Inorganica Chimica Acta, 71 (1983) 41–48

Ring Contraction and Double α-Addition of Cationic $(C_5H_5)Mo(CO)_2$ (Schiff Base Chelate) Complexes: The Crystal and Molecular Structures of $(\eta^5\text{-}C_5H_5)Mo(CO)[\eta^2\text{-}NH(CH_3)\text{-}C(NC_5H_4)C_6H_5][\eta^2\text{-}OCH(C_6H_5)]$

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Received October 15, 1982

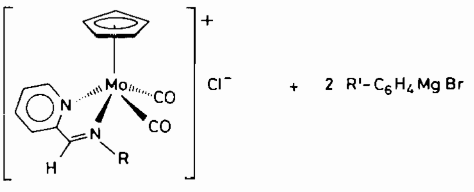
The structure of racemic $[\eta^5\text{-}C_5H_5)]Mo(CO)\text{-}[\eta^2\text{-}NH(CH_3)C(NC_5H_4)C_6H_5][\eta^2\text{-}OCH_6H_5]$ *was determined from single crystal X-ray diffraction data. The compound crystallizes in space group* $P\bar{1}$ *(z = 2) with* a = 9.035(6), b = 12.314(6), c = 13.220(5) Å, $\alpha = 65.91(4)$, $\beta = 71.40(4)$, $\gamma = 72.42(4)°$; *cell volume* 1246.97 Å^3. *The Mo atom sits at the center of a Cp-capped trigonal pyramid with a terminal carbonyl group, an* η^2*-aminomethylene and an* η^2*-benzaldehyde moiety as basal ligands. Structural features indicate that both* η^2*-ligands act as π-acids, accepting Mo electron density through their hetero atoms.*

Introduction

When cationic complexes [1] of the type *1* derived from the Schiff bases of 2-pyridine carbaldehyde and $C_5H_5Mo(CO)_3Cl$ are reacted with excess CH_3Li, C_6H_5Li or $R''C_6H_4MgBr$, a 1:1 nucleophilic addition is accompanied by ring contraction [2] to yield the η-aminomethylene complexes 2.

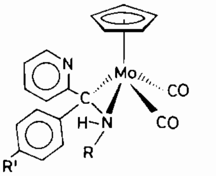
The rearrangement from *1* to *2* occurs by exchange of R' for H at the azomethine carbon, addition of H to the imine nitrogen, and cleavage of the Mo–N(pyridine) bond followed by formation of the Mo–C bond in the three-membered ring. Crystal and molecular structures of two such 1:1 addition complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(u^2\text{-}NH(R)C(C_5H_4N)\text{-}R'$; with I: $R = CH_3$, $R' = CH(CH_3)_2$, and II: $R = CH(CH_3)(C_6H_5)$, $R' = C_6H_5]$ were recently reported by Reisner and Bernal [3].

When the Schiff base complex *1* ($R = CH_3$) is reacted with excess $p\text{-}R''C_6H_4MgBr$ ($R'' = H, CH_3$), the reaction sequence does not stop at stage *2*, but proceeds with additional attack on one terminal CO ligand producing an η^2-coordinated benzaldehyde *3*. Whereas the formation of a carbene from a M–C=O group requires the attack of a nucleophile on C and an electrophile on O, the direct conversion of –C≡O to η^2-benzaldehyde requires double α-addition. The reaction products *3a* and *3b* have been investigated by IR, H and ^{13}C NMR spectra and *3a* by a preliminary X-ray study [4]. In this report, we present the crystal and molecular structures of *3a* or III: $C_5H_5Mo(CO)_2 = [\eta^2\text{-}C(C_5H_5N)\text{-}(C_6H_5)NHCH_3][\eta^2\text{-}OCHC_6H_5]$, the first η^2-benzaldehyde complex to be structurally characterized.



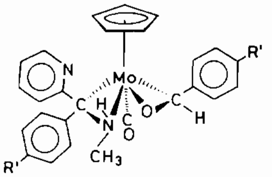
(1)

$R = CH_3$, C_6H_5, $CH(CH_3)_2$, $CH_2C_6H_5$, $CH(CH_3)C_6H_5$



(2)

$R' = H, CH_3, OCH_3, Cl$



(3a), R' = H ; (3b), R' = CH_3

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TABLE I. Crystallographically Important Data Collection and Processing Information.

Empirical Formula		$C_{26}H_{24}O_2N_2Mo$
Molecular Weight		492.43 amu
Cell Constants	a = 9.035(6) Å	α = 65.91(4)°
	b = 12.314(6) Å	β = 71.40(4)°
	c = 13.220(5) Å	γ = 72.42(4)°
Unit Cell Volume		1246.97 $Å^3$
Space Group		$P\bar{1}$
Density (calculated $Z = 2$)		1.311 gm/cm^3
Absorption Coefficient (Mo-Kα)		4.79 cm^{-1}
Radiation Used for Data Collection		MoK_α (λ = 0.71069 Å)
Scanning Range for 2θ		$4.0° \leq 2\theta \leq 45°$
Crystal Approximately Along		arbitrary direction
Standards for Intensity Control[a]		[432] and [154]
(measured every 2 hrs. of exposure time)		
Scan Width for Each Reflection		$\Delta\theta = (0.90 + 0.35 \tan\theta)$
Maximum Scan Time		5 min.
Prescan Acceptance Criterion for Classifying 'observed' Reflections		$\sigma(Ipre)/Ipre < 1.90$
Scan Technique		θ:2θ
Total Number of Reflections Collected[b]		3154
Number of Contributing Reflections in the Last Cycle of Least-Squares		2182
Number of Variables		301
Weighting Scheme		Unit Weights
Largest Parameter Shift in the Last Cycle of Least-Squares		0.2 × esd
Largest Peak in Final Difference Fourier		0.82 e/$Å^3$
Final R(F)[c]		0.0459
Final R_w(F)[d]		0.0674

[a] A least-squares fit of the 103 pairs of intensity standards indicated a small but definite decay in intensity during approximately two weeks of data collection. Intensity data were corrected during data reduction with $I_{corr} = I_{obs} + 0.00118\ I_{obs}\ T + 0.000001\ I_{obs}\ T^2$, where T is the accumulated exposure time in hours. [b] A total of 3154 reflections were collected of which 2202 having $I \geq 2\sigma(I)$ were classified as 'observed' and were used in the solution and refinement stages. During refinement, an additional 21 low-angle reflections were omitted from the data set due to apparent secondary extinction effects. [c] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [d] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Experimental

The synthesis, spectra and physical properties of III were previously reported by Brunner and Wachter [2a]. Also, the instrumental and procedural details of data collection were identical to those described in detail elsewhere [5], and will not be repeated here. Intensity data were collected on an ENRAF-NONIUS computer-controlled CAD-4 diffractometer employing the OS/4 version of computer software. Relevant data collection and processing information is summarized in Table I.

Solution and Refinement

Data reduction was accomplished using a locally written program [6], with Lorentz and polarization factors applied in converting intensities to structure factor amplitudes. No absorption corrections were made due to the relatively low absorption coefficient and uniform crystal shape. Standard deviations of the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{tot} + 2\Sigma I_{BG}$. Standard deviations in structure factor amplitudes, $\sigma(|F_o|)$, were estimated as $\sigma(|F_o|) = (I)/2\ Lp|F_o|$. After data reduction all data processing was carried out using the SHELX-76 system of computer programs [7].

Positional parameters for the Mo atom were derived from a three-dimensional Patterson map, while all remaining atoms were located in subsequent difference maps using Fourier calculations phased by the partial structure. Nitrogen atoms N(1) and N(2) were identified by their thermal parameters (*i.e.*, when refined as 'carbons' these atoms displayed iso-

TABLE II. Atomic Coordinates and Thermal Parameters (×10, Mo × 10, H × 10).

Atom	x/a	y/b	z/c	U11	U22	U33	U12	U13	U23
Mo	0.1564(1)	0.2004(1)	0.0985(1)	378(4)	471(5)	460(6)	−56(3)	−134(3)	−212(4)
O1	0.5186(8)	0.1059(7)	0.0676(7)	45(5)	65(5)	93(6)	−5(4)	−12(4)	−31(4)
O2	0.1204(8)	0.3732(6)	0.1018(6)	51(4)	53(4)	62(5)	−3(3)	−13(4)	−27(4)
N1	0.1062(17)	0.1544(13)	0.2794(13)	42(7)	65(8)	74(8)	3(6)	−28(6)	−34(6)
N2	−0.1792(9)	0.1002(8)	0.3220(7)	41(5)	73(6)	61(6)	−13(4)	−7(4)	−30(5)
C1	0.178(1)	0.148(1)	−0.055(1)	64(7)	81(9)	46(8)	−12(7)	−18(6)	−32(7)
C2	0.056(2)	0.103(1)	0.027(1)	128(13)	63(8)	85(11)	−22(9)	−65(10)	−27(8)
C3	−0.066(2)	0.199(2)	0.039(1)	65(8)	153(14)	54(9)	−52(9)	−24(7)	−30(9)
C4	−0.008(1)	0.304(1)	−0.36(1)	75(8)	78(8)	56(8)	−1(7)	−38(7)	−25(7)
C5	0.145(1)	0.265(1)	−0.093(1)	43(6)	58(7)	55(7)	−5(5)	−14(5)	−16(6)
C6	0.379(1)	0.139(1)	0.088(1)	43(6)	49(6)	65(8)	−5(5)	−14(5)	−22(5)
C7	0.279(1)	0.347(1)	0.075(1)	47(6)	48(6)	66(8)	−7(5)	−15(6)	−25(6)
C8	0.366(1)	0.416(1)	−0.040(1)	50(6)	52(6)	66(8)	−11(5)	−14(6)	−30(6)
C9	0.531(1)	0.396(1)	−0.065(1)	60(7)	65(7)	75(9)	−19(6)	−24(6)	−23(7)
C10	0.615(2)	0.460(1)	−0.169(1)	64(8)	79(9)	89(11)	−28(7)	−13(8)	−27(8)
C11	0.533(2)	0.547(1)	−0.249(1)	99(11)	80(9)	65(9)	−44(8)	1(8)	−13(7)
C12	0.370(2)	0.570(1)	−0.224(1)	76(9)	77(8)	65(9)	−23(7)	−17(7)	−3(7)
C13	0.287(1)	0.505(1)	−0.123(1)	61(7)	56(7)	68(9)	−7(6)	−21(6)	−18(6)
C14	0.207(2)	0.163(1)	0.341(1)	62(8)	78(9)	64(10)	−30(7)	−9(8)	−28(8)
C15	0.111(1)	0.047(1)	0.258(1)	42(5)	51(6)	49(7)	−12(4)	−10(5)	−25(5)
C16	−0.052(1)	0.016(1)	0.294(1)	44(6)	59(7)	46(7)	−15(5)	−10(5)	−18(5)
C17	−0.324(1)	0.075(1)	0.350(1)	37(6)	85(9)	96(10)	−10(6)	−7(6)	−43(7)
C18	−0.355(1)	−0.027(1)	0.353(1)	43(7)	97(10)	92(10)	−24(7)	−12(6)	−33(8)
C19	−0.227(1)	−0.114(1)	0.325(1)	69(8)	89(9)	88(10)	−40(7)	−20(7)	−29(7)
C20	−0.071(1)	−0.093(1)	0.294(1)	57(7)	67(7)	75(9)	−21(6)	−18(6)	−27(6)
C21	0.234(1)	−0.066(1)	0.298(1)	39(5)	51(6)	44(7)	−17(5)	−9(5)	−12(5)
C22	0.334(1)	−0.124(1)	0.223(1)	45(6)	51(6)	57(7)	−7(5)	−7(5)	−24(5)
C23	0.437(1)	−0.232(1)	0.260(1)	61(7)	58(7)	68(9)	−14(6)	−3(6)	−24(7)
C24	0.444(1)	−0.282(1)	0.372(1)	63(8)	57(8)	111(13)	−6(6)	−32(8)	−17(9)
C25	0.344(2)	−0.225(1)	0.448(1)	91(10)	81(9)	65(9)	−31(8)	−40(8)	3(7)
C26	0.240(1)	−0.119(1)	0.411(1)	54(7)	57(7)	54(8)	−12(5)	−16(6)	−12(6)
H1	0.281(1)	0.096(1)	−0.081(1)	9(2)					
H2	0.050(2)	0.016(1)	0.071(1)	9(2)					
H3	−0.174(2)	0.195(2)	0.092(1)	9(2)					
H4	−0.064(1)	0.390(1)	−0.046(1)	9(2)					
H5	0.217(1)	0.319(1)	−0.153(1)	9(2)					
H7	0.325(11)	0.300(8)	0.157(8)	6(3)					
H9	0.590(1)	0.333(1)	−0.007(1)	8(2)					
H10	0.734(2)	0.445(1)	−0.186(1)	8(2)					
H11	0.593(2)	0.595(1)	−0.325(1)	8(2)					
H12	0.312(2)	0.633(1)	−0.282(1)	8(2)					
H13	0.168(1)	0.523(1)	−0.107(1)	8(2)					
HN2	0.051(12)	0.172(10)	0.277(10)	0(4)					
H14A	0.316(13)	0.144(9)	0.292(9)	7(2)					
H14B	0.169(14)	0.143(11)	0.403(10)	7(2)					
H14C	0.223(12)	0.253(10)	0.303(8)	7(2)					
H17	−0.417(1)	0.136(1)	0.371(1)	9(1)					
H18	−0.468(1)	−0.037(1)	0.372(1)	9(1)					
H19	−0.245(1)	−0.191(1)	0.329(1)	9(1)					
H20	0.023(1)	−0.155(1)	0.274(1)	9(1)					
H22	0.330(1)	−0.086(1)	0.141(1)	9(1)					
H23	0.505(1)	−0.272(1)	0.205(1)	9(1)					
H24	0.521(1)	−0.360(1)	0.399(1)	9(1)					
H25	0.349(2)	−0.262(1)	0.530(1)	9(1)					
H26	0.167(1)	−0.080(1)	0.467(1)	9(1)					

TABLE III. Structural Parameters.

a. Bonding distances (Å)

Mo–O(2)	2.070(8)	Mo–C(1)	2.304(16)
Mo–N(1)	2.145(16)	Mo–C(2)	2.298(21)
Mo–C(6)	1.900(10)	Mo–C(3)	2.382(17)
Mo–C(7)	2.261(13)	Mo–C(4)	2.379(13)
Mo–C(15)	2.203(8)	Mo–C(5)	2.349(12)
C(1)–C(2)	1.346(19)	O(1)–C(6)	1.185(12)
C(2)–C(3)	1.375(20)	O(2)–C(7)	1.333(12)
C(3)–C(4)	1.397(20)	N(1)–C(14)	1.448(27)
C(4)–C(5)	1.392(14)	N(1)–C(15)	1.447(23)
C(5)–C(1)	1.291(17)	C(15)–C(16)	1.513(15)
		C(15)–C(21)	1.514(12)
C(8)–C(9)	1.388(15)	C(16)–N(2)	1.364(12)
C(9)–C(10)	1.374(16)	N(2)–C(17)	1.335(15)
C(10)–C(11)	1.381(19)	C(17)–C(18)	1.347(23)
C(11)–C(12)	1.369(20)	C(18)–C(19)	1.393(17)
C(12)–C(13)	1.356(15)	C(19)–C(20)	1.405(18)
C(13)–C(8)	1.399(15)	C(20)–C(16)	1.399(19)
C(21)–C(22)	1.387(16)	C(24)–C(25)	1.399(22)
C(22)–C(23)	1.371(13)	C(25)–C(26)	1.362(15)
C(23)–C(24)	1.357(23)	C(26)–C(21)	1.376(16)
N(1)–H(100)	0.48(10)	C(14)–H(14A)	1.01(10)
C(7)–H(7)	1.15(10)	C(14)–H(14B)	0.75(11)
(C–H) aromatic	1.00	C(14)–H(14C)	1.05(12)

b. Selected bond angles (°)

N(1)–Mo–C(6)	92.7(5)	C(6)–Mo–C(15)	88.8(3)
N(1)–Mo–C(7)	89.9(6)	C(6)–Mo–C(7)	69.9(4)
N(1)–Mo–O(2)	81.9(5)	C(6)–Mo–O(2)	104.5(4)
O(2)–Mo–C(7)	35.5(3)	N(1)–Mo–C(15)	38.8(6)
C(7)–O(2)–Mo	80.0(6)	C(15)–N(1)–Mo	72.7(8)
Mo–C(6)–O(1)	171.5(1.0)	Mo–C(15)–N(1)	68.4(6)
O(2)–C(7)–C(8)	119.6(8)	N(1)–C(15)–C(16)	122.2(9)
O(2)–C(7)–H(7)	108.5(4.2)	N(1)–C(15)–C(21)	118.7(1.1)
C(8)–C(7)–H(7)	127.5(4.7)	C(16)–C(15)–C(21)	110.6(8)
C(5)–C(1)–C(2)	111(1)	C(13)–C(8)–C(9)	118(1)
C(1)–C(2)–C(3)	108(1)	C(8)–C(9)–C(10)	121(1)
C(2)–C(3)–C(4)	106(1)	C(9)–C(10)–C(11)	120(1)
C(3)–C(4)–C(5)	107(1)	C(10)–C(11)–C(12)	120(1)
C(4)–C(5)–C(1)	109(1)	C(11)–C(12)–C(13)	121(1)
		C(12)–C(13)–C(8)	121(1)
C(20)–C(16)–N(2)	121(1)	C(26)–C(21)–C(22)	118(1)
C(16)–N(2)–C(17)	117(1)	C(21)–C(22)–C(23)	121(1)
N(2)–C(17)–C(18)	126(1)	C(22)–C(23)–C(24)	120(1)
C(17)–C(18)–C(19)	118(1)	C(23)–C(24)–C(25)	119(1)
C(18)–C(19)–C(20)	120(1)	C(24)–C(25)–C(26)	120(1)
C(19)–C(20)–C(16)	118(1)	C(25)–C(26)–C(21)	121(1)

(continued on facing page)

TABLE III. *(continued)*

c. Selected torsional angles (°)	
Mo–O(2)–C(7)–C(8)	112.79
O(2)–C(7)–C(8)–C(13)	–1.76
Mo–N(1)–C(15)–C(16)	–110.30
N(1)–C(15)–C(16)–N(2)	9.90
Mo–N(1)–C(15)–C(21)	118.57
N(1)–C(15)–C(21)–C(26)	58.48

TABLE IV. Least-Squares Planes[a] and Deviations Atoms from Those Planes (Å).

(a) Plane defined by C(1) through C(5)					
(–0.6110)x + (–0.3026)y + (–0.7315)z = (–1.265)					
C(1)	0.0072	C(2)	–0.0131	C(3)	0.0137
C(4)	–0.0095	C(5)	0.0017	Mo	–2.081
(b) Plane defined by Mo, O(2) and C(7)					
(–0.2133)x + (0.0498)y + (–0.9757)z = (–1.570)					
C(6)	–0.3363	O(2)	–0.3722		
(c) Plane defined by Mo, N(1) andC(15)					
(0.9507)x + (–0.3102)y + (–0.0063)z = (1.710)					
(d) Plane defined by C(6), CO and NC[b]					
(–0.5572)x + (0.0247)y + (–0.8300)z = (–3.405)					
(e) Plane defined by C(8) through C(13)					
(–0.2930)x + (–0.8768)y + (–0.3812)z = (–5.424)					
C(8)	0.0068	C(9)	–0.0083	C(10)	0.0011
C(11)	0.0076	C(12)	–0.0090	C(13)	0.0018
O(2)	–0.1449	C(7)	–0.0506	H(7)	–0.4338
(f) Plane defined by C(16), N(2), C(17), C(18), C(19) and C(20)					
(–0.2390)x + (0.1052)y + (–0.9653)z = (–3.366)					
C(16)	0.0040	N(2)	–0.0041	C(17)	–0.0006
C(18)	0.0052	C(19)	–0.0052	C(20)	0.0006
H(100)	0.1229	N(1)	0.0150		
(g) Plane defined by C(21) through C(26)					
(0.8305)x + (0.5302)y + (–0.1704)z = (2.446)					
C(21)	0.0081	C(22)	0.0016	C(23)	–0.0087
C(24)	0.0059	C(25)	0.0041	C(26)	–0.0112

Angles between planes

Plane 1	Plane 2	Angle (°)
(a)	(d)	19.92
(a)	(e)	43.68
(a)	(f)	34.88
(b)	(c)	102.24

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[a] Planes are expressed in the form ax + by + cz = d in orthogonal space where vectors x, y and z are parallel to unit cell vectors a, b and c* respectively. [b] The points CO and NC represent the midpoints of the C(7)–O(2) and N(1)–C(15) bonds. Points C(6), CO and NC define the basal plane for this pseudo-trigonal pyramidal complex.

tropic thermal parameters which were low as compared to similarly bonded carbon atoms). With all heavy atoms present and with individual isotropic thermal parameters assigned, blocked least-squares refinement yielded the conventional agreement parameter: R = 0.0824. The inclusion of hydrogen atoms together with anisotropic refinement of all heavy atoms reduced this to R = 0.0572.

TABLE V. Structural Parameters for η^2-Aminomethylene Complexes.

Compound	Distance (Å)					
	Mo–Cp	Mo–CO	Mo–N	Mo–C	C–N	Ref.
I	2.077	1.932(13)	2.178(8)	2.223(12)	1.418(16)	3
II	2.022	1.937(8)	2.177(6)	2.259(6)	1.446(8)	3
III	2.081	1.900(10)	2.145(16)	2.203(8)	1.447(23)	This work

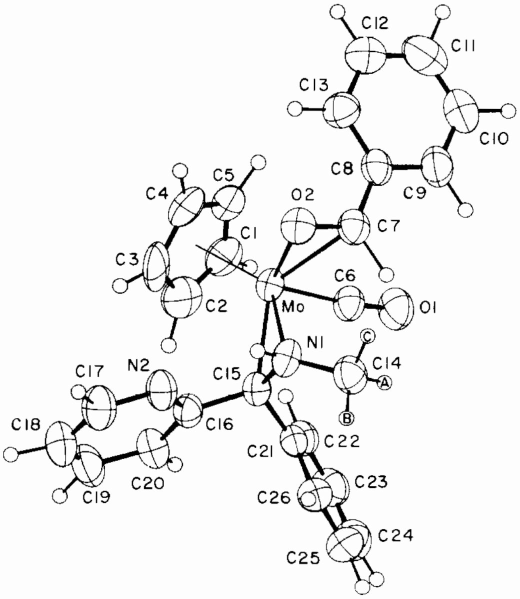

Fig. 1. Labeled view of the title compound. Heavy atoms are represented by 50 percent probability ellipsoids, while hydrogen atoms are shown as spheres of arbitrary size.

Although all of the hydrogen atoms were located in difference maps, only five chemically significant hydrogens were actually refined in the final stages: The aminomethylene, H(100), and benzaldehyde H(7), hydrogens were refined as individual isotropic atoms while the methyl hydrogens, H(14A,B,C), were refined using a single group isotropic thermal parameter. Hydrogens belonging to phenyl, pyridine and cyclopentadiene groups were refined in the SHELX floating mode where calculated hydrogen positions [d(C–H) = 1.00 Å] are allowed to shifts as their parent carbons refine. Three group isotropic thermal parameters were assigned to the aromatic hydrogen atoms.

The final stages of blocked least-squares refinement included 2182 reflections and 301 parameters yielding the final agreement parameters: $R = 0.0459$ and $R_w = 0.0674$. The largest parameter shifts during the last cycle were smaller than 0.2 times their respective ESD's. In the final difference Fourier map, the largest residual peak had a value of 0.82 e/Å^3. Final positional and thermal parameters appear in Table II. Structural parameters for III are listed

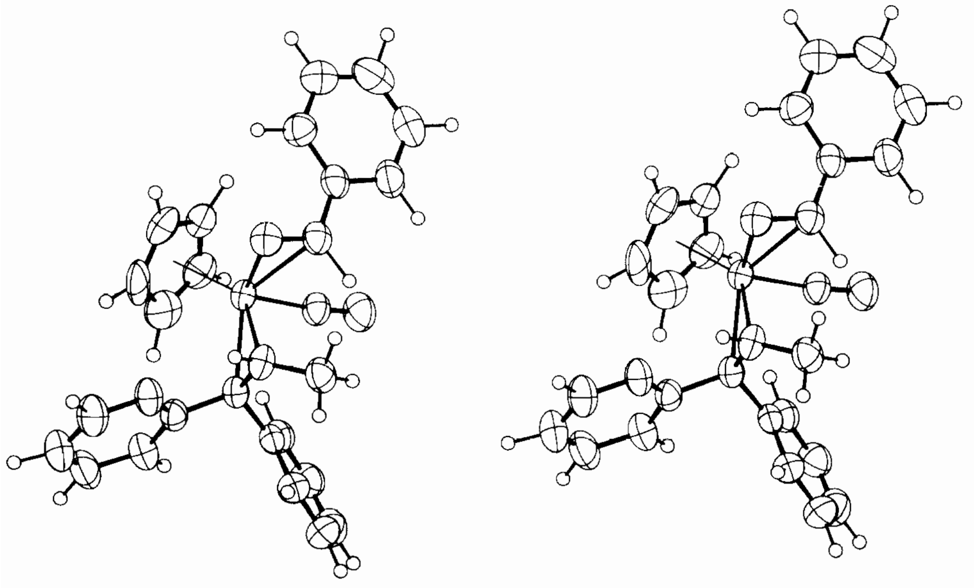

Fig. 2. Stereo view of the title compound.

TABLE VI. Structural Parameters for η^2-Carboxy Complexes

Compound	Distance (Å)			
	M–C	M–O	C–O	Ref.
III	2.261(13)	2.070(8)	1.333(12)	This work
$[Ph_3P]_2Ni[\eta^2\text{-}OC(CF_3)_2]$	1.89(2)	1.87(1)	1.32(2)	10
$[Et_3P]_2Ni[\eta^2\text{-}OC(Ph)_2]$	1.974(2)	1.849(2)	1.335(4)	9
$(OC)_2[Ph_3P]_2Os[\eta^2\text{-}OCH_2]$	2.191(7)	2.038(7)	1.59(1)	11

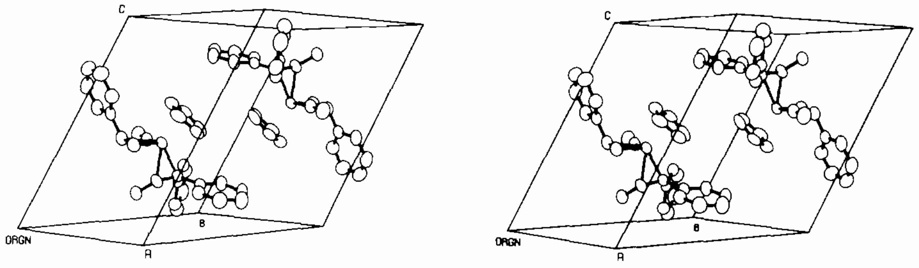

Fig. 3. Stereo view depicting the molecular packing.

in Tables III–V. Figures 1–3 depict the molecular geometry and crystal packing.

Results and Discussion

The geometry of III may be described as a distorted Cp-capped trigonal pyramid. As depicted in Fig. 1, the two η^2-ligands and the molybdenum atom form a pair of three-membered ligand planes which are almost perpendicular [the dihedral angle between planes Mo–O(2)–C(7) and Mo–N(1)–C(15) is 102.24°], while the terminal CO ligand lies just 0.36 Å out of the Mo–O(2)–C(7) plane (see Table IV). Since the four ligands differ, the Mo site in III is chiral and inspection of Fig. 1 shows two C sites and one N site in the surrounding ligands also to be chiral. Although, theoretically, 16 stereoisomers should be possible, only two enantiomers (that depicted in Fig. 1 and its mirror image) have been isolated in the solid state as the racemic mixture III.

Most of the bonding in III is identical to that described earlier [3] for the simple η^2-aminomethylene compounds I and II. Table V shows that for all three compounds, Mo–N distances are shorter than Mo–C (aminomethylene). In each case, the shorter Mo–N distance may be explained in terms of enhanced π-donation to nitrogen by the metal [8]. The high π-acidity of the aminomethylene ligand is reflected in the N–C distances, all of which correspond, within experimental error, to unit bond order.

As with compounds I and II, the orientation of the pyridine group in III is determined by the formation of an intramolecular hydrogen bond. The N(1)–H(100) group lies close to the plane of the pyridine ring (see Table IV), with intramolecular contacts [N(1)···N(2) = 2.66, and N(2)···H(100) = 2.13 Å] consistent with those reported for I and II. Thus, the weak intramolecular hydrogen bonding in III results in the pyridine and methyl groups always being *trans*-oriented across the Mo–N(1)–C(15) plane.

The most striking structural feature in III is the presence of a neutral η^2-coordinated benzaldehyde ligand. The carbonyl group lies close to the plane of its attached phenyl ring, resulting in an O(2)–C(7)–C(13) torsional angle of only −1.76°. The refined aldehyde hydrogen is further removed from this plane (plane e in Table IV) reflecting the distortion of the aldehyde group upon coordination to Mo. The C(7)–(O7) distance, 1.33(1) Å, is identical to that found for η^2-benzophenone described by Tsou *et al.* [9]. This distance is significantly longer than the 1.204 Å reported by Coppens *et al.* [10] for the carbonyl group in uncoordinated *o*-nitrobenzaldehyde. For all of the η^2-coordinated carboxy ligands listed in Table VI, deviations between M–C and Mo–O distances, lengthening of the C–O bonds, and distortion of the carboxyl carbon atoms toward sp^3 hybridization can all be explained in terms of back donation of metal electron density into the carbonyl π orbital.

Acknowledgements

We thank the Robert A. Welch Foundation and the U.S. National Science Foundation for operational support. I. Bernal thanks NATO and the Alexander von Humboldt Foundation for providing the opportunity to visit Germany to collaborate with Professor Henri Brunner and his associates, whom we thank for the crystals we used in this study.

References

1 (a) H. Brunner and W. A. Herrmann, *Angew. Chem., 84,* 442 (1972);
(b). H. Brunner and W. A. Herrmann, *Chem. Ber., 105,* 3600 (1972).
2 (a) H. Brunner and J. Wachter, *J. Organometal. Chem., 113,* C58 (1976);
(b) H. Brunner, H. Schwägerl, J. Wachter, G. M. Reisner and I. Bernal. *Angew. Chem., 90,* 478 (1978).
3 G. M. Reisner and I. Bernal, *Inorg. Chim. Acta, 51,* 201 (1981).
4 H. Brunner, J. Wachter, I. Bernal and M. W. Creswick, *Angew. Chem., 91,* 920 (1979).
5 G. M. Reisner, I. Bernal and G. R. Dobson, *J. Organometal. Chem., 157,* 23 (1978).
6 Program REDUCE, J. Korp, University of Houston, 1975.
7 G. Sheldrick, 'SHELX-76 System of Computer Programs', Cambridge, 1976.
8 (a) E. W. Abel, R. J. Rowley, R. Mason and K. M. Thomas, *J. Chem. Soc. Chem. Commun.,* 72 (1974).
(b) E. W. Abel and R. J. Rowley, *J. Chem. Soc. Dalton Trans.,* 1096 (1975).
9 T. T. Tsou, J. C. Huffman and J. K. Kochi, *Inorg. Chem., 18,* 2311 (1979).
10 R. Countryman and B. R. Penfold, *J. Cryst. Mol. Struct., 2,* 281 (1972).
11 K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden and W. R. Roper, *J. Am. Chem. Soc., 101,* 503 (1979).
12 P. Coppens and G. M. J. Schmidt, *Acta Crystallogr., 17,* 573 (1964).