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Characterization of Bis(2,2′-bipyridine) and Bis(1,10-phenanthroline) Derivatives of Molybdenum and Tungsten Carbonyls. Crystal and Molecular Structure of *cis*-Dicarbonylbis(2,2′-bipyridine)molybdenum(0)

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Improved syntheses of *cis*-[M(CO)$_2$(bpy)$_2$] and *cis*-[Mo(CO)$_2$(phen)$_2$] are reported (M = Mo, W; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline). The IR, visible, and NMR spectra of the complexes are discussed, as well as their electrochemical and general properties. Pertinent comparisons with the complexes *cis*-[M(CO)$_2$(PR$_3$)$_4$] or M(CO)$_4$(biL) (PR$_3$ = general tertiary phosphine ligand; biL = bpy, phen) are noted. Most noteworthy is the very low average C–O stretching frequency, ca. 1750 cm^{-1}, which indicates considerable $M(d) \rightarrow CO(\pi^*)$ back-bonding. The structure of *cis*-[Mo(CO)$_2$(bpy)$_2$], determined by a single-crystal X-ray diffraction study, revealed short Mo–C (1.93 (1) Å) and Mo–N (2.19 (4) Å) bonds, consistent with the presence of strong $M(d) \rightarrow CO(\pi^*)$, bpy($\pi^*$) back-bonding. The bpy ligand appears to be slightly distorted as a result of $M(d) \rightarrow bpy(\pi^*)$ bonding. Crystal data at −162 °C are a = 26.830 (12) Å, b = 9.467 (3) Å, c = 8.756 (3) Å, β = 119.91 (1)°, Z = 4, and d_{calcd} = 1.600 g cm^{-3} with space group $P2_1/a$.

Introduction

The reaction chemistry of *cis*-[M(CO)$_2$(dmpe)$_2$] (M = Mo, W; dmpe = 1,2-bis(dimethylphosphino)ethane) has been investigated by one of us recently.[2] As an extension of this work, it was decided to explore the chemistry of the analogous *cis*-[M(CO)$_2$(biL)$_2$] (biL = 2,2′-bipyridine or 1,10-phenanthroline) complexes. These have been previously prepared by Behrens,[3] though very little further work has been carried out on them.[4]

An unusual feature of these complexes is that the infrared spectra of the solid complexes show two ν(CO) absorptions at very low frequencies for terminal CO ligands (ca. 1770 and ca. 1720 cm^{-1}) when compared with those of other *cis*-[M(CO)$_2$L$_4$] complexes. These low frequencies are even lower than those observed for the complex Mo(O-*t*-Bu)$_2$(py)$_2$(CO)$_2$ (py = pyridine) (1908 and 1768 cm^{-1}), whose frequencies are unusually low for MoX$_2$L$_2$(CO)$_2$ complexes.[5] For the latter complex, the separation of the two ν(CO) absorptions by 140 cm^{-1} is also remarkable. Both of these attributes can be at least partially ascribed to the strong π-donating abilities of the alkoxide ligands, which in turn cause the Mo(II) center to be a strong π donor. The resultant geometry of this d^4 complex is severely distorted from octahedral, with the cis CO ligands moved toward one another ($\angle$CMoC = 72°) and the trans O-*t*-Bu ligands bending away from the CO groups ($\angle$OMoO = 156°).[5] This distortion has been rationalized in terms of a displacement along a C_{2v} mode, along which there is a double minimum in the total energy of the molecule.[6]

Further evidence of the strong π-donating ability of the Mo(OR)$_2$ moiety is seen in the complex Mo(O-*i*-Pr)$_2$(bpy)$_2$. The crystal structure and resonance Raman spectra of this Mo(II) species show that there is extensive π donation from the metal into the π^* orbitals of the bipyridine ligands, such that they adopt a bi(2*H*-pyrid-2-ylidene) configuration.[7] This behavior is reminiscent of that of low-valent metal–bpy complexes, such as M(bpy)$_3$ (M = Cr, Mo, W). Though the molybdenum and tungsten species have not been extensively characterized,[8] for Cr(bpy)$_3$, it was found that extensive π donation from the metal to the bipyridine ligands occurs such that it might be best to characterize this complex as Cr^{III}(bpy$^-$·)$_3$.[9]

The low values of ν(CO) in the complexes M(CO)$_2$(biL)$_2$ clearly indicate that the metal is a strong π donor in this coordination environment. One then might expect that some of the unusual attributes noted above could be present in these complexes. Here are reported an improved preparation of *cis*-[M(CO)$_2$(bpy)]$_2$ and the results of spectroscopic measurements on these molecules and on *cis*-[Mo(CO)$_2$(phen)$_2$]. Where appropriate, comparisons are made with *cis*-[M(CO)$_4$(biL)] complexes. The crystal and molecular structure of *cis*-[Mo(CO)$_2$(bpy)$_2$] determined at 91 K is also reported.

Results and Discussion

Synthesis and General Properties. It was found that, by use of Behren's method[3] for the synthesis of *cis*-[M(CO)$_2$(biL)$_2$], a tedious, inefficient purification by extraction with hot benzene was necessary to remove the last traces of *cis*-[M(CO)$_4$(biL)] from the product. This problem was avoided by first preparating pure *cis*-[M(CO)$_4$(biL)] (readily obtained in high yield from the reaction between *cis*-[Mo(CO)$_4$(norbornadiene)] and biL[10]) and then reacting it with excess biL in boiling tetralin. The darkly colored crystalline, highly air-sensitive complexes precipitate from the reaction mixture upon cooling. The *cis*-[M(CO)$_2$(biL)$_2$] complexes are insoluble in solvents such as pentane, benzene, diethyl ether, and tetrahydrofuran. Even in more polar solvents, such as methyl cyanide and dimethyl sulfoxide, *cis*-[M(CO)$_2$(biL)$_2$] is much less soluble than *cis*-[M(CO)$_4$(biL)]. *cis*-[M(CO)$_2$(phen)$_2$] is more soluble in solvents of lower polarity than *cis*-[M(CO)$_2$(bpy)$_2$].

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Table I. Carbonyl Stretching Frequencies for Representative *cis*-[Mo(CO)$_2$L$_4$] Complexes[a]

complex	Mo oxidn state	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	solvent	ref
Mo(CO)$_2$(bpy)$_2$	0	1782, 1723	59	CH$_3$CN	b
Mo(CO)$_2$(phen)$_2$	0	1795, 1728	67	CH$_2$Cl$_2$	b
Mo(CO)$_2$(dmpe)$_2$	0	1838, 1766	72	CH$_2$Cl$_2$	12a
Mo(CO)$_2$(dppm)$_2$	0	1845, 1784	61	Nujol	12b
Mo(CO)$_2$(dppe)$_2$	0	1852, 1786	66	DCE	12c
Mo(CO)$_2$(PF$_3$)$_4$	0	2040, 2008	32	CH$_2$Cl$_2$	13
Mo(CO)$_2$(O-*t*-Bu)$_2$(py)$_2$	2	1908, 1768	140	Nujol	15
Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$	2	1925, 1865	60	KBr	14a
Mo(CO)$_2$(S$_2$CN-*i*-Pr$_2$)$_2$	2	1934, 1842	92	CH$_2$Cl$_2$	14b
Mo(CO)$_2$(PPh$_3$)$_2$Br$_2$	2	1965, 1890	75	KBr	14c
Mo(CO)$_2$(PPh$_3$)(S$_2$CNEt$_2$)$_2$	2	1945, 1860	85	KBr	14d

[a] Abbreviations used: bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, dmpe = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, py = pyridine, DCE = 1,2-dichloroethane. [b] This work.

Solutions of *cis*-[M(CO)$_2$(biL)$_2$] are markedly photosensitive. For example, a solution of *cis*-[Mo(CO)$_2$(bpy)$_2$] in carefully deaerated dimethyl sulfoxide changed color from deep purple to orange-brown on standing in a sealed tube for 12 h in daylight (not direct sunlight); a deep blue solution of *cis*-[Mo(CO)$_2$(phen)$_2$] in dichloromethane decomposed within minutes of being exposed to direct sunlight. Consequently, the solid complexes *cis*-[M(CO)$_2$(biL)$_2$] and their solutions in carefully deaerated, dry solvents were always handled in subdued or indirect light; in particular, solutions of these complexes were shielded by black paper wherever possible.

The solid complexes are rather involatile. Heating *cis*-[Mo(CO)$_2$(bpy)$_2$] for several hours at 500 K under vacuum (10^{-2} torr) resulted in a small deposit of bpy, which was collected on a cold finger (77 K). However, an electron impact mass spectrum of this complex contained an intense molecular ion (*m*/*e* 466 (100%)), together with ions of lower intensity formed by sequential loss of CO ligands (*m*/*e* 438 (18%), 410 (14%)). Attempts to record mass spectra for *cis*-[M(CO)$_4$(bpy)] (M = Cr, Mo, W), *cis*-[Mo(CO)$_4$(phen)], and *cis*-[Mo(CO)$_2$(phen)$_2$] were not successful, even when the fast atom bombardment technique (FABMS)[11] was used. Qualitatively, the tungsten complexes *cis*-[W(CO)$_2$(biL)$_2$] are more fragile than their molybdenum analogues.

IR Spectra. The infrared spectra of the pure *cis*-[Mo(CO)$_2$(biL)$_2$] complexes have been recorded in solution, and the values for the ν(CO) frequencies are given in Table I. The observations of the very low values for these complexes as measured in the solid-state (mull) spectra[3,4] are confirmed. For comparison, the values for various other *cis*-[Mo(CO)$_2$L$_4$] complexes,[12,13] as well as for various dicarbonyl Mo(II) complexes,[5,14] are included in Table I. The values for $\Delta\nu$, the energy difference between the two ν(CO) bands, are also included.

One point illustrated by these data is that the ν(CO) stretching frequencies for the *cis*-[Mo(CO)$_2$(biL)$_2$] (biL = bpy, phen) complexes are lower than for the other Mo(0) dicarbonyl complexes containing phosphine ligands. The present data suggest that the π acidity of the ligands increases in the order bpy < phen < dmpe < dppm < dppe < PF$_3$, as expected.

A second interesting point raised by the data in Table I concerns the splitting between the two ν(CO) stretching frequencies. Previously it has been suggested[15] that the splitting will increase as the average value of ν(CO) decreases because of increased coupling between the C–O stretching modes which results from the increased strength of the M–C bonds. From inspection of the data in Table I, it is clear that the splitting is most pronounched for Mo(O-*t*-bu)$_2$(py)$_2$(CO)$_2$ and a general trend with decreasing average ν(CO) value is not apparent. Other features are obviously important in determining this splitting, one of which is probably the C–M–C bond angle.[13] As of yet, there is insufficient data to evaluate such a premise though.

Saito et al.[9a] have examined the IR spectra of numerous metal–bpy complexes, especially those with metals in unusually low oxidation states where complexes of the type M^{n+}(bpy) may be better described as M$^{(n+1)+}$(bpy$^{-}\cdot$); i.e. the bpy is reduced. On the basis of characteristic IR properties, they classified the various complexes into three categories where the bpy ligands were in a normal, reduced, or intermediate oxidation state. The complexes with "normal" bpy ligands exhibited a weak band above 1600 cm^{-1} and no bands in the 1550–1600- or 950–1000-cm^{-1} regions. Complexes containing "reduced" bpy ligands did not have a band above 1600 cm^{-1} but exhibited an intermediate band in the 1550–1600-cm^{-1} region and a strong band in the 950–1000-cm^{-1} region. Complexes with "intermediate" bpy ligands exhibited bands in all three regions. The IR spectrum of *cis*-[Mo(CO)$_2$(bpy)$_2$] shows a weak band at 1602 cm^{-1}, a medium band at 1585 cm^{-1}, and a strong band at 972 cm^{-1}. Thus, the complex falls into the intermediate bpy category. Given the low oxidation potential of this complex (vide infra) and the low ν(CO) values which indicate the strong π donor properties of the Mo center, this is not a surprising result. This clearly indicates the presence of significant Mo(4d) → bpy(π^*) back-bonding.

NMR Spectra. In order to observe the proton NMR spectra of the rather insoluble *cis*-[Mo(CO)$_2$(biL)$_2$] complexes, extensive use of Fourier transform methods has been made. At a glance the low-resolution spectra appear quite simple, apparently consisting of two doublets and two triplets, which seemed to suggest a trans configuration[16] in contrast to IR data and the X-ray study, which unequivocally reveal the cis configuration in the solid state. The conflict was resolved by observation of the high-resolution NMR: one of the triplets was clearly seen to consist of two superimposed doublets. This establishes that the two pyridine rings are not equivalent and confirms the cis configuration. The remaining simplicity of the spectra presumably results from accidental degeneracies.

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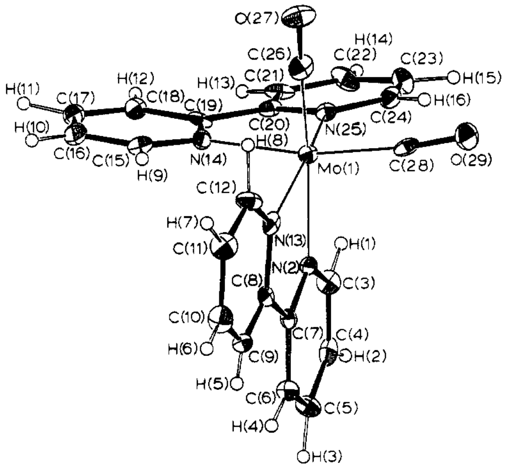

Figure 1. ORTEP view of the *cis*-[$Mo(CO)_2(bpy)_2$] molecule showing the atom-numbering scheme.

The NMR spectral data are given in the Experimental Section.

Electronic Spectra. The electronic spectra of *cis*-[$Mo(CO)_2(biL)_2$] in solution have been recorded. In addition to the usual $\pi \rightarrow \pi^*$ transitions of biL, there are Mo(4d) $\rightarrow$ biL(π^*) charge-transfer transitions in the visible region. In contrast to the visible absorption spectra of *cis*-[$Mo(CO)_4(biL)$], which show only weak absorption below ca. 500 nm, the *cis*-[$Mo(CO)_2(biL)_2$] compounds show significant absorption throughout the visible region. Obviously, replacing two CO ligands by the much weaker π acid biL increases the ease of oxidation of the metal center, shifting the charge-transfer absorptions to lower energy. The spectra are solvent dependent but, because of the difficulty experienced in preparing solutions and the restricted solubilities of the complexes, this was not investigated quantitatively. For *cis*-[$Mo(CO)_2(bpy)_2$] in dimethyl sulfoxide solution, the absorption maxima in the visible region are observed at λ_{max} 414 (log ϵ 3.5), 500 (3.6), and 720 (3.2) nm and for *cis*-[$Mo(CO)_2(phen)_2$] in dichloromethane solution at λ_{max} 376 (3.7), 468 (3.6), 578 (3.9), and 716 (3.8) nm. The values for the latter complex compare reasonably well with values previously reported for the complex in benzene solution.[4c]

Electrochemistry. Electrochemical measurements on *cis*-[$Mo(CO)_2(bpy)_2$] by cyclic voltammetry (glassy-carbon electrode) in acetonitrile solution (vs. the saturated calomel electrode) show a reversible reduction, $E_{1/2}^{red} = -1.68$ V, and a reversible oxidation, $E_{1/2}^{ox} = -0.54$ V, as previously reported.[17] These were shown to be one-electron couples by coulometry. A second, irreversible oxidation, $E_{1/2}^{ox} = +0.3$ V, is also observed. Comparisons with other *cis*-[$Mo(CO)_2(biL)_2$] systems (biL = bidentate phosphine ligands)[12,18,19] show that the oxidations can be assigned as being metal centered and that the reduction is probably bpy centered. The complex *cis*-[$W(CO)_2(bpy)_2$] shows no reduction wave out to −2.0 V. This increased resistance to reduction possibly indicates a much greater M(d) $\rightarrow$ bpy(π^*) back-bonding for tungsten relative to that for molybdenum.

The tungsten analogue is also slightly more difficult to oxidize. In acetonitrile solution, there is a reversible one-electron oxidation, $E_{1/2}^{ox} = -0.44$ V, and a second irreversible oxidation, $E_{1/2}^{ox} = +0.3$ V. The similarity of metal oxidation potentials for Mo and W in *cis*-[$Mo(CO)_2(biL)_2$] complexes (biL = bidentate phosphine ligands) has been noted previously.[12b,18,19] Comparison of the oxidation potentials in solution for *cis*-[$Mo(CO)_{6-2n}(biL)_n$] ($n = 1, 2$; biL = bpy, dmpe) shows that, for $n = 1$, the values of $E_{1/2}^{ox}$ are very similar (bpy, +0.62 V; dmpe, +0.61 V[19]), but for $n = 2$, the bpy complex is very much easier to oxidize (bpy, −0.54 V; dmpe, −0.23 V[19]). No indication of a cis to trans isomerization of [$Mo(CO)_2(biL)_2$] upon oxidation was observed for biL = bpy, phen, as has been previously found for biL = bidentate phosphines.[18]

Table II. Fractional Coordinates and Isotropic Thermal Parameters for *cis*-[$Mo(CO)_2(bpy)_2$][a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	3629.4 (3)	3442 (1)	4373 (1)	10
N(2)	4498 (2)	3782 (6)	6738 (7)	12
C(3)	4764 (3)	2853 (8)	8064 (8)	14
C(4)	5302 (3)	3103 (8)	9495 (10)	17
C(5)	5584 (3)	4345 (9)	9566 (9)	18
C(6)	5323 (3)	5297 (9)	8229 (9)	17
C(7)	4770 (3)	4991 (7)	6800 (8)	12
C(8)	4448 (3)	5969 (8)	5320 (8)	12
C(9)	4652 (3)	7277 (8)	5157 (10)	16
C(10)	4329 (3)	8151 (8)	3770 (10)	19
C(11)	3795 (3)	7684 (9)	2507 (10)	19
C(12)	3606 (3)	6369 (8)	2677 (9)	16
N(13)	3918 (2)	5480 (6)	4029 (7)	12
N(14)	3252 (2)	4245 (6)	5957 (7)	14
C(15)	3061 (3)	5567 (8)	5866 (9)	15
C(16)	2810 (3)	6041 (9)	6819 (10)	18
C(17)	2750 (3)	5072 (8)	7929 (9)	17
C(18)	2943 (3)	3723 (8)	8027 (9)	14
C(19)	3187 (3)	3297 (8)	7022 (8)	12
C(20)	3359 (3)	1855 (7)	6920 (9)	12
C(21)	3353 (3)	757 (8)	7961 (9)	16
C(22)	3497 (3)	−570 (8)	7742 (10)	19
C(23)	3638 (3)	−836 (8)	6441 (10)	18
C(24)	3636 (3)	291 (8)	5441 (9)	15
N(25)	3506 (2)	1640 (6)	5628 (7)	11
C(26)	2904 (3)	3489 (8)	2214 (9)	16
O(27)	2473 (2)	3553 (6)	820 (6)	22
C(28)	3853 (3)	2313 (8)	2972 (9)	13
O(29)	3948 (2)	1526 (6)	2089 (6)	20

atom	10^3x	10^3y	10^3z	$10B_{iso}$, Å^2
H(1)	456 (2)	199 (6)	806 (8)	6 (13)
H(2)	544 (3)	234 (8)	1031 (9)	18 (15)
H(3)	595 (3)	473 (8)	1043 (9)	21 (15)
H(4)	548 (3)	623 (8)	815 (9)	22 (16)
H(5)	494 (2)	755 (6)	596 (7)	0 (12)
H(6)	446 (3)	896 (8)	366 (9)	20 (16)
H(7)	352 (2)	822 (6)	155 (7)	0 (11)
H(8)	318 (3)	605 (8)	176 (10)	35 (18)
H(9)	311 (3)	620 (7)	514 (8)	15 (15)
H(10)	269 (3)	701 (9)	676 (10)	36 (19)
H(11)	253 (3)	546 (8)	856 (10)	32 (18)
H(12)	290 (3)	302 (7)	878 (9)	13 (15)
H(13)	327 (2)	93 (6)	883 (7)	0 (12)
H(14)	353 (2)	−135 (6)	846 (7)	2 (12)
H(15)	378 (3)	−172 (9)	621 (10)	35 (19)
H(16)	371 (3)	30 (8)	444 (8)	18 (15)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

Molecular Structure of *cis*-[$Mo(bpy)_2(CO)_2$]. An ORTEP view of the molecule giving the atom-numbering scheme is shown in Figure 1. Final atomic coordinates and thermal parameters are given in Table II. Complete listings of bond distances and angles are given in Tables III and IV, respectively. The molecule has approximate C_2 symmetry, but this is not crystallographically imposed. The coordination environment of the metal atom is octahedral, though there are slight distortions from this, most noticeably those required by

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Table III. Bond Distances (Å) for the *cis*-[Mo(CO)$_2$(bpy)$_2$] Molecule

A	B	dist	A	B	dist
Mo(1)	N(2)	2.239 (5)	C(4)	C(5)	1.382 (11)
Mo(1)	N(13)	2.155 (6)	C(5)	C(6)	1.362 (10)
Mo(1)	N(14)	2.220 (5)	C(6)	C(7)	1.415 (9)
Mo(1)	N(25)	2.143 (6)	C(7)	C(8)	1.471 (9)
Mo(1)	C(26)	1.922 (7)	C(8)	C(9)	1.390 (10)
Mo(1)	C(28)	1.935 (7)	C(9)	C(10)	1.364 (11)
O(27)	C(26)	1.193 (8)	C(10)	C(11)	1.376 (11)
O(29)	C(28)	1.188 (8)	C(11)	C(12)	1.379 (11)
N(2)	C(3)	1.343 (9)	C(15)	C(16)	1.381 (10)
N(2)	C(7)	1.343 (9)	C(16)	C(17)	1.403 (11)
N(13)	C(8)	1.383 (8)	C(17)	C(18)	1.364 (11)
N(13)	C(12)	1.350 (9)	C(18)	C(19)	1.394 (9)
N(14)	C(15)	1.340 (9)	C(19)	C(20)	1.457 (10)
N(14)	C(19)	1.366 (8)	C(20)	C(21)	1.389 (10)
N(25)	C(20)	1.387 (8)	C(21)	C(22)	1.357 (11)
N(25)	C(24)	1.355 (9)	C(22)	C(23)	1.389 (10)
C(3)	C(4)	1.381 (10)	C(23)	C(24)	1.378 (10)

Table IV. Bond Angles (deg) for the *cis*-[Mo(CO)$_2$(bpy)$_2$] Molecule

A	B	C	angle
N(2)	Mo(1)	N(13)	73.7 (2)
N(2)	Mo(1)	N(14)	87.8 (2)
N(2)	Mo(1)	N(25)	89.8 (2)
N(2)	Mo(1)	C(26)	169.5 (3)
N(2)	Mo(1)	C(28)	99.0 (2)
N(13)	Mo(1)	N(14)	95.0 (2)
N(13)	Mo(1)	N(25)	160.5 (2)
N(13)	Mo(1)	C(26)	95.7 (3)
N(13)	Mo(1)	C(28)	99.2 (2)
N(14)	Mo(1)	N(25)	73.5 (2)
N(14)	Mo(1)	C(26)	93.0 (2)
N(14)	Mo(1)	C(28)	165.5 (3)
N(25)	Mo(1)	C(26)	100.5 (3)
N(25)	Mo(1)	C(28)	93.5 (3)
C(26)	Mo(1)	C(28)	82.6 (3)
Mo(1)	N(2)	C(3)	124.3 (5)
Mo(1)	N(2)	C(7)	116.9 (4)
C(3)	N(2)	C(7)	118.7 (6)
Mo(1)	N(13)	C(8)	118.7 (4)
Mo(1)	N(13)	C(12)	124.9 (5)
C(8)	N(13)	C(12)	116.3 (6)
Mo(1)	N(14)	C(15)	124.3 (5)
Mo(1)	N(14)	C(19)	117.0 (4)
C(15)	N(14)	C(19)	118.6 (6)
Mo(1)	N(25)	C(20)	118.8 (4)
Mo(1)	N(25)	C(24)	125.0 (4)
C(20)	N(25)	C(24)	115.6 (6)
N(2)	C(3)	C(4)	122.4 (7)
C(3)	C(4)	C(5)	119.2 (7)
C(4)	C(5)	C(6)	119.3 (7)
C(5)	C(6)	C(7)	119.2 (7)
N(2)	C(7)	C(6)	121.2 (6)
N(2)	C(7)	C(8)	115.6 (6)
C(6)	C(7)	C(8)	123.1 (6)
N(13)	C(8)	C(7)	115.0 (6)
N(13)	C(8)	C(9)	120.8 (6)
C(7)	C(8)	C(9)	124.2 (6)
C(8)	C(9)	C(10)	121.6 (7)
C(9)	C(10)	C(11)	117.7 (8)
C(10)	C(11)	C(12)	119.6 (7)
N(13)	C(12)	C(11)	123.9 (7)
N(14)	C(15)	C(16)	123.7 (7)
C(15)	C(16)	C(17)	117.7 (7)
C(16)	C(17)	C(18)	119.0 (7)
C(17)	C(18)	C(19)	120.9 (7)
N(14)	C(19)	C(18)	120.1 (7)
N(14)	C(19)	C(20)	115.0 (5)
C(18)	C(19)	C(20)	124.9 (6)
N(25)	C(20)	C(19)	114.5 (6)
N(25)	C(20)	C(21)	121.8 (6)
C(19)	C(20)	C(21)	123.7 (6)
C(20)	C(21)	C(22)	120.2 (7)
C(21)	C(22)	C(23)	119.8 (7)
C(22)	C(23)	C(24)	117.6 (7)
N(25)	C(24)	C(23)	124.9 (7)
Mo(1)	C(26)	O(27)	175.6 (6)
Mo(1)	C(28)	O(29)	173.3 (6)

the small bite angle (73.6°) of the bpy ligands. The configuration is found to be cis as originally predicted on the basis of the IR data.[3]

There are rather short Mo–C bond lengths, 1.93 (1) Å (averaged), which together with the low values of $\nu(CO)_{av}$ (1753 cm^{-1}) indicate extensive Mo(4d) → CO(π^*) back-bonding. These values can be compared with those for Mo(CO)$_6$ (Mo–C$_{av}$ = 2.06 (2) Å,[20] $\nu(CO)_{av}$ = 2016 cm^{-1} [15a]), Mo(CO)$_3$(bpy)(py) (Mo–C$_{av}$ = 1.965 (10) Å,[21] $\nu(CO)_{av}$ = 1872 cm^{-1} [22]), and Mo(CO)$_3$(dien) (Mo–C$_{av}$ = 1.943 (20) Å,[20] $\nu(CO)_{av}$ = 1805 cm^{-1} [15b]). The Mo–N distances, which range from 2.14 to 2.24 Å, are on the average slightly shorter than those previously observed for a Mo(0)–bpy complex (Mo(CO)$_3$(bpy)(py), Mo–N(bpy)$_{av}$ = 2.235 (7) Å).[21] This can be attributed to increased M(d) → bpy(π^*) back-bonding as has been suggested previously.[7,23,24] Further, the Mo–N bond lengths involving the nitrogen atoms trans to CO ligands are significantly longer than those trans to nitrogen atoms. The latter are cis to the CO ligands. The π^* orbitals of the pyridine rings trans to a CO ligand overlap with a Mo(dπ) orbital that also overlaps with two CO(π^*) orbitals, whereas those of the pyridine rings trans to one another overlap with a Mo(dπ) orbital that only overlaps with one CO(π^*) orbital. Thus, the Mo(dπ) → bpy(π^*) back-bonding should be weakest to pyridine ligands that are trans to the CO ligands, accounting for the longer bond lengths.

In two cases, it has been noted that extensive M(d) → bpy(π^*) back-bonding results in a rather distinctive distortion of the bpy ligand.[7,23] It is therefore of interest to examine the structure of the bpy ligands of the present complex, since there is obviously extensive Mo(4d) → CO(π^*) back-bonding.

A detailed comparison is not possible in the present study due to distortions that occur in the molecule. A least-squares plane analysis indicates the pyridine ring associated with N(14)–C(19) is "bent" by nearly 10° with respect to the plane of pyridine containing C(20)–N(25). The pyridine rings themselves are all planar within experimental error, the largest deviation being 0.02 Å from an idealized C$_5$N plane. The electronic effects of one long and one short Mo–N bond per bpy ligand, along with the distortion described above, tend to render average distances within the bpy less meaningful than would be found for a molecule with higher symmetry. With these cautions in mind, we present in Table V the bpy parameters for the present structure along with other representative bpy parameters. Points worthy of note in examining the data presented in Table V are as follows. First, the structural parameters for bpy itself are nearly identical with the average parameters obtained by averaging the C–C and C–N distances in 128 well-determined M(bpy)$_x$L$_y$ complexes. The only significant difference is a shortening of the central C–C bond distance by ca. 0.02 Å upon complexation. Second, the two previously reported structures with well-established Md-to-bpy π^* bonding[7,23] are distinctly different from the above and agree with each other within experimental error. Third, the bpy parameters in *cis*-[Mo(CO)$_2$(bpy)$_2$] lie between these two extremes. As has been poined out by a reviewer,

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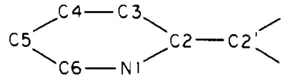
(25) The structure of the bpy ligand in Fe(η^6-toluene)(bpy)[23] is virtually identical with that in *cis*-[Mo(O-*i*-Pr)$_2$(bpy)$_2$].[7]

Table V. Comparison of bpy Interatomic Distances (Å) in Free 2,2'-Bipyridine, *cis*-[Mo(CO)$_2$(bpy)$_2$], and Other Selected Compounds



	N1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-N1	C2-C2'
bpy[a]	1.346 (2)	1.394 (2)	1.385 (2)	1.383 (3)	1.384 (2)	1.341 (2)	1.490 (2)
ML$_x$(bpy)$_y$[b]	1.353	1.394	1.384	1.380	1.390	1.348	1.467
Mo(CO)$_2$(bpy)$_2$							
min	1.343 (9)	1.389 (10)	1.357 (10)	1.376 (11)	1.378 (10)	1.340 (9)	1.457 (10)
max	1.387 (8)	1.415 (9)	1.364 (11)	1.403 (11)	1.381 (10)	1.355 (9)	1.471 (9)
av 1[c]	1.370	1.397	1.362	1.387	1.380	1.347	1.464
av 2[c]	1.385 ± 2	1.289 ± 1	1.361 ± 7	1.382 ± 13	1.379 ± 1	1.352 ± 5	
av 3[c]	1.354 ± 23	1.405 ± 21	1.363 ± 2	1.392 ± 21	1.381 ± 0	1.341 ± 3	
Fe(η^6-toluene)(bpy)[d]	1.383 (2)	1.409 (2)	1.370 (3)	1.406 (3)	1.368 (2)	1.371 (2)	1.417 (3)
Mo(O-*i*-Pr)$_2$(bpy)$_2$[a]	1.380 (10)	1.412 (7)	1.365 (7)	1.415 (5)	1.358 (4)	1.376 (5)	1.424 (4)

[a] Reference 7. [b] These values represent the average geometrical parameters for 128 "well-determined" bpy complexes located in the June 1980 release of the Cambridge Crystal Data File. Complexes with large residuals (>0.08) or larger discrepancies in chemically equivalent bonds were excluded. [c] Av 1 is a simple average for the four equivalent bonds in the present complex (two for C2-C2'); av 2 represents the side with the shorter M-N distance, and av 3 is the average of the two py rings for the longer M-N bond. The ±*n* represents the difference between the two values averaged (see text). [d] Reference 23.

the quoted esd's encompass both of the two extremes. That is to say, statistically we cannot base conclusions concerning the nature of the bpy ligand on crystallographic evidence alone. Nevertheless, we believe the trends observed in the structure, which lie between the extremes for a bpy ligand, corroborate the IR spectral evidence for the existence of appreciable Md-to-bpy π^* bonding in *cis*-[Mo(CO)$_2$(bpy)$_2$]. The magnitude of the back-bonding in *cis*-[Mo(CO)$_2$(bpy)$_2$] appears less than that in Mo(O-*i*-Pr)$_2$(bpy)$_2$, despite the formal oxidation states, 0 vs. +2, and d^n configurations, t_{2g}^6 vs. t_{2g}^4, because of the presence of the strongly π-acceptor carbonyl ligands.

Finally, it is interesting to note that the C-Mo-C angle is rather acute (82.6°). Since there are no obvious steric requirements for this, this must result for electronic reasons. Such an explanation can be found in a recent theoretical analysis by Kubâcek and Hoffmann,[6] though their paper dealt predominantly with distortions occurring in d^4 octahedral complexes (see Figure 6 of that work and related discussion). For an octahedral complex with two cis CO ligands and the other four ligands at rigorously octahedral angles, it is calculated that the optimum C-M-C angle for a low-spin d^6 complex should be 90° (or slightly greater). However, if the other four ligands are not at the idealized positions, this result is subject to change. In particular, if the two ligands that are mutually trans (cis to both CO ligands) are bent back away from the CO ligands, it becomes favorable for the C-M-C angle to become acute. For the present complex, the small bite angle of the bpy ligands results in the two trans nitrogens being bent back away from the CO ligands ($\angle$N-Mo-N = 160.5°). The acute C-Mo-C angle is apparently a consequence of this. These distortions are comparable to those found in Mo(CO)$_2$(O-*t*-Bu)$_2$(py)$_2$, where the two trans alkoxide oxygens subtend an angle of 156° about the metal (away from the CO ligands) and the C-M-C angle is 72°.[5] It should be kept in mind that this latter complex is d^4 (vs. the present d^6) and thus has additional reasons for undergoing such a distortion.[6]

Experimental Section

Preparation of *cis*-[Mo(bpy)$_2$(CO)$_2$]. *cis*-[Mo(CO)$_4$(bpy)] (6.6 g, 18.1 mmol) and 2,2'-bipyridine (8.55 g, 54.8 mmol) were placed in a three-neck round-bottomed nitrogen-filled flask. Dry, deaerated tetralin (150 mL) was added to the flask under a strong countercurrent of nitrogen. This mixture was heated while nitrogen gas was bubbled *directly* into the tetralin solution through a wide (1.5 cm i.d.) mouth pipette. The temperature of the mixture was slowly (over ca. 3 h) raised to the boiling point, during which time the color darkened appreciably. The mixture was heated at reflux for 0.5 h; then the heat was removed and the reaction vessel was allowed to cool to room temperature, during which time the flow of nitrogen through the solution was maintained. (If the above reaction times are substantially exceeded, lower yields of a powdery, pyrophoric material are isolated in which finely divided molybdenum is mixed with *cis*-[Mo(CO)$_2$(bpy)$_2$].)

When the reaction vessel had cooled to room temperature, the flask was sealed and placed in an icebox for at least 3 h to complete crystallization. The reaction mixture was filtered, and the solid residue was washed with petroleum ether (bp 40-60 °C) (3 × 100 mL). The remaining black, highly crystalline solid was then extracted with boiling benzene under nitrogen, until the drainings from the sinter were no longer red (produced by *cis*-[Mo(CO)$_4$(bpy)]). This extraction typically required 8 h. The pure complex *cis*-[Mo(CO)$_2$(bpy)$_2$] was dried under vacuum; yield 4.94 g, 59% based on *cis*-[Mo(CO)$_4$(bpy)]. Anal. Calcd for $C_{22}H_{16}N_4O_2Mo$: C, 56.9; H, 3.5; N, 12.1; Mo, 20.7. Found: C, 56.5; H, 3.5; Mo, 20.5; N, 11.9. NMR data (in C_2H_6SO solution, δ vs. Me$_4$Si): 7.46 (dd, 2 H), 7.54 (dd, 2 H) 8.01 (td, 4 H), 8.44 (dt, 4 H), 8.66 (dm, 4 H).

Preparation of *cis*-[Mo(CO)$_2$(phen)$_2$] and *cis*-[W(CO)$_2$(bpy)$_2$]. These were prepared in a similar manner described above, except from Mo(CO)$_4$(phen) and W(CO)$_4$(bpy), respectively.

Measurements. IR spectra were recorded on either a Perkin-Elmer 457 or 683 spectrophotometer. UV-visible spectra were measured with a Pye Unicam SP800 spectrophotometer. NMR spectra were recorded with a Bruker WP80 or a JEOL PS 100 FT spectrometer. The electrochemical apparatus has been described elsewhere.[26]

X-ray Structural Determination for *cis*-[Mo(CO)$_2$(bpy)$_2$]. General procedures were described previously.[27]

A black crystal of dimensions 0.12 × 0.10 × 0.09 mm was selected and transferred to the cold stream of the goniostat under an atmosphere of dry nitrogen. The cell dimensions obtained from 36 reflections at -162 °C with Mo Kα (λ = 0.71069 Å) were a = 26.830 (12) Å, b = 9.467 (3) Å, c = 8.756 (3) Å, β = 119.91 (1)°, Z = 4, and d_{calcd} = 1.600 g cm^{-3} with space group $P2_1/a$.

A total number of 2953 reflections were collected by using standard moving-crystal-moving-detector techniques with the following values: scan speed, 4.0 deg min^{-1}; scan width, 2.0 + dispersion; single background time at extremes of scan, 4 s; aperture size, 3.0 × 4.0 mm. The limits of data collection were $6° < 2\theta < 45°$. Of the 2953 reflections, 2530 were unique, and the number of $F > 2.33\sigma(F)$ was 1994.

The structure was solved by a combination of direct methods and Fourier techniques. All hydrogen atoms were located in a difference Fourier synthesis phased on the refined non-hydrogen atom parameters. The final full-matrix refinement included isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms, as well as positional parameters and an overall scale factor. The linear absorption coefficient was 6.882 cm^{-1}. Final residues were $R(F)$ = 0.0475 and $R_w(F)$ = 0.0436.

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Registry No. *cis*-$[Mo(bpy)_2(CO)_2]$, 29643-27-4; *cis*-$[Mo(CO)_2(phen)_2]$, 29643-29-6; *cis*-$[W(CO)_2(bpy)_2]$, 29643-28-5; $Mo(CO)_4(bpy)$, 15668-64-1; $Mo(CO)_4(phen)$, 15740-78-0; $W(CO)_4(bpy)$, 15668-66-3.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factor tables for the $Mo(bpy)_2(CO)_2$ molecule (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Reactions of Metal–Metal Multiple Bonds. 13.[1] Reactions of Diazoalkanes with Hexaalkoxides of Dimolybdenum and Ditungsten ($M\equiv M$). Preparation and Characterization of $Mo_2(O\text{-}i\text{-}Pr)_6(N_2CPh_2)_2(py)$, $W_2(O\text{-}t\text{-}Bu)_6(N_2C(p\text{-}tol)_2)_2$, and $Mo(O\text{-}t\text{-}Bu)_4(N_2CPh_2)$

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Received August 18, 1983

Various aryl-substituted diazomethanes have been found to react with $M_2(OR)_6$ ($M\equiv M$) compounds in hydrocarbon solvents at room temperature. A variety of products are formed, depending on M (Mo or W) and the alkoxy ligand, but in no instance is there evidence of alkylidene formation. The dinuclear center serves as a source of electrons for the reduction of the diazoalkane to a 2− ligand, i.e. to a hydrazone-type NNCRR′ ligand. In the reaction between $Mo_2(O\text{-}t\text{-}Bu)_6$ and Ph_2CN_2 the $M\equiv M$ bond is cleaved, and the mononuclear compound $Mo(O\text{-}t\text{-}Bu)_4(NNCPh_2)$ has been isolated as a crystalline compound. The molecule has a trigonal-bipyramidal central MoO_4N moiety with short Mo–N (1.797 (3) Å) and long Mo–O (1.944 (3) Å) bonds in the axial positions. The equatorial Mo–O bond distances are 1.889 (3) Å (averaged). Related reactions involving $W_2(O\text{-}t\text{-}Bu)_6$ and Ar_2CN_2 yield $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}NNCAr_2)_2$ compounds where Ar = Ph and *p*-tolyl (*p*-tol). The molecular structure of the *p*-tolyl derivative reveals a central $[O_3W\text{-}\mu\text{-}N]_2$ moiety based on the fusing of two trigonal-bipyramidal units sharing a common equatorial–axial edge formed by the agency of a pair of $NNCAr_2^{2-}$ ligands. The W–W and N–N distances are respectively 2.675 (1) and 1.410 (16) Å, indicative of single bonds. In the presence of donor ligands (pyridine or $HNMe_2$) the less sterically demanding isopropoxy and neopentoxy Mo_2 compounds form adducts of formula $Mo_2(OR)_6(N_2CAr_2)_2(L)$. The molecular structure of the compound $Mo_2(O\text{-}i\text{-}Pr)_6(NNCPh_2)_2(py)$ has three O-*i*-Pr ligands bridging a Mo–Mo single bond (2.662 (1) Å), with one terminal $NNCPh_2^{2-}$ ligand coordinated to each molybdenum atom. NMR and IR data are reported and the present results are compared and contrasted to related work involving mono- and dinuclear transition-metal complexes. Crystal data: for $Mo(O\text{-}t\text{-}Bu)_4(NNCPh_2)$, $a = 17.652$ (10) Å, $b = 12.366$ (6) Å, $c = 9.060$ (3) Å, $\alpha = 76.95$ (3)°, $\beta = 87.92$ (3)°, $\gamma = 124.92$ (2)°, $V = 1545$ (1) Å^3, $d_{calcd} = 1.252$ g cm^{-3}, and space group $P\bar{1}$; for $W_2(O\text{-}t\text{-}Bu)_6(NNC(p\text{-}tol)_2)_2$(hexane), $a = 23.672$ (5) Å, $b = 12.214$ (2) Å, $c = 21.221$ (6) Å, $\beta = 97.24$ (1)°, $V = 6086$ (1) Å^3, $d_{calcd} = 1.459$ g cm^{-3}, and space group $C2/c$; for $Mo_2(O\text{-}i\text{-}Pr)_6(NNCPh_2)_2(py)$, $a = 12.512$ (8) Å, $b = 14.795$ (9) Å, $c = 14.099$ (8) Å, $\beta = 109.51$ (2)°, $V = 2460$ (1) Å^3, $d_{calcd} = 1.369$ g cm^{-3}, and space group $P2_1$.

Introduction

Various transition metals are known to catalytically decompose diazomethane to polymethylene or ethylene.[2] Silver oxide, copper powder, and copper salts are also used in the catalytic formation of carbenes from diazoalkanes in organic syntheses. Diazoalkane metal complexes have been synthesized by reactions involving coordinated dinitrogen ligands with *gem*-dihalides,[3] acids,[4] and ketones[5] and by ligand displacement or substitution reactions involving the direct interaction between a diazoalkane and an unsaturated metal center.[6] Examples of the latter are reactions involving dinuclear compounds such as $Cp_2Mo_2(CO)_4$, which contains a $Mo\equiv Mo$ bond and yields various adducts depending upon the diazoalkane.[7] Diazoalkane complexes are often the precursors to metal alkylidene complexes by the thermally or photochemically induced elimination of dinitrogen. As part of a continuing study of the chemistry of $(RO)_3M\equiv M(OR)_3$ compounds, where M = Mo and W,[8] we describe here our studies of their reactions with aryl-substituted diazomethanes. A preliminary report of a part of this study has appeared.[9]

Results and Discussions

Syntheses. The isolated new diazoalkane compounds have been obtained from the reactions shown in eq 1–3.

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