Acknowledgment. Support of this research by the National Science Foundation (Grant CHE82-06117) is gratefully acknowledged.

Registry No. (η^3-C_3H_5)Mo(CO)$_2$(bpy)Cl, 86022-48-2; (η^3-2-MeC_3H_4)Mo(CO)$_2$(bpy)Cl, 86022-49-3; (η^3-C_3H_5)Mo(CO)$_2$(bpy)(O_2CCF_2) (isomer A), 57811-34-4; (η^3-2-MeC_3H_4)Mo(CO)$_2$(bpy)(O_2CCF_3), 80974-03-4; (η^3-C_6H_5)Mo(CO)$_2$(dppm)Cl, 62662-28-6; (η^3-C_3H_5)Mo(CO)$_2$(dppe)Cl, 62742-80-7; (η^3-2-MeC_3H_4)Mo(CO)$_2$(dppe)Cl, 86167-35-3; (η^3-C_3H_5)Mo(CO)$_2$(dpae)Cl, 66615-65-4; (η^3-(C_3H_5)W(CO)$_2$(dppe)Cl, 62662-31-1; (η^3-C_3H_5)Mo(CO)$_2$(bpy)(O_2CCF_3) (isomer B), 81027-38-5.

Studies of Molybdenum Compounds. 4. Synthesis and Structure of Dibenzyl(2,2′-bipyridyl)dioxomolybdenum(VI)

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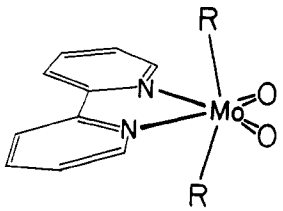
Dibenzyl(2,2′-bipyridyl)dioxomolybdenum(VI), synthesized by the reaction of benzylmagnesium chloride with dioxodibromo(2,2′-bipyridyl)molybdenum(VI), crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.961 (3) Å, b = 12.862 (2) Å, and c = 16.156 (5) Å with Z = 4. Its structure was resolved by Patterson and Fourier methods. The three-dimensional X-ray data were measured with the θ–2θ scan technique with a scintillation detector. The structure was refined by full-matrix least-squares calculations to give $R(F_o)$ = 0.067 and $R_w(F_o)$ = 0.104 for 1582 unique observations above 2σ. The structure of the Mo(O)$_2$(bpy) moiety is coplanar as in other complexes of this type. However, the Mo–N bonds are shorter, the C–Mo–C bond angle of 155.5° is wider, and the Mo–C bonds of 2.25 (2) Å are longer than in the corresponding dimethyl or dineopentyl derivatives. Although indefinitely stable at room temperature in the solid state, the complex exhibits a tendency to decompose with Mo–C bond cleavage in solution under aerobic conditions. This is attributed to the occurrence of spontaneous Mo–C bond cleavage reactions induced by thermal motions of the coordinated bpy ligand.

Introduction

In previous papers of this series[1,2] we described the synthesis and structure of two new dialkyl derivatives of dioxomolybdenum(VI) of composition $R_2Mo(O)_2$(bpy) (bpy = 2,2′-bipyridyl), with R = CH_3 (1) and $CH_2C(CH_3)_3$ (2), respectively. Because of the steric demands of the neo-



R = $-CH_3$ 1
$-CH_2C(CH_3)_3$ 2
$-CH_2C_6H_5$ 3

pentyl groups in 2 the C–Mo–C bond angle decreased and the Mo–C bond length increased as compared to 1. We have sence prepared dibenzyl(2,2′-bipyridyl)dioxomolybdenum, 3, to study both electronic and steric effects on Mo–C bond labilization in complexes of this type. Complex 3 was found to be less stable thermally (mp 155 °C dec) than the corresponding alkyl derivatives and exhibits sensitivity to O_2 in solution. Complex 3 also has an unusual ^{1}H NMR spectrum, suggesting an interaction of the benzyl phenyl moieties with the coordinated bpy ligand. This unique structural feature was confirmed by the X-ray crystallographic structure determination to be described in the following.

Experimental Section

Reagents and Chemicals. All reagents and chemicals obtained from commercial sources were of analytical or reagent grade purity and were used without further purification. Tetrahydrofuran (Mallinckrodt) was dried over potassium and distilled immediately prior to use. The argon was of 99.998% purity and was dried by passage over KOH pellets. Mo(O)$_2$Br$_2$(bpy) was prepared according to Hull and Stiddard.[3]

Synthesis of Mo(O)$_2$($CH_2C_6H_5$)$_2$(bpy), 3. Benzylmagnesium chloride was prepared in tetrahydrofuran by using 30 cm^3 (0.25 mol) of freshly distilled benzyl chloride diluted to 200 cm^3 with THF added dropwise to 12 g (0.5 mol) of Mg in 300 cm^3 of THF. The addition was done over 5 h under an atmosphere of nitrogen and at 0 °C. The resulting Grignard reagent was 0.4 M. A stirred suspension of 7 g of Mo(O)$_2$Br$_2$(bpy) in 100 cm^3 of dry THF and under an atmosphere of nitrogen was cooled to −10 °C in a dry ice/acetone/water bath. To this suspension, 80 cm^3 of the 0.4 M benzylmagnesium chloride was added dropwise. The Grignard was added in 1 h, and the reaction was kept cold for another 2 h after which it was allowed to warm to room temperature. The entire solution was added to 1 L of water and stirred. An orange

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(2) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Ross, F.; Ross, D.; Schlemper, E. O. *Organometallics* **1983**, *2*, 481.
(3) Hull, C. G.; Stiddard, M. H. B. *J. Chem. Soc.* **1966**, 1633.

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Table I. Summary of Physical Properties of Complexes 1, 2, and 3

phys property	1	2	3
mp, °C	230 dec	180 dec	155 dec
IR $\nu_{Mo=O}$,[a] cm^{-1}	934, 905	922, 890	915, 885
UV-vis λ_{max}, nm (ϵ)[b]	345 (2000)	365 (1900)	356 (7800)
	303 (19 600)	304 (18 500)	308 (20 800)
	293 (17 000)	292 (18 500)	296 (18 000)
	283 s (10 300)	283 s (14 300)	276 s (11 000)
	245 (24 900)	250 (25 400)	236 (26 400)
energy of Mo-C bond,[c] kJ M^{-1}	347.6	328.3	336.5

[a] In KBr. [b] Measured in CH_2Cl_2. [c] Calculated from the lowest energy transition in the UV spectrum.

Table II. Summary of ^1H NMR Data

protons	chem shifts,[a] ppm (intensities) 1	2	3
CH_3	0.58 (6) s	0.95 (18) s	
CH_2		1.15 (4) s	3.10 (4) s
phenyl[b] C's 13, 17 and 20, 24			5.95 (4) dd
C's 14, 15, 16 and 21, 22 23			6.50 (6) m
bpy C's 1 and 10	9.39	9.60	9.36
C's 2 and 9	7.71 (8)	7.50 (8)	7.32 (8)
C's 3 and 8	7.77	7.61	7.63
C's 4 and 7	8.42	8.20	7.80

[a] Chemical shifts are relative to Me_4Si, measured in $CDCl_3$. [b] See Figure 1 for proton positions.

precipitate was collected by vacuum filtration, dried, and recrystallized from diethyl ether/benzene: mp 155 °C dec; yield 50% based on 1. Anal. Calcd for $C_{24}H_{24}MoN_2O_2$: C, 61.77; H, 4.77; Mo, 20.58; N, 6.01; O, 6.86; mol wt 466.28. Found: C, 62.04; H, 4.92; Mo, 20.61; N, 5.98; O, 6.45; mol wt 490 (cryoscopic in benzene).

Physical Properties. Absorption characteristics in the UV–vis and infrared spectra and comparison with those of complexes 1 and 2 are summarized in Table I. Fourier transform ^1H NMR spectra were obtained for a solution of 3 in $CDCl_3$ using a Nicolet-360 spectrometer. Chemical shifts and intensities of the observed signals are given in Table II.

Aerobic Decompsoition of 3. A 6-mg sample of 3 was weighed into two 10-cm^3 serum-capped vials. One was flushed with argon and serum capped, and the other was capped with an atmosphere of air. The reaction was initiated by injecting 5 cm^3 of anhydrous, argon-flushed methanol into each bottle. These were placed on a shaker, and the change in color was monitered visually and spectrally. The aerobic reaction solution became completely colorless overnight. There was no spectral change of the anaerobic sample during the same period. Benzaldehyde was detected in the aerobic sample solution by conversion to the 2,4-dinitrophenylhydrazone by adding 2 cm^3 of a saturated (4 mg/cm^3) solution of 2,4-dinitrophenylhydrazine in 2 N HCl plus 5 cm^3 of water. The derivatized product was extracted into hexane and identified against standards by thin-layer chromatography on Silica gel using benzene as the elutant.

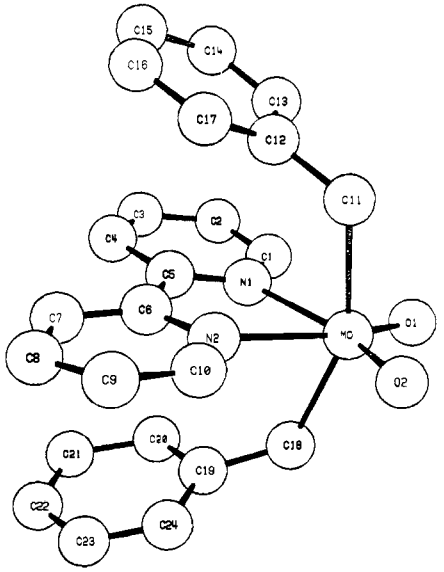

Figure 1. Perspective view of $Mo(O)_2(CH_2C_6H_5)_2(bpy)$ with the atoms numbered.

Structural Analysis. An outline of crystallographic and data collection parameters is given in Table III. A crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm was mounted on an Enraf-Nonius CAD4 automated diffractometer for data collection. The orthorhombic $P2_12_12_1$ unit cell dimensions were determined by a least-squares fit of 25 reflections obtained by automatic centering on the diffractometer. Intensity data (294 K) were measured by the θ–2θ step scan technique with Mo K_α radiation (λ = 0.7107 Å) from a graphite monochromator. A total of 3167 Bragg reflections were examined out to 2θ = 45°. The intensities were, in general, quite weak which limits the accuracy of the final structure parameters. The intensities of three standard reflections measured after each 8000 s of X-ray exposure showed no systematic change during data collection. Orientation was maintained by checking the centering of three reflections after every 200 reflections and recentering 25 reflections and calculating a new orientation matrix if any of the three were significantly off center. Several ψ scans indicated that the transmission varied by less than 2% so no absorption correction was applied. Averaging of equivalent reflections yielded 1582 reflections of the type *hkl* and

Table III. Crystallographic and Data Collection Parameters

space group	$P2_12_12_1$	diffractometer	Enraf-Nonius CAD-4
a, Å	9.961 (3)	cryst size, mm	0.1 × 0.1 × 0.1
b, Å	12.862 (2)	λ, Å (Mo Kα)	0.710 73
c, Å	16.156 (5)	μ, cm^{-1}	6.4
V, Å^3	2069 (1)	absorptn correctn	none
ρ_{calcd}, g/cm^3	1.497 (1)	transmissn range	estd from ψ scans (0.98-1.00)
Z	4	scan speed	variable to maintain 3% counting statistics to a max time of 120 s/scan
f_w	466.4		
$R(F_o)$	0.067	θ-2θ scan	96 steps/scan
$R_w(F_o)$	0.104	background	16 steps/each side
total no. of observns	3167	peak	64 steps
no. of unique observatns above 2σ (includes unequal Friedel pairs)	1582	scan width (θ)	0.55 + 0.35 tan θ

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B1,2)	B(1,3)	B(2,3)
Mo	−0.2393 (2)	−0.2150 (1)	−0.0927 (1)	0.0092 (2)	0.00402 (9)	0.00345 (6)	0.0038 (4)	−0.0015 (3)	0.0014 (2)
O(1)	−0.306 (2)	−0.273 (1)	−0.009 (1)	0.016 (2)	0.007 (1)	0.0058 (8)	0.012 (3)	0.002 (2)	0.009 (2)
O(2)	−0.108 (2)	−0.286 (1)	−0.130 (1)	0.017 (2)	0.008 (1)	0.0045 (8)	0.014 (3)	−0.003 (2)	−0.002 (2)
N(1)	−0.391 (2)	−0.085 (1)	−0.079 (1)	0.008 (2)	0.003 (1)	0.0019 (7)	−0.001 (2)	−0.003 (2)	0.001 (2)
N(2)	−0.201 (2)	−0.089 (1)	−0.191 (1)	0.009 (2)	0.006 (1)	0.0017 (7)	0.005 (3)	0.002 (2)	0.001 (2)
C(1)	−0.488 (2)	−0.092 (2)	−0.021 (1)	0.010 (3)	0.004 (2)	0.0014 (9)	−0.002 (4)	0.004 (3)	−0.002 (2)
C(2)	−0.589 (3)	−0.021 (2)	−0.019 (1)	0.013 (3)	0.010 (2)	0.0022 (10)	−0.007 (5)	0.003 (3)	−0.002 (3)
C(3)	−0.589 (2)	0.066 (2)	−0.070 (2)	0.011 (3)	0.005 (2)	0.0054 (14)	0.003 (4)	0.008 (3)	−0.004 (3)
C(4)	−0.491 (2)	0.074 (2)	−0.129 (1)	0.013 (3)	0.003 (1)	0.0035 (10)	0.002 (4)	−0.004 (3)	0.001 (2)
C(5)	−0.390 (2)	−0.006 (2)	−0.132 (1)	0.007 (2)	0.002 (1)	0.0023 (9)	0.000 (3)	−0.002 (2)	0.001 (2)
C(6)	−0.277 (2)	−0.005 (1)	−0.193 (1)	0.009 (3)	0.004 (1)	0.0018 (7)	0.001 (4)	−0.002 (3)	0.003 (2)
C(7)	−0.252 (3)	0.079 (2)	−0.243 (1)	0.012 (2)	0.007 (1)	0.0053 (10)	−0.015 (5)	−0.013 (3)	0.005 (2)
C(8)	−0.140 (2)	0.069 (2)	−0.301 (1)	0.006 (3)	0.016 (3)	0.0024 (10)	−0.010 (5)	0.004 (3)	0.005 (3)
C(9)	−0.075 (2)	−0.023 (2)	−0.303 (2)	0.007 (3)	0.014 (3)	0.0040 (13)	0.005 (5)	0.005 (3)	0.001 (3)
C(10)	−0.107 (3)	−0.095 (2)	−0.247 (1)	0.013 (3)	0.005 (2)	0.0035 (11)	0.004 (4)	0.002 (3)	−0.001 (3)
C(11)	−0.387 (3)	−0.268 (2)	−0.189 (2)	0.012 (3)	0.010 (2)	0.0069 (14)	0.002 (5)	0.003 (4)	−0.008 (3)
C(12)	−0.492 (2)	−0.195 (2)	−0.225 (1)	0.009 (2)	0.003 (2)	0.0033 (9)	0.000 (3)	−0.006 (3)	−0.001 (2)
C(13)	−0.611 (2)	−0.188 (2)	−0.186 (1)	0.009 (3)	0.006 (2)	0.0048 (12)	0.001 (4)	−0.005 (3)	−0.004 (3)
C(14)	−0.705 (2)	−0.123 (2)	−0.220 (2)	0.010 (3)	0.013 (2)	0.0046 (11)	−0.013 (4)	0.002 (3)	−0.010 (3)
C(15)	−0.683 (3)	−0.069 (3)	−0.294 (2)	0.009 (3)	0.027 (5)	0.0066 (17)	0.009 (7)	−0.006 (4)	−0.006 (5)
C(16)	−0.567 (3)	−0.080 (2)	−0.331 (2)	0.017 (4)	0.011 (3)	0.0030 (11)	−0.003 (6)	−0.006 (3)	0.005 (3)
C(17)	−0.471 (2)	−0.147 (2)	−0.302 (2)	0.011 (3)	0.007 (2)	0.0041 (12)	−0.002 (4)	−0.005 (3)	−0.004 (3)
C(18)	−0.127 (2)	−0.098 (2)	−0.015 (2)	0.009 (3)	0.009 (2)	0.0051 (13)	0.010 (4)	0.006 (3)	0.003 (3)
C(19)	−0.101 (2)	0.013 (2)	−0.034 (1)	0.011 (3)	0.006 (2)	0.0022 (9)	−0.003 (4)	−0.004 (3)	−0.001 (2)
C(20)	−0.195 (2)	0.088 (2)	−0.010 (1)	0.012 (3)	0.008 (2)	0.0023 (9)	−0.003 (4)	−0.004 (3)	−0.004 (2)
C(21)	−0.176 (3)	0.193 (2)	−0.043 (2)	0.016 (4)	0.008 (2)	0.0106 (19)	−0.005 (5)	0.013 (4)	−0.007 (4)
C(22)	−0.069 (3)	0.216 (2)	−0.078 (2)	0.028 (5)	0.007 (2)	0.0117 (23)	−0.018 (6)	0.004 (6)	−0.004 (5)
C(23)	0.025 (3)	0.136 (3)	−0.103 (2)	0.023 (4)	0.016 (3)	0.0040 (14)	−0.025 (5)	−0.004 (5)	0.005 (4)
C(24)	0.011 (2)	0.039 (2)	−0.081 (2)	0.012 (3)	0.009 (2)	0.0031 (11)	−0.010 (4)	0.002 (3)	−0.004 (3)

atom[b]	x	y	z	atom[b]	x	y	z
HC(1)	−0.4877 (0)	−0.1502 (0)	0.0197 (0)	HC(14)	−0.7923 (0)	−0.1114 (0)	−0.1918 (0)
HC(2)	−0.6650 (0)	−0.0278 (0)	0.0216 (0)	HC(15)	−0.7521 (0)	−0.0271 (0)	−0.3220 (0)
HC(3)	−0.6588 (0)	0.1191 (0)	−0.0671 (0)	HC(16)	−0.5398 (0)	−0.0323 (0)	−0.3782 (0)
HC(4)	−0.4911 (0)	0.1329 (0)	−0.1687 (0)	HC(17)	−0.3942 (0)	−0.1648 (0)	−0.3344 (0)
HC(7)	−0.3114 (0)	0.1424 (0)	−0.2396 (0)	H1C(18)	−0.1717 (0)	−0.1008 (0)	0.0392 (0)
HC(8)	−0.1170 (0)	0.1297 (0)	−0.3345 (0)	H2C(18)	−0.0391 (0)	−0.1308 (0)	−0.0050 (0)
HC(9)	−0.0102 (0)	−0.0358 (0)	−0.3474 (0)	HC(20)	−0.2686 (0)	0.0703 (0)	0.0305 (0)
HC(10)	−0.0478 (0)	−0.1574 (0)	−0.2447 (0)	HC(21)	−0.2448 (0)	0.2479 (0)	−0.0390 (0)
H1C(11)	−0.3332 (0)	−0.2901 (0)	−0.2359 (0)	HC(22)	−0.0384 (0)	0.2852 (0)	−0.0872 (0)
H2C(11)	−0.4326 (0)	−0.3249 (0)	−0.1674 (0)	HC(23)	0.0992 (0)	0.1557 (0)	−0.1410 (0)
HC(13)	−0.6308 (0)	−0.2277 (0)	−0.1345 (0)	HC(24)	0.0785 (0)	−0.0134 (0)	−0.0976 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(B1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl]$. [b] $B = 5.0000\ (0)$ Å^2.

Table V. Selected Interatomic Bond Distances (Å)

Mo-O(1)	1.68 (1)	N(1)-C(1)	1.35 (2)
-O(2)	1.71 (1)	N(1)-C(5)	1.33 (2)
-C(11)	2.24 (2)	N(2)-C(6)	1.32 (2)
-C(18)	2.26 (2)	N(2)-C(10)	1.30 (2)
-N(1)	2.27 (1)	av N-C	1.33 (2)
-N(2)	2.30 (1)		
		C(12)-C(13)	1.34 (2)
C(1)-C(2)	1.36 (3)	C(13)-C(14)	1.38 (3)
C(2)-C(3)	1.40 (3)	C(14)-C(15)	1.40 (3)
C(3)-C(4)	1.36 (3)	C(15)-C(16)	1.31 (3)
C(4)-C(5)	1.43 (3)	C(16)-C(17)	1.37 (3)
C(6)-C(7)	1.38 (2)	C(17)-C(12)	1.41 (3)
C(7)-C(8)	1.46 (3)	C(19)-C(20)	1.40 (2)
C(8)-C(9)	1.35 (3)	C(20)-C(21)	1.46 (3)
C(9)-C(10)	1.35 (3)	C(21)-C(22)	1.25 (3)
av bpy C-C	1.39 (4)	C(22)-C(23)	1.44 (4)
		C(23)-C(24)	1.31 (3)
C(5)-C(6)	1.49 (2)	C(24)-C(19)	1.40 (3)
C(11)-C(12)	1.52 (3)	av phenyl C-C	1.37 (6)
C(18)-C(19)	1.47 (3)		

Table VI. Selected Interatomic Bond Angles (deg)[a]

O(1)-Mo-O(2)	110.2 (6)	N(1)-Mo-C(11)	81.3 (6)
N(1)-Mo-N(2)	69.9 (5)	N(1)-Mo-C(18)	77.6 (5)
C(11)-Mo-C(18)	155.5 (8)	N(2)-Mo-C(11)	80.8 (8)
		N(2)-Mo-C(18)	80.3 (6)
O(1)-Mo-N(1)	89.4 (5)		
O(2)-Mo-N(2)	90.5 (6)	Mo-N(1)-C(1)	120 (1)
O(1)-Mo-N(2)	159.1 (5)	Mo-N(1)-C(5)	120 (1)
O(2)-Mo-N(1)	160.4 (6)	Mo-N(2)-C(6)	119 (1)
		Mo-N(2)-C(10)	123 (1)
O(1)-Mo-C(11)	99.6 (8)		
O(1)-Mo-C(18)	92.6 (8)	N(1)-C(5)-C(6)	115 (1)
O(2)-Mo-C(11)	95.6 (7)	N(2)-C(6)-C(5)	115 (1)
O(2)-Mo-C(18)	100.1 (7)		
Mo-C(11)-C(12)	123 (1)		
Mo-C(18)-C(19)	128 (1)		

[a] For average values the average deviation from the mean is given rather than the least squares standard deviation.

$hk\bar{l}$ which had $F_o > 2\sigma(F_o)$; these were used to solve and refine the structure ($\sigma^2(F_o^2) = \sigma(\text{counting})^2 + (0.05F_o^2)^2$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$).

The structure was solved by Patterson and Fourier methods. Least-squares refinement, minimizing $\sum\omega(|F_o| - |F_c|)^2$, where $\omega = 1/(\sigma(F_o))^2$, converged with $R = \sum||F_o| - |F_c||/\sum F_o = 0.067$ and $R^w = [\sum(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2} = 0.104$. Refinement of the other enantiomers gave $R = 0.068$ and was therefore rejected. Hydrogen atoms were located and held in near "ideal" X-ray positions. The largest shift on the last cycle was 0.09 times its esd, and the error in an observation of unit weight was 2.25. Atomic scattering factors were taken from ref 4 and included anomalous scattering effects in F_c. Final atomic positional and thermal parameters are included in Table IV. Selected interatomic distances and angles are given in Tables V and VI.

(4) "International Tables for Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

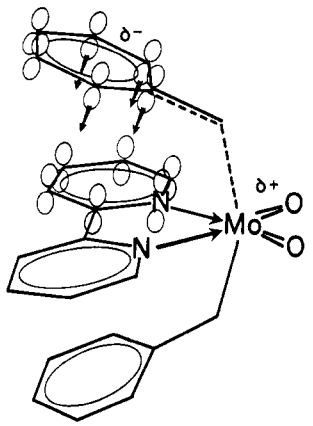

Figure 2. Qualitative representation of the π-electron system interaction between the benzyl rings and the bpy pyridine rings.

Discussion

Complex **3** is the first aralkyl derivative of this series of complexes and exhibits a number of interesting structural features. Like **1** and **2**, **3** has a *cis*-Mo–O_2 moiety and a *trans*-Mo–R_2 moiety. The Mo–O bonds and the O–Mo–O angle are isostructural in all three compounds, but there is a significant lengthening in the Mo–C bonds to 2.25 (2) Å compared with 2.194 (2) Å (**1**) and 2.237 (5) Å (**2**). The C–Mo–C angle has increased from 149° in **1** and 145° in **2** to 155.5° in **3**. This, along with the widening of the Mo–C–C angle to 126° compared to 119° in **2**, is indicative of resonance effects which increase the electron density on the benzyl phenyl rings and weaken the Mo–C bonds. The high electron density apparently forces the benzyl phenyl moieties away from the *cis*-MoO_2 oxygen atoms to positions of close contact above and below the bpy pyridine rings. The phenyl planes are nearly parallel with the bpy plane (dihedral angles of 19.1 and 23.1°) and the average distances between these planes are 3.104 and 3.205 Å (Figure 1). The resulting interaction of the π-electron systems increases the electron density on the bpy ligand (Figure 2), which in turn is transferred to the molybdenum atom through increased $d\pi$–$p\pi$ back-bonding, as evidenced by the shortening of the Mo–N bonds from 2.33 Å in **1** and **2** to 2.28 Å in **3**. Finally, the increased charge density on molybdenum is in part shifted onto the oxygen atoms. This effect is not noticeable in the Mo=O bond lengths, but it is seen in the IR spectrum, namely, in the shift of the 2 Mo–O stretching frequencies to lower energy (see Table I). The UV–vis absorption spectrum in solution indicates a shift of the absorptions corresponding to coordinated bpy to higher energies. Compared to **1**, the Mo–C bond strength in **3** is weakened by about 11.1 kJ M^{-1}, as estimated from the λ_{max} of the first low-energy absorption. However compared to **2**, the Mo–C bond is stronger by about 8.2 kJ M^{-1}, indicating that the electronic Mo–C bond labilization in **3** is smaller than the steric labilization in **2**.

The interactions between the benzyl phenyl groups and the bpy pyridine rings appears unaffected by different organic solvents as is indicated by ^1H NMR measurements. The absence of a temperature dependence of the ^1H NMR spectra (temperature range 0–55 °C) demonstrates furthermore that the free rotation of the benzyl phenyl groups remains impaired even at higher temperatures. The spectrum shows an upfield shift of the phenyl protons compared to nonligated aromatic compounds to 6.50 ppm for the protons on carbons 14, 15, 16 and 21, 22, 23 and 5.95 ppm for the protons on carbons 13, 17 and 20, 24 (see Figure 1 for numbering of atoms). There is also an upfield shift of the four bpy resonances compared with the dialkyl derivatives (Table II) which is consistent with the expected overlap of the π systems.

Although **3** appears to be indefinitely stable on storage in the crystalline state and in solution under strictly anaerobic conditions, there is a tendency toward spontaneous Mo–C bond homolysis at room temperature as exhibited by the oxygen sensitivity of **3** in solution. Under strictly anaerobic conditions this Mo–C bond cleavage occurs as well, but the recombination of the $PhCH_2\cdot$ and $\cdot Mo(O)_2(CH_2Ph)(bpy)$ radicals takes place with high efficiency. In the presence of O_2, which acts as a free radical scavenger, the spontaneous decomposition occurs via oxidation of these radicals. This decomposition is accelerated on exposing aerobic solutions of **3** to visible or UV light.

The Mo–C bond lability of **3** is reminiscent of the behavior of benzylcobalamin[5] and is another example of a "mechanochemical" bond cleavage reaction. As a result of the structurally interlocked nature of **3** thermal movement of the coordinated bpy ligand can cause further weakening or rupture of one of the Mo–C bonds. Spontaneous Mo–C bond cleavage does not occur in **2**. In this complex both neopentyl moieties are orientated away from the bpy ligand and hence protected against mechanochemical Mo–C bond cleavage.

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Registry No. **3**, 86307-86-0; $Mo(O)_2Br_2(bpy)$, 25411-14-7; benzyl chloride, 100-44-7.

Supplementary Material Available: Tables of weighted least-squares planes and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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