o)$]. Almost all F values with $2\theta > 42.3^\circ$ were very small and subsequently discarded. It was suspected that this was caused by large thermal motion effects as was later verified on refinement. A total of 1588 reflections were used in the final refinement. Lattice constants were obtained by a least squares refinement of $\pm 2\theta$ for 11 strong independent reflections.

The molybdenum atom was positioned from a Patterson map. Electron density maps generated by the program ALLS¹⁴ were used to locate the remaining non-hydrogen atoms. Isotropic refinement of these positions by full matrix least squares techniques followed by anisotropic refinement gave a conventional residual index (R) of 10.7 and a weighted R factor at 13.3. Comparatively large thermal disorder prevented further refinement. Because the main goal of this work was the definition of the stereochemistry of the phosphorus ligands, low temperature data were not sought. Hydrogen positions on carbons C₂ and C₈ on the phosphorinane rings were calculated assuming a carbon hydrogen bond length of 1.05 Å and a hydrogen-carbon-hydrogen bond angle of 109.54°. A computer drawing¹⁵ of the title complex is shown in Figure 1. Intramolecular bond distances and angles, fractional coordinates and final thermal parameters are given in Tables I, II, and III, respectively.

DISCUSSION

From Figure 1 it is seen that the molybdenum atom occupies the axial position of the six-membered ring of each of the phosphorus ester ligands, thus confirming that coordination of **1a** proceeds by retention of the phosphorus configuration. Because the average 118.8° POC ring angles and the 100.8° OPO ring angles in the ligands are greater and smaller than the tetrahedral angle, respectively, the P(OC)₂ moiety

FIGURE 1 Computer drawing of *cis*-(**1a**)₂Mo(CO)₄.

of the chair-form of the ring is somewhat flattened. This also permits severe 1,3 interactions of axial hydrogens and the Mo(CO)₄ moiety to be avoided.

For each ligand the C—O bond of the equatorial methoxy group is directed approximately parallel to but away from the axial P—Mo bond. This conformation of the CH₃O group does not appear to be necessitated by intra or intermolecular steric considerations. In fact the spatial arrangement of both P(OC)₃ moieties in the complex is quite similar to that encountered in P(OMe)₃ ligands in other complexes whose molecular structures have been determined.¹⁶ Thus it may be that although the conformation of the free ligand **1a** is thermodynamically unstable relative to **1b**, stabilization of the **1a** configuration may occur upon complexation. Further work is underway to test this hypothesis.

The bond lengths and angles summarized in Table I are not unreasonable but large thermal parameters (Table III) preclude a more detailed discussion of the structure.

TABLE I
Intramolecular bond distances (Å) and angles (°)

P ₁ —Mo	2.459(7)	C ₇ —C ₈	1.51(5)	O ₄ —P ₂ —O ₅	102.6(10)
P ₂ —Mo	2.468(7)	C ₈ —C ₉	1.53(4)	O ₄ —P ₂ —O ₆	102.9(10)
C _A —Mo	2.00(3)	O ₁ —C ₆	1.51(3)	O ₅ —P ₂ —O ₆	100.2(9)
C _B —Mo	2.06(3)	P ₁ —Mo—P ₂	90.0(2)	P ₂ —O ₄ —C ₁₂	122.7(16)
C _C —Mo	2.02(3)	P ₁ —Mo—C _A	93.9(8)	P ₁ —O ₁ —C ₆	120.2(16)
C _D —Mo	2.05(3)	P ₁ —Mo—C _B	179.1(7)	P ₁ —O ₂ —C ₁	120.0(17)
O ₁ —P ₁	1.55(2)	P ₁ —Mo—C _C	89.2(8)	P ₁ —O ₃ —C ₃	115.4(18)
O ₂ —P ₁	1.62(2)	P ₁ —Mo—C _D	85.9(8)	P ₂ —O ₅ —C ₇	117.1(17)
O ₃ —P ₁	1.61(2)	P ₂ —Mo—C _A	92.0(8)	P ₂ —O ₆ —C ₉	122.6(16)
O ₄ —P ₂	1.58(2)	P ₂ —Mo—C _B	90.1(7)	Mo—C _A —O _A	175.1(25)
O ₅ —P ₂	1.62(2)	P ₂ —Mo—C _C	178.4(8)	Mo—C _B —O _B	177.2(21)
O ₆ —P ₂	1.58(2)	P ₂ —Mo—C _D	88.6(8)	Mo—C _C —O _C	178.0(26)
C ₁₂ —O ₄	1.47(3)	C _A —Mo—C _B	87.0(10)	Mo—C _D —O _D	177.6(25)
C ₁ —O ₂	1.46(4)	C _A —Mo—C _C	89.5(10)	O ₂ —C ₁ —C ₂	103.4(24)
C ₇ —O ₅	1.46(4)	C _A —Mo—C _D	179.4(11)	O ₂ —C ₁ —C ₄	107.2(25)
C ₃ —O ₃	1.50(4)	C _B —Mo—C _C	90.7(11)	O ₃ —C ₃ —C ₂	106.0(28)
C ₉ —O ₆	1.45(3)	C _B —Mo—C _D	93.2(10)	O ₅ —C ₇ —C ₈	104.2(23)
C _A —O _A	1.13(3)	C _C —Mo—C _D	89.6(11)	O ₅ —C ₇ —C ₁₁	101.2(25)
C _B —O _B	1.08(3)	Mo—P ₁ —O ₁	110.3(7)	O ₆ —C ₉ —C ₈	103.4(20)
C _C —O _C	1.13(4)	Mo—P ₁ —O ₂	118.1(7)	O ₆ —C ₉ —C ₁₀	107.1(21)
C _D —O _D	1.13(4)	Mo—P ₁ —O ₃	120.2(7)	C ₁ —C ₂ —C ₃	110.9(27)
C ₂ —C ₁	1.54(5)	Mo—P ₂ —O ₄	112.3(7)	C ₂ —C ₁ —C ₄	111.6(29)
C ₄ —C ₁	1.56(5)	Mo—P ₂ —O ₅	117.3(7)	C ₈ —C ₇ —C ₁₁	111.7(24)
C ₃ —C ₂	1.44(5)	Mo—P ₂ —O ₆	119.2(7)	C ₅ —C ₃ —C ₂	110.4(29)
C ₉ —C ₁₀	1.57(4)	O ₁ —P ₁ —O ₂	101.3(10)	C ₈ —C ₉ —C ₁₀	107.8(23)
C ₅ —C ₃	1.60(5)	O ₁ —P ₁ —O ₃	102.8(10)	C ₉ —C ₈ —C ₇	110.9(24)
C ₇ —C ₁₁	1.68(5)	O ₂ —P ₁ —O ₃	101.4(10)	C ₅ —C ₃ —O ₃	99.6(26)

TABLE II
Final atomic positional parameters

	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.2789(2)	0.1636(2)	0.1813(1)
P ₁	0.2450(6)	−0.0015(7)	0.0882(3)
P ₂	0.1657(6)	0.0274(6)	0.2433(3)
O _A	0.5051(20)	0.0361(24)	0.2594(11)
O _B	0.3147(16)	0.3780(21)	0.2986(10)
O _C	0.4149(19)	0.3402(22)	0.0979(12)
O _D	0.0540(18)	0.3069(23)	0.1029(11)
C _A	0.4212(24)	0.0767(31)	0.2307(14)
C _B	0.3054(20)	0.3038(24)	0.2585(14)
C _C	0.3679(24)	0.2758(27)	0.1285(14)
C _D	0.1333(26)	0.2537(27)	0.1298(13)
C ₁	0.4248(25)	−0.1534(43)	0.0889(14)
C ₂	0.3453(31)	−0.2736(30)	0.0874(17)
C ₃	0.2693(35)	−0.2517(32)	0.1315(18)
C ₄	0.5106(26)	−0.1788(39)	0.0435(18)
C ₅	0.1842(40)	−0.3749(34)	0.1275(20)
C ₆	0.1259(25)	−0.0288(31)	−0.0385(14)
C ₇	0.2367(32)	0.0678(34)	0.3752(15)
C ₈	0.2450(27)	−0.0828(32)	0.3839(14)

TABLE II (continued)

C ₉	0.2916(22)	−0.1471(27)	0.3269(14)
C ₁₀	0.2937(31)	−0.3034(29)	0.3382(15)
C ₁₁	0.1814(29)	0.1393(35)	0.4357(16)
C ₁₂	−0.0411(24)	−0.0760(32)	0.2254(15)
O ₁	0.1638(15)	0.0567(18)	0.0246(8)
O ₂	0.3450(14)	−0.0463(20)	0.0567(9)
O ₃	0.1892(16)	−0.1447(16)	0.0979(9)
O ₄	0.0416(12)	0.0055(18)	0.2006(8)
O ₅	0.1461(15)	0.0869(17)	0.3146(8)
O ₆	0.2052(15)	−0.1196(16)	0.2661(9)
H ₁ —C ₈	0.1648	−0.1219	0.3826
H ₂ —C ₈	0.2987	−0.1051	0.4310
H ₁ —C ₂	0.2986	−0.2874	0.0373
H ₂ —C ₂	0.3932	−0.3599	0.1035

TABLE III

Final thermal parameters^a

	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Mo	0.0073(2)	0.0090(3)	0.0031(1)	0.0002(2)	0.0017(1)	0.0000(1)
P ₁	0.0089(7)	0.0106(8)	0.0030(2)	0.0014(6)	0.0020(3)	0.0009(3)
P ₂	0.0080(6)	0.0111(9)	0.0030(2)	0.0003(6)	0.0020(3)	−0.0004(4)
O _A	0.010(2)	0.023(4)	0.005(1)	0.003(3)	0.002(1)	−0.001(1)
O _B	0.013(2)	0.021(3)	0.004(1)	0.001(2)	0.002(1)	−0.006(1)
O _C	0.018(2)	0.019(3)	0.006(1)	0.000(2)	0.006(1)	0.003(2)
O _D	0.010(2)	0.022(4)	0.005(1)	0.000(2)	0.000(1)	0.000(1)
C _A	0.006(3)	0.019(4)	0.003(1)	0.002(3)	0.001(1)	−0.002(2)
C _B	0.006(2)	0.010(3)	0.003(1)	0.003(2)	0.001(1)	0.000(1)
C _C	0.011(2)	0.015(3)	0.004(1)	0.004(3)	0.004(1)	0.001(2)
C _D	0.009(3)	0.016(4)	0.002(1)	−0.001(3)	0.001(1)	−0.002(1)
C ₁	0.011(3)	0.024(7)	0.004(1)	0.008(4)	0.002(1)	0.001(2)
C ₂	0.022(4)	0.011(4)	0.004(1)	0.011(3)	0.003(2)	0.003(2)
C ₃	0.018(5)	0.017(5)	0.008(2)	0.006(4)	0.007(2)	0.006(2)
C ₄	0.014(3)	0.028(7)	0.007(2)	0.007(4)	0.007(2)	0.003(3)
C ₅	0.029(7)	0.015(5)	0.007(2)	−0.002(5)	0.006(3)	0.003(2)
C ₆	0.014(3)	0.016(5)	0.004(1)	0.006(3)	−0.001(1)	−0.001(2)
C ₇	0.025(5)	0.015(5)	0.002(1)	−0.002(4)	0.004(2)	−0.004(2)
C ₈	0.009(3)	0.024(5)	0.003(1)	−0.008(3)	−0.001(1)	0.001(2)
C ₉	0.007(2)	0.019(4)	0.003(1)	0.002(3)	0.001(1)	0.002(2)
C ₁₀	0.021(4)	0.011(4)	0.005(1)	0.002(3)	0.003(2)	0.004(2)
C ₁₁	0.014(4)	0.021(5)	0.005(1)	−0.011(4)	−0.001(1)	−0.001(2)
C ₁₂	0.011(3)	0.025(5)	0.005(1)	−0.011(3)	0.004(1)	0.001(2)
O ₁	0.013(2)	0.015(3)	0.003(1)	0.004(2)	0.002(1)	0.000(1)
O ₂	0.006(2)	0.020(3)	0.005(1)	0.000(2)	0.004(1)	−0.002(1)
O ₃	0.013(2)	0.010(2)	0.005(1)	0.001(2)	0.003(1)	0.001(1)
O ₄	0.007(1)	0.018(2)	0.004(1)	0.001(2)	0.000(1)	0.001(1)
O ₅	0.013(2)	0.013(2)	0.003(1)	−0.001(1)	0.003(1)	0.000(1)
O ₆	0.011(2)	0.009(2)	0.004(1)	0.001(2)	0.003(1)	0.001(1)

^a The β_{ij} are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l\beta_{23} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and the U.S. Department of Energy, Office of Basic Energy Sciences, Material Science Division.

REFERENCES AND NOTES

1. M. G. B. Drew, J. Rodgers, D. W. White and J. G. Verkade, *J. Chem. Soc.*, **D**, 227 (1971).
2. J. Rodgers, D. W. White and J. G. Verkade, *J. Chem. Soc.*, **A**, 77 (1971).
3. J. G. Verkade, *Phosphorus and Sulfur*, **2**, 251 (1976).
4. L. J. Vande Griend, J. G. Verkade, J. F. M. Pennings and H. M. Buck, *J. Am. Chem. Soc.*, **99**, 2459 (1977).
5. R. D. Kroshefsky, R. Weiss and J. G. Verkade, *Inorg. Chem.*, **18**, 469 (1979).
6. R. F. Hudson and J. G. Verkade, *Tetrahedron Letters*, 3231 (1975).
7. R. V. Hodges, F. A. Houle, J. L. Beauchamp, R. A. Montag and J. G. Verkade, *J. Am. Chem. Soc.*, **102**, 932 (1980).
8. D. Z. Denney and D. B. Denny, *J. Amer. Chem. Soc.*, **88**, 1830 (1966).
9. L. J. Vande Griend and J. G. Verkade, *Inorg. and Nucl. Lett.*, **9**, 1137 (1973).
10. L. W. Yarbrough and J. G. Verkade, to be published.
11. Y. Gultneh and J. G. Verkade, to be published.
12. J. A. Mosbo and J. G. Verkade, *J. Am. Chem. Soc.*, **95**, 4659 (1973).
13. F. Takusagawa and R. A. Jacobson, *Acta Crystallogr.*, **B34**, 213 (1978).
14. R. L. Lapp and R. A. Jacobson, *ALLS, A Generalized Crystallographic Program*, Ames Laboratory, U.S. Department of Energy Report IS4708, (Iowa State University, Ames, Iowa 1979).
15. C. A. Johnson, *ORTEP II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, U.S. Atomic Energy Commission Report ORNL-3794 (Second Revision with Supplemental Instructions) (Oak Ridge, National Laboratory, Oak Ridge, Tennessee, 1971).
16. R. M. Kirchner and J. Ibers, *Inorg. Chem.*, **13**, 1667 (1974); A.D.U. Hardy and G. A. Simm, *J. Chem. Soc. Dalton*, 1900 (1972); R. A. Marsh, J. Howard and P. Woodward, *J. Chem. Soc. Dalton*, 778 (1973); J. C. Atwood and D. J. Darensbourg, *Inorg. Chem.*, **16**, 2314 (1977); R. A. Loghry and S. H. Simonsen, *Inorg. Chem.*, **17**, 1986 (1978); D. Ginderow, *Acta Cryst.*, **B30**, 2798 (1974); L. J. Vande Griend, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, **14**, 710 (1975); J. H. Meiners, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, **14**, 632 (1975); D. S. Milbrath, J. P. Springer, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, **14**, 2665 (1975); R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey and R. Bau, *J. Am. Chem. Soc.*, **98**, 4491 (1976).