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Quadruply Bonded Pairs of Metal Atoms Bridged by Amidines. I. Preparation and Structure of Tetrakis(*N*,*N*'-diphenylbenzamidinato)dimolybdenum(II)

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When molybdenum hexacarbonyl is heated with *N*,*N*'-diphenylbenzamidine, PhC(NPh)(NHPh), a red, air-stable crystalline precipitate is formed in the reaction solution. Analytical, spectroscopic, and X-ray crystallographic data show it to be $Mo_2[PhC(NPh)_2]_4$, with an Mo–Mo distance of 2.090 (1) Å. A strong Raman band at 410 cm^{-1} can be associated primarily with the stretching of the Mo≣Mo bond. The molecule shows no tendency to form adducts with other donors, presumably because of severe steric blocking of the coaxial positions. Crystallographic data are as follows: space group $I4_1cd$; unit cell dimensions a = 18.976 (4) Å and c = 35.894 (8) Å. There are 8 molecules in the unit cell and crystallographic symmetry 2 (C_2) is imposed. The structure was refined to discrepancy indices of R_1 = 0.056 and R_2 = 0.078. Only the Mo atom was refined anisotropically. The structure is analogous to that of $Mo_2(O_2CR)_4$ molecules, as expected, since an amidinato group $RNC(R)NR^-$ is isoelectronic and isostructural with $OC(R)O^-$. The Mo–Mo distance is essentially identical with those in $Mo_2(O_2CR)_4$ compounds. The analogous tetrakis(*N*,*N*'-di-*p*-tolylbenzamidino)dimolybdenum has also been isolated. It has a strong Raman line at 413 cm^{-1} and is presumed to be isostructural with the molecule just described. Attempts to prepare similar chromium and tungsten compounds were unsuccessful, though other compounds, also described, were isolated.

Introduction

The remarkable ability of carboxylato ions to serve as bridging ligands in binuclear complexes with metal–metal bonds is now well-known.[2-4] The most common type of compound involves four bridging carboxyl groups, but those with only two[5,6] or one[7] are also known. The O···O distance is approximately 2.3 Å and the oxygen atoms have their donor orbitals directed roughly parallel to each other so that excellent overlap can occur if the two metal atoms are also about 2.3 Å apart. However, the situation is a flexible one and variations in the M–M distance in the range 2.0–2.7 Å can be tolerated with only slight loss of overlap. In practice M–M distances in $M_2(O_2CR)_4$ structures are known from a lower limit[8,9] of 2.090 (4) Å in $Mo_2(O_2CCF_3)_4$ and 2.093 (1) Å in $Mo_2(O_2CCH_3)_4$, to an upper limit[10] of 2.716 (2) Å in $[Cu_2(O_2CH)_4(NCS)_2]^{2-}$.

From the RCO_2^- group there are several natural extrapolations to isostructural and isoelectronic groups which should also be expected to yield a large class of binuclear complexes. One such structural and electronic analog to RCO_2^- is the amidinato group $RC(NR')(NR'')^-$ where the O atoms are replaced by NR' and NR''. In this paper we report the preparation and characterization of the first M_2(amidinato)$_4$ type complex, namely, the dimolybdenum(II) compound, with a quadruple Mo-to-Mo bond, in which the amidinato ligand is the *N*,*N*'-biphenylbenzamidino ion $\{C_6H_5C[N(C_6H_5)]_2\}^-$. Unsuccessful attempts to prepare chromium and tungsten analogs will also be described.

Experimental Section

Preparations. All reactions and manipulations of solutions containing the product were carried out in an atmosphere of nitrogen. Hydrocarbon solvents were dried over sodium wire. *N*,*N*'-Diphenylbenzamidine and its *p*-tolyl analog were prepared by a literature method.[11] Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer.

Tetrakis(*N*,*N*'-diphenylbenzamidinato)dimolybdenum (1). A solution of molybdenum hexacarbonyl (0.250 g, 0.93 mmol) and the amidine (0.750 g, 2.75 mmol) in petroleum ether (bp 100–120°, 50 ml) was heated under reflux for 27.5 hr. A red precipitate had formed and this was separated by decantation. The precipitate was washed well with hexane and dried under vacuum to give tetrakis(*N*,*N*'-diphenylbenzamidenato)dimolybdenum (0.096 g, 0.075 mmol, 16%). The material thus prepared gave satisfactory analyses. A sample was recrystallized from CH_2Cl_2–hexane to obtain the red crystals required for the structural study. These decomposed without melting at ca. 230° under vacuum.

Anal. Calcd for $C_{76}H_{60}Mo_2N_8$: C, 71.47; H, 4.70; Mo, 15.4; N, 8.78; M, 1276. Found: C, 71.9; H, 4.66; Mo, 16.4; N, 9.18; M, 1185, 1231.

Tetrakis(*N*,*N*'-di-*p*-tolylbenzamidinato)dimolybdenum (2). Molybdenum carbonyl (0.532 g, 2.00 mmol) and the amidine (0.606 g, 2.00 mmol) in petroleum ether (bp 100–120°, 40 ml) were heated under reflux for 17 hr. The solution was filtered while hot and the orange powder which had precipitated was washed well with hexane (in which it is slightly soluble) and dried under vacuum to give **tetrakis(*N*,*N*'-di-*p*-tolylbenzamidinato)dimolybdenum** (0.35 g, 0.25 mmol, 25%). The material decomposes in chlorinated solvents.

Anal. Calcd for $C_{84}H_{76}Mo_2N_8$: C, 72.62; H, 5.48; N, 8.07. Found: C, 72.5; H, 5.16; N, 7.92.

Reaction of Chromium Hexacarbonyl with *N*,*N*'-Diphenylbenzamidine. Chromium hexacarbonyl (1.09 g, 4.6 mmol), the amidine (1.5 g, 5.5 mmol), and petroleum ether (100–120°, 40 ml) were heated under reflux for 52 hr. The hot liquid was decanted from the crystalline precipitate which had formed. The precipitate which appeared to be a mixture of red and yellow crystals was ground up and extracted thoroughly with acetone until the extracts were colorless. The red, acetone-insoluble residue (0.781 g, mp 308–309°) proved to be insoluble in all solvents tried. It was therefore washed well with hexane, dried under vacuum, and submitted for analysis.

Anal. Calcd for $C_{76}H_{60}Cr_2N_8$: C, 76.77; H, 5.05; N, 9.43. Found: C, 76.88; H, 5.15; N, 9.64.

This compound, **3**, thus has the composition $(Ph_3CN_2)_4Cr_2$, but lack of solubility would suggest that it may not consist of simple dinuclear molecules analogous to those in compounds **1** and **2**.

Petroleum ether (bp 60–80°) was added to the yellow acetone extract. Slow reduction of the volume under vacuum caused the deposition of yellow needles. A further quantity of yellow solid was obtained when the reaction solution, which had originally been decanted, was cooled to room temperature. This material was washed with hexane and the two batches were combined and recrystallized from CH_2Cl_2–hexane to give yellow, slightly air-sensitive needles of compound **4**, *N,N'*-diphenylbenzamidinetricarbonylchromium (0.549 g, 1.32 mmol, 29%); mp 164–166° dec.

Anal. Calcd for $C_{22}H_{16}CrN_2O_3$: C, 64.71; H, 3.92; N, 6.86. Found: C, 64.4; H, 4.32; N, 6.89.

In CH_2Cl_2 solution the compound has strong CO stretching bands at 1964 and 1883 (br) cm^{-1}, and the mass spectrum has a multiplet centered around m/e 405 with its most intense component at m/e 408. This corresponds precisely to $(C_{19}H_{16}N_2)^{52}Cr(CO)_3$. The infrared spectrum also has a weak peak at 3405 cm^{-1} indicative of an N–H bond but shifted some 100 cm^{-1} to higher frequency from that in the free amidine.

Reactions of Tungsten Hexacarbonyl. The carbonyl (0.723 g, 2.05 mmol), *N,N'*-diphenylbenzamidine (0.556 g, 2.04 mmol) and petroleum ether (bp 100–120°, 25 ml) were heated under reflux for 22 hr. The hot reaction mixture was filtered and the precipitate was washed with hexane and dried. Recrystallization of the brown solid from CH_2Cl_2–hexane afforded red crystals (0.22 g), mp 250–251° dec, of compound **5**. Thin-layer chromatography indicated that this consisted of only one component.

Anal. Calcd for $C_{54}H_{40}N_5O_3W_2$: C, 55.20; H, 3.41; N, 5.96; mol wt 1174. Found: C, 53.6; H, 3.28; N, 5.79; m/e for P^+ 1174.

In dichloromethane solution, carbonyl stretching bonds were found at 1960 (s), 1880 (s), and 1867 (s) cm^{-1}. There was no evidence for any other reaction product.

Reaction of $W(CO)_6$ (0.7 g) with the di-*p*-tolylamidine (1.8 g) in refluxing petrolum ether (bp 100–120°) for 24 hr give a very dark solution and traces of a precipitate. The solution had ir absorption bands at ca. 1927 (s, sh), 1917 (s), and ca. 1905 (s, sh) cm^{-1} in addition to the band due to unreacted $W(CO)_6$. The reaction mixture was evaporated to dryness and extracted with hexane to give a brown residue which appeared to decompose on further attempts at purification. Its ir spectrum had broad peaks in the CO stretching region. No further work was done with this material.

X-Ray Crystallography. A large crystal of **1**, ca. 0.5 × 0.5 × 0.7 mm, was mounted on a glass fiber with the long axis parallel to the ϕ axis and was examined on the diffractometer. The crystal belonged to the tetragonal system; systematic absences (hkl for $h + k + l \neq 2n$, $0kl$ for $k, l \neq 2n$, hhl for $2h + l \neq 4n$) uniquely indicated space group $I4_1cd$. The half-height widths (ω scans) of several strong reflections were measured as <0.15°. Accurate cell constants were obtained by carefully centering 15 reflections in a range $2° < 2\theta < 2°$; the cell constants and calculated volume are $a = 18.976$ (4) Å, $c = 35.894$ (8) Å, and $V = 12925$ (5) Å^3. For $Z = 8$, the calculated density is 1.32 g cm^{-3}; a value 1.33 ± 0.02 g cm^{-3} was determined by flotation in a CCl_4–hexane mixture. A crystallographic twofold axis is imposed on the molecule.

Two data sets were collected for this compound. The first data set was collected on a Syntex $P\bar{1}$ diffractometer at 3 ± 1° with Mo Kα radiation in the range $0° < 2\theta \leq 50°$, using step ω scans with a variable scan rate of 1.0–24.0° min^{-1}. One complete octant of data was collected; the 2742 unique data ($F_o° > 3\sigma(F_o^2)$ and $k \geq h$) were used in the solution and refinement[12] of the structure. The parameter p used in data reduction was set at 0.05. One standard reflection was measured every 200 reflections; its intensity did not change with time. The second data set was collected on a Syntex $P\bar{1}$ diffractometer at 24 ± 1° with Mo Kα radiation. The θ–2θ scan technique with a variable scan rate of 3.0–24.0° min^{-1} was used to collect 3226 hkl reflections ($k \geq h$, $l \geq 0$) in the range $0° < 2\theta \leq 50°$ and 229 $hk\bar{l}$ reflections ($k \geq h$) in the range $0 < 2\theta \leq 20°$.[13] The parameter p was set at 0.07. Four standard reflections, remeasured every 100 reflections, maintained constant intensity throughout the data collection.

The absorption coefficient is 3.4 cm^{-1}; no absorption correction was made. No extinction correction was necessary. In each data set, a few reflections (four or five) exceeded the maximum counting rate of the detector and were omitted from the data set.

In space group $I4_1cd$, the z coordinate of one atom must be fixed to define the origin; the z coordinate of the unique Mo atom was chosen to be 0. This choice introduces a false inversion center at the origin and a false mirror plane at $z = 0$. The x and y coordinates of the Mo atom were obtained from a three-dimensional Patterson function; the positions so determined (0.055, 0, 0) gave rise to *mmm* pseudosymmetry at the origin. One nitrogen atom was also located from the Patterson map. Two cycles of refinement on the atomic positions produced $R_1 = \sum \| F_o| - |F_c \| / \sum |F_o| = 0.59$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2\}^{1/2} = 0.67$. Three additional light atoms were located in a difference Fourier map. When the positions of these five atoms were refined, the Mo atom shifted to its final position; at this point $R_1 = 0.36$ and $R_2 = 0.43$. The structure was built up by successive cycles of Fourier calculations (both F_o and difference syntheses) and least-squares refinement or structure factor calculations. Because of the pseudosymmetry, the process of completing the structure was more arduous than normal. Isotropic refinement converged with residuals $R_1 = 0.072$ and $R_2 = 0.105$; two cycles of full-matrix refinement with anisotropic thermal parameters for the core atoms (Mo, N, and bridging C) gave $R_1 = 0.064$ and $R_2 = 0.092$.

Although the structure appeared in general to be reasonable, there remained some nagging difficulties: the temperature factors for the atoms in rings 1 and 3 (those on the twofold axis) were quite large, and these rings were severely distorted from a planar, hexagonal configuration. Also the error in an observation of unit weight was high (2.75). A comparison of preliminary θ–2θ scan data, taken to establish the space group, with the ω-scan data revealed that some reflections which were absent ($I < 2\sigma$) in the θ–2θ scans had been measured with intensities as great as 10σ in the ω scans. Since this result suggested that other reflections could also have been mismeasured, the θ–2θ data were remeasured.

The new data set at 24 ± 1° was used for a new isotropic refinement. There was no significant improvement in the structure. After several attempts to improve the positions of the offending atoms had failed, the two rings were removed, and the remaining atoms were refined to convergence. A difference map then revealed two sets of peaks in the regions occupied by rings 1 and 3, with one set of peaks approximately twice as intense as the other. When both sets of peaks were included with occupation factors of 0.65 and 0.35, the residuals fell to $R_1 = 0.068$ and $R_2 = 0.095$, and the error in an observation of unit weight dropped from 2.80 to 2.10. Further refinement with anisotropic thermal parameters for Mo converged with $R_1 = 0.056$ and $R_2 = 0.078$ and the error in an observation of unit weight equal to 1.73.

The choice of enantiomorph is important in a polar space group. When structure was refined in the space group of opposite polarity, the residuals increased to $R_1 = 0.16$ and $R_2 = 0.21$, and the error in an observation of unit weight rose to 4.7. The temperature factors of several carbon atoms, including those in the disordered rings, changed dramatically. This worsening of the residuals, as well as the other forms of unsatisfactory behavior of the structure upon changing the enantiomorph are more extreme than normally expected, but we have accepted the initial choice of polarity as correct and terminated the refinement, since all features of interest in the structure have doubtless been determined to useful accuracy.

An examination of the final model indicates that although the disordered model produces some improvements, there still exist some problems. In particular, the minor conformer of ring 1 has not refined to a reasonable geometry, and both C14 and C34 have large temperature factors. It is possible that these rings exhibit a fluttering motion such that C14 and C34 move in an arc bisected by the twofold axis. We have established that the structure of the amidine complex is like that of $Mo_2(OAc)_4$ rather than $Mo_2(allyl)_4$, and we have obtained a good value for the Mo–Mo distance; our interest in this structure does not extend further.

Scattering factors for neutral Mo, N, and C were taken from Cromer's tabulation.[14]

Anomalous dispersion effects for Mo were included in F_c;[15] $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[16]

Table I lists the final values of $|F_o|$ and $|F_c|$.[17] The atomic positions and thermal parameters are listed in Table II.

Results

Figure 1 gives a schematic representation of the structure. The actual structure is shown in the stereopair of Figure 2. The large number of phenyl groups and their varying ori-

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

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.05350 (3)	−0.01330 (3)	0.0000 (0)	0.00216 (1)	0.00225 (2)	0.000638 (5)	0.00087 (3)	0.00006 (3)	0.00014 (4)
Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
N1	0.0557 (4)	−0.0208 (4)	0.0592 (2)	3.6 (1)	C42	0.1368 (6)	0.0698 (6)	−0.0973 (3)	5.3 (2)
N1′	0.0604 (3)	−0.0066 (4)	−0.0602 (3)	3.8 (2)	C43	0.2065 (6)	0.0850 (6)	−0.1109 (3)	6.6 (3)
N2	0.0863 (4)	0.0950 (3)	0.0034 (2)	3.8 (1)	C44	0.2615 (7)	0.0404 (6)	−0.1025 (3)	6.4 (3)
N2′	0.0307 (4)	−0.1240 (3)	−0.0045 (2)	3.7 (1)	C45	0.2505 (7)	−0.0214 (6)	−0.0822 (3)	6.6 (3)
C1	0.0000 (0)	0.0000 (0)	0.0781 (3)	3.1 (2)	C46	0.1832 (6)	−0.0390 (5)	−0.0689 (3)	5.0 (2)
C11	0.0000 (0)	0.0000 (0)	0.1216 (4)	4.9 (3)	C51	0.1528 (5)	0.1147 (5)	0.0200 (3)	4.0 (2)
C12[b]	0.0657 (9)	0.0366 (9)	0.1365 (5)	5.2 (4)	C52	0.2156 (5)	0.0960 (5)	−0.0002 (3)	5.2 (2)
C13[b]	0.0624 (13)	0.0417 (13)	0.1778 (7)	8.6 (6)	C53	0.2792 (7)	0.1116 (7)	0.0171 (3)	7.0 (3)
C12′[c]	−0.043 (1)	−0.018 (1)	0.1428 (8)	3.9 (5)	C54	0.2829 (7)	0.1452 (7)	0.0504 (4)	7.6 (3)
C13′[c]	0.033 (6)	−0.060 (7)	0.166 (5)	2.8 (5)	C55	0.2229 (7)	0.1598 (7)	0.0704 (4)	7.1 (3)
C14	0.0000 (0)	0.0000 (0)	0.1949 (9)	12.7 (7)	C56	0.1558 (5)	0.1463 (6)	0.0545 (3)	5.2 (2)
C21	0.1101 (5)	−0.0627 (5)	0.0767 (3)	4.2 (2)	C6	0.0357 (4)	0.1449 (4)	−0.0003 (3)	4.2 (2)
C22	0.1801 (6)	−0.0404 (6)	0.0719 (3)	5.7 (2)	C61	0.0570 (5)	0.2216 (4)	−0.0016 (3)	4.5 (2)
C23	0.2386 (8)	−0.0829 (8)	0.0882 (4)	8.4 (3)	C62	0.0299 (6)	0.2640 (7)	0.0281 (4)	7.2 (3)
C24	0.2180 (7)	−0.1476 (7)	0.1036 (4)	7.6 (3)	C63	0.0533 (9)	0.3373 (9)	0.0309 (4)	10.0 (4)
C25	0.1505 (6)	−0.1697 (7)	0.1065 (4)	6.8 (3)	C64	0.0979 (8)	0.3584 (7)	0.0038 (5)	9.2 (4)
C26	0.0928 (6)	−0.1256 (6)	0.0935 (3)	5.2 (2)	C65	0.1196 (8)	0.3179 (8)	−0.0294 (4)	8.9 (4)
C3	0.0000 (0)	0.0000 (0)	−0.0811 (4)	5.0 (3)	C66	0.1032 (6)	0.2450 (6)	−0.0285 (3)	6.1 (3)
C31	0.0000 (0)	0.0000 (0)	−0.1194 (4)	4.4 (3)	C71	0.0802 (5)	−0.1716 (5)	−0.0213 (3)	4.3 (2)
C32[b]	0.0316 (9)	−0.0647 (9)	−0.1380 (5)	5.7 (4)	C72	0.1444 (6)	−0.1820 (5)	−0.0019 (4)	5.9 (2)
C33[b]	0.0288 (9)	−0.0636 (9)	−0.1773 (5)	5.6 (4)	C73	0.1981 (7)	−0.2252 (7)	−0.0197 (4)	7.4 (3)
C32′[c]	0.027 (1)	−0.044 (1)	−0.1436 (8)	4.0 (5)	C74	0.1840 (7)	−0.2535 (6)	−0.0537 (4)	7.6 (3)
C33′[c]	0.017 (1)	−0.034 (1)	−0.1914 (7)	3.3 (4)	C75	0.1195 (7)	−0.2432 (7)	−0.0734 (4)	7.8 (3)
C34	0.0000 (0)	0.0000 (0)	−0.1996 (8)	11.3 (7)	C76	0.0678 (6)	−0.1994 (6)	−0.0561 (3)	5.6 (2)
C41	0.1275 (5)	0.0078 (5)	−0.0764 (2)	3.9 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Refined with 65% occupancy. [c] Refined with 35% occupancy.

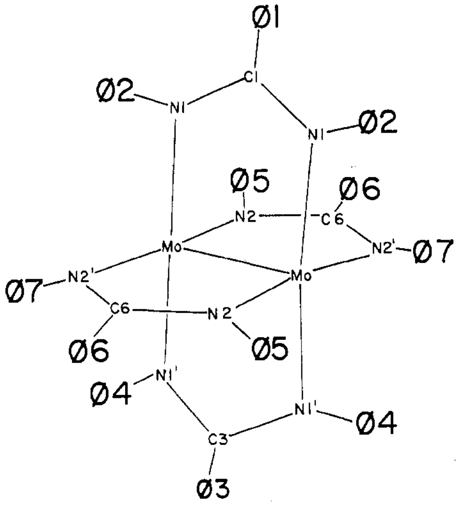

Figure 1. Structure of tetrakis(N,N'-diphenylbenzamidinato)-dimolybdenum. The drawing illustrates the atomic numbering scheme.

entations make it impossible to find any uncluttered, monoptic view of the complete structure. However, the stereopair, seen through a suitable magnifying viewer, provides a very clear three-dimensional picture.

The interatomic distances are listed in Table III and bond angles around the core atoms are given in Table IV.

Discussion

The structure of compound **1**, $Mo_2[PhC(NPh)_2]_4$, in its general features, is as expected, namely, analogous to the well-known dimetal tetracarboxylato structure. The central skeleton, that which is left after deleting the phenyl groups (Figure 1), has essentially D_{4h} symmetry. For the molecule as a whole this symmetry is degraded to C_2 by the fact that all of the phenyl groups are rotationally oriented so as to be neither parallel nor perpendicular to the $\overline{\text{NCNMoMo}}$ plane.

Compound **1** forms easily, though not in particularly high yield, by reaction of the amidine PhC(NPh)(NHPh) with $Mo(CO)_6$ in petroleum ether at 100–120°. The formation of this product appeared to be independent of the initial mole ratio of reactants ($Mo(CO)_6$:amidine) from 1:1 to 1:3, and no other product was isolated. Compound **2**, obtained from a similar reaction using N,N'-di-p-tolylbenzamidine, appears virtually certain, on the basis of analysis and other properties to have the analogous structure. It is highly significant that both **1** and **2** have strong Raman bands, at 410 and 413 cm^{-1}, respectively, which are characteristic of compounds with quadruply bonded pairs of molybdenum atoms.[18]

The Mo–Mo distance in **1**, 2.090 (1) Å, is identical, within the small esd's with those found[8,9] in $Mo_2(O_2CCH_3)_4$ and

Table III. Bond Distances (Å)

Mo–Mo	2.090 (1)	C31–C32	1.51 (2)
Mo–N1	2.125 (9)	C32–C33	1.41 (3)
Mo–N1′	2.163 (10)	C33–C34	1.54 (2)
Mo–N2	2.149 (5)	C41–C42	1.40 (1)
Mo–N2′	2.149 (5)	C41–C46	1.41 (1)
N1–C1	1.32 (1)	C42–C43	1.44 (1)
N1–C21	1.45 (1)	C43–C44	1.38 (1)
N1′–C3	1.38 (1)	C44–C45	1.39 (1)
N1′–C41	1.43 (1)	C45–C46	1.40 (1)
N2–C6	1.36 (1)	C51–C52	1.44 (1)
N2–C51	1.44 (1)	C51–C56	1.37 (1)
N2′–C6	1.33 (1)	C52–C53	1.39 (2)
N2′–C71	1.44 (1)	C53–C54	1.35 (1)
C1–C11	1.56 (2)	C54–C55	1.37 (2)
C3–C31	1.37 (2)	C55–C56	1.42 (1)
C6–C61	1.51 (1)	C61–C62	1.43 (1)
C11–C12	1.52 (2)	C61–C66	1.38 (1)
C12–C13	1.48 (3)	C62–C63	1.46 (2)
C13–C14	1.55 (2)	C63–C64	1.35 (2)
C21–C22	1.40 (1)	C64–C65	1.47 (2)
C21–C26	1.38 (1)	C65–C66	1.42 (2)
C22–C23	1.49 (2)	C71–C72	1.42 (1)
C23–C24	1.40 (2)	C71–C76	1.38 (1)
C24–C25	1.35 (1)	C72–C73	1.45 (1)
C25–C26	1.45 (1)	C73–C74	1.36 (2)
		C74–C75	1.43 (2)
		C75–C76	1.43 (1)

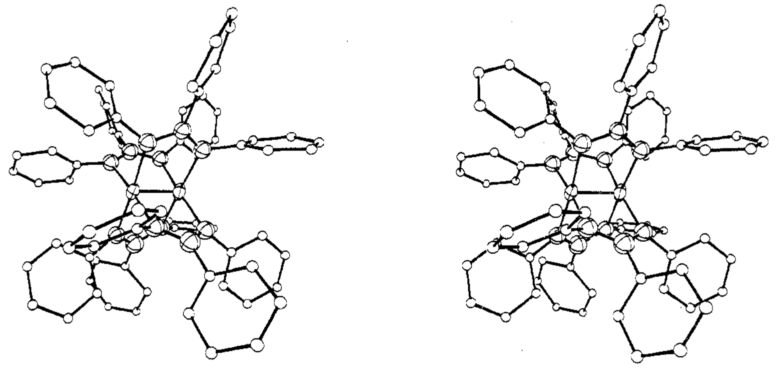

Figure 2. Stereopair view of the molecular structure of $(Ph_3CN_2)_4Mo_2$ produced by the program ORTEP.[12]

Table IV. Bond Angles (deg) around Core Atoms

Mo-Mo-N1	92.0 (2)	Mo-N1-C21	119.0 (5)
Mo-Mo-N1′	92.6 (2)	Mo-N1′-C41	118.3 (6)
Mo-Mo-N2	92.9 (2)	Mo-N2-C51	121.6 (5)
Mo-Mo-N2′	92.3 (2)	Mo-N2′-C71	120.9 (5)
N1-Mo-N1′	175.3 (2)	C1-N1-C21	120.8 (8)
N1-Mo-N2	90.1 (3)	C3-N1′-C41	120.2 (10)
N1-Mo-N2′	90.8 (3)	C6-N2-C51	118.6 (6)
N1′-Mo-N2	89.0 (3)	C6*-N2′-C71	118.7 (6)
N1′-Mo-N2′	89.7 (3)	N1-C1-N1*	118 (1)
N2-Mo-N2′	174.7 (2)	N1′-C3-N1′*	114 (1)
Mo-N1-C1	118.6 (7)	N2-C6-N2′*	118 (1)
Mo-N1′-C3	119.9 (8)	N1-C1-C11	121 (1)
Mo-N2-C6	117.2 (5)	N1′-C3-C31	123 (1)
Mo-N2′-C6*	118.3 (4)	N2-C6-C61	119 (1)
		N2′C6-C61	123 (1)

$Mo_2(O_2CCF_3)_4$. There is no doubt that the Mo–Mo bond is essentially the same.

While molybdenum carboxylates form weak adducts with donor molecules such as pyridine[19,20] compound **1** was found to be inert to pyridine, CO under pressure, and triphenylphosphine. In view of the structure, this can be attributed to steric blocking of the coaxial positions by the *N*-phenyl groups.

The reactions of $Cr(CO)_6$ and $W(CO)_6$ with *N,N*′-diphenylbenzamidine did not yield analogs to **1**. With tungsten the only isolable product, **5**, was a small quantity of red, air-stable crystals. The analytical data and presumed parent ion peak in the mass spectrum do not seem to fit any reasonable structure, the molecular formula being $C_{54}H_{40}N_5O_3W_2$. The presence of three intense absorptions in the ir spectrum in the region characteristic of terminal CO ligands might suggest that an (η^6-arene)W(CO)$_3$ group forms a part of the molecule.

The reaction of $Cr(CO)_6$ gave a yellow soluble product which can be identified fairly definitely as an arenechromium tricarbonyl species. Which of the three possible isomers it is remains uncertain, but NMR data give some indication that the complexed phenyl group may be the one attached to the carbon atom.

The other product of the reaction with $Cr(CO)_6$ was a red microcrystalline solid for which no solvent could be found. The infrared spectrum of this substance, **3**, is generally similar to the spectra of **1** and **2**, and the microanalytical data correspond satisfactorily to the dinuclear formula $(Ph_3CN_2)_4Cr_2$. The extreme insolubility is difficult to understand if this is indeed the chromium analog of **1**, but that possibility cannot be entirely ruled out.

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Registry No. Tetrakis(*N,N*′-diphenylbenzamidinato)dimolybdenum, 54755-06-5; tetrakis(*N,N*′-di-*p*-tolylbenzamidinato)dimolybdenum, 55517-30-1; *N,N*′-diphenylbenzamidinetricarbonylchromium, 55517-29-8; $C_{76}H_{60}Cr_2N_8$, 55569-90-9; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6.

Supplementary Material Available. Table I, observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40591G-9-75.

References and Notes

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