temperature parameters (Table A), rates for the forward and reverse processes and equilibrium constants (Table B), and a list of observed and calculated structure amplitudes (Table C) (15 pages). Ordering information is given on any current masthead page.

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(1) Issued as N.R.C.C. No. 17810.
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Dimolybdenum Tetraacetate and the Octachlorodimolybdate(II) Anion as Reagents for Preparing Mononuclear Molybdenum(II) Complexes. Geometry of the Hepta(methylisocyano)molybdenum(II) Cation

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Received March 21, 1979

Abstract: The reactions of $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_8$ with alkyl isocyanides causes scission of the Mo—Mo quadruple bond to give $[Mo(CNR)_7]^{2+}$ ions, where R = CH_3, $(CH_3)_3C$, or C_6H_{11}, which can be isolated by using large anions such as BF_4^- and PF_6^-. For the case where R = CH_3, we have structurally characterized the product $[Mo(CNCH_3)_7](BF_4)_2$. The structure of this compound has been determined by X-ray crystallography. It crystallizes in space group *Pbcn* with unit cell dimensions of a = 11.660 (4) Å, b = 18.733 (4) Å, c = 22.610 (5) Å, and Z = 8. The $[Mo(CNCH_3)_7]^{2+}$ cation possesses no crystallographic symmetry. It comes closest to having a capped octahedral (CO) arrangement, although there are two orientations that can be viewed as distorted forms of the capped trigonal prismatic structure, and one that is a distorted form of 4:3 coordination. This is the first example of a homoleptic ML_7 species with a CO structure.

Introduction

The reactions of multiply bonded dimetal species, such as $Mo_2(O_2CCH_3)_4$, may all be classified as either (A) those in which the M-M multiple bond is retained, possibly with some change in bond order, or (B) those in which the metal atoms become separated. We include under B cases where a binuclear structure is retained but only by virtue of bridging ligands, with the M-M bond order being reduced, effectively to zero, as when $Re_2Cl_8^{2-}$ reacts[2] with ligands such as $SC(NH_2)_2$ and $Ph_2PCH_2CH_2PPh_2$.

Reactions of type B are not only interesting because of their bearing on the nature of the M-M multiple bonds but for the practical reason that they can afford efficient synthetic methods to prepare more conventional complexes. In some cases, entirely new kinds of complexes have been so obtained, such as the 14-electron metal nitrosyls $Mo_2(OR)_6(NO)_2$, which are prepared[3] by the action of NO on $Mo_2(OR)_6$, and the 17-electron species *trans*-$Re(CO)_2Cl_2(PR_3)_2$ which are formed[4] upon reacting CO with $Re_2Cl_4(PR_3)_4$. In other cases, multiply bonded M_2 species which are themselves easy to prepare and handle provide excellent starting materials for new synthetic routes to previously known compounds.

We report here an exemplary case of a class B reaction leading to a compound that is of considerable interest in its own right. In 1973, Novotny and Lippard[5] reported the preparation of $[Mo(CNR)_7]^{2+}$ ions by the reaction of $Mo(CO)_6$ with the isocyanide and iodine, or by alkylation of $[Mo(CN)_8]^{4-}$, and later Lewis and Lippard carried out an X-ray crystallographic

0002-7863/79/1501-6588$01.00/0

structure study[6] of $[Mo(CNCMe_3)_7](PF_6)_2$. We describe here a very convenient and general preparative method for $[Mo(CNR)_7]^{2+}$ ions, summarized by reaction 1 and a structural characterization of the $[Mo(CNCH_3)_7]^{2+}$ ion that throws new light on the important but incompletely studied question of the structures of homoleptic seven-coordinate complexes.

$$Mo_2(O_2CCH_3)_4 \text{ or } Mo_2Cl_8{}^{4-} + RNC \rightarrow [Mo(CNR)_7]^{2+} \qquad (1)$$

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: CH_3NC,[7] $K_4Mo_2Cl_8$,[8] and $Mo_2(O_2CCH_3)_4$.[9] Cyclohexyl and *tert*-butyl isocyanides and other reagents and solvents were obtained from commercial sources and used as received.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere and solvents were deoxygenated by purging with N_2 gas prior to use.

A. Reactions of $K_4Mo_2Cl_8$. (i) **$[Mo(CNCH_3)_7](PF_6)_2$.** A mixture of CH_3NC (0.50 mL, 8.94 mmol) and $K_4Mo_2Cl_8$ (1.0 g, 1.58 mmol) in 5 mL of anhydrous methanol was allowed to stand at room temperature for 4 days. The reaction mixture was filtered to remove a mixture containing unreacted $K_4Mo_2Cl_8$ and a small quantity of KCl (~0.72 g), and KPF_6 (0.20 g) was then added to the orange-brown filtrate. The latter was stirred and chilled to 5 °C for a short time and the resulting canary yellow precipitate filtered off, recrystallized from acetone-isopropyl alcohol (10:1 by volume) or acetone-diethyl ether (20:1 by volume), washed with diethyl ether, and dried in vacuo, yield 0.59 g (~90% based upon the actual amount of $K_4Mo_2Cl_8$ consumed). Anal. Calcd for $C_{14}H_{21}F_{12}MoN_7P_2$: C, 25.0; H, 3.1; N, 14.6. Found: C, 24.6; H, 3.0; N, 14.3. This yellow complex decomposes slowly in air, turning a yellow-green color. It is soluble in dichloromethane, chloroform, acetone, and many other polar solvents.

A variation in the reaction procedure involved an increase in the proportion of CH_3NC used. When $K_4Mo_2Cl_8$ (0.51 g, 0.80 mmol) and CH_3NC (1.0 mL, 17.8 mmol) were reacted at room temperature by using the procedure described previously, virtually no $K_4Mo_2Cl_8$ remained unreacted and $[Mo(CNCH_3)_7](PF_6)$ could be isolated in high yield (0.71 g, 66%). Use of reflux conditions caused a much more rapid consumption of the $K_4Mo_2Cl_8$, the reaction being complete after approximately 1 h. Addition of KPF_6 to the chilled reaction filtrate afforded $[Mo(CNCH_3)_7](PF_6)_2$ in 50% yield. Anal. Found: C, 25.3; H, 3.3; N, 14.4.

(ii) **$[Mo(CNCH_3)_7](BF_4)_2$.** This complex could be obtained in 50% yield by using procedures similar to those described in A(i) but with use of $NaBF_4$ as the precipitating agent. Anal. Calcd for $C_{14}H_{21}B_2F_8MoN_7$: C, 30.2; H, 3.8; B, 3.9. Found: C, 29.6; H, 3.9; B, 3.0.

(iii) **$[Mo(CNCMe_3)_7](PF_6)_2$.** The reaction between a suspension of $K_4Mo_2Cl_8$ (0.20 g, 0.32 mmol) and *tert*-butyl isocyanide (0.25 mL, 2.36 mmol) in refluxing methanol (25 mL) was carried out for 1 h. The reaction mixture was cooled and filtered and KPF_6 (0.20 g) added to the dark yellow-brown filtrate. The resulting yellow complex was filtered off, washed with methanol and diethyl ether, and dried in vacuo, yield 0.15 g (27%). Anal. Calcd for $C_{35}H_{63}F_{12}MoN_7P_2$: C, 43.4; H, 6.6; N, 10.1. Found: C, 43.3; H, 6.6; N, 9.9.

(iv) **$[Mo(CNC_6H_{11})_7](PF_6)_2$.** A bright yellow complex approximating to this stoichiometry was obtained by a procedure analogous to A(iii). Anal. Calcd for $C_{49}H_{70}F_{12}MoN_7P_2$: C, 51.2; H, 6.75; N, 8.53. Found: C, 50.15; H, 6.4; N, 8.65.

B. Reactions of $Mo_2(O_2CCH_3)_4$. The reactions between mixtures of $Mo_2(O_2CCH_3)_4$, $Pb(NO_3)_2$ (added to precipitate $Pb(O_2CCH_3)_2$), and the appropriate alkyl isocyanide in refluxing methanol were carried out by using the same procedure as that described in section A. The yellow complexes $[Mo(CNR)_7](PF_6)_2$, where R = CH_3, CMe_3, or C_6H_{11}, were obtained generally in slightly lower yields than those encountered in the reactions involving $K_4Mo_2Cl_8$.

(i) **$[Mo(CNCH_3)_7](PF_6)_2$.** Anal. Calcd for $C_{14}H_{21}F_{12}MoN_7P_2$: C, 25.0; H, 3.1; N, 14.6. Found: C, 24.7; H, 3.3; N, 13.8.

(ii) **$[Mo(CNCMe_3)_7](PF_6)_2$.** Anal. Calcd for $C_{35}H_{63}F_{12}MoN_7P_2$: C, 43.4; H, 6.6; N, 10.1. Found: C, 42.8; H, 6.9; N, 9.7.

(iii) **$[Mo(CNC_6H_{11})_7](PF_6)_2$.** Anal. Calcd for $C_{49}H_{70}F_{12}MoN_7P_2$: C, 51.2; H, 6.75; N, 8.5. Found: C, 51.1; H, 6.7; N, 8.4.

Infrared and ^1H NMR spectroscopy confirmed that these complexes were identical with those obtained in section A.

Physical Measurements. Spectroscopic characterizations were carried out by using the instrumentation described previously[10] with the exception of infrared spectra which were recorded on a Digilab FTS 20B spectrometer.

X-Ray Structure Determination. Data were recorded at 21 ± 2 °C on a Syntex $P\bar{1}$ automated diffractometer by using Mo $K\alpha$ radiation with a graphite crystal monochromator in the incident beam. The automatic centering and indexing procedures used have been described previously.[11] Data were recorded by using a modified version of the standard Syntex θ-2θ collection program.[12] Three standard reflections were measured after every 97 data points. Data used were corrected for Lorentz and polarization effects. Systematic absences uniquely determined the space group to be *Pbcn* (no. 60) with unit cell dimensions of: a = 11.660 (4) Å, b = 18.733 (4) Å, c = 22.610 (5) Å, V = 4939 (4) Å^3. With this unit cell volume, the only reasonable value of Z is 8, making the asymmetric unit one $[Mo(CNCH_3)_7](BF_4)_2$ formula unit. Using 2124 unique data with $I > 3\sigma(I)$, the structure was solved by heavy atom techniques and refined to convergence employing anisotropic thermal parameters for the Mo, C, and N atoms, isotropic thermal parameters for the B and F atoms, and neglecting hydrogen atoms. The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$, where a value of $p = 0.07$ was used as described previously.[11] The final residuals were $R_1 = 0.078$, $R_2 = 0.115$, and the esd of an observation of unit weight was 2.60. The data reduction and structure refinement were carried out by using the Enraf-Nonius structure determination package on the PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas. The atomic positional and thermal parameters are given in Table I. Tables of observed and calculated structure factors are available as supplementary material.

Results

Synthesis and Characterization. The reactions between $Mo_2(O_2CCH_3)_4$ or $K_4Mo_2Cl_8$ and methyl, *tert*-butyl, and cyclohexyl isocyanide provide a novel route to the homoleptic isocyanide derivatives of molybdenum(II), $[Mo(CNR)_7]^{2+}$, species which may be isolated as salts by using the $BF_4{}^-$ and $PF_6{}^-$ anions. These "one-pot" reactions afford the desired complexes in yields in excess of 50% with use of judicious reaction conditions (see Experimental Reaction Conditions) and are rapid (less than 1 h) when carried out under reflux. Since the starting materials ($Mo_2(O_2CCH_3)_4$ or $K_4Mo_2Cl_8$) are readily available because of their use in the synthesis of many derivatives of molybdenum(II) containing Mo-Mo multiple bonds,[13] we find that this synthetic route is preferred over the alternative methods developed by Lippard and co-workers,[5] namely, iodine oxidation of $Mo(CO)_6$ in the presence of RNC and the alkylation of $[Mo(CN)_8]^{4-}$.

The spectral characterizations of the complexes leave no doubt as to their identity. Electronic absorption spectral measurements on methanol solutions of the three $PF_6{}^-$ salts are very similar, and the absorption maxima compare very favorably with data published by Lippard[5] for $[Mo(CNCMe_3)_7](PF_6)_2$. An intense charge-transfer band (L → M?) is located at ~250 nm with one or two weak, poorly defined shoulders located between 270 and 300 nm. The lowest energy absorption at 410 (± 5) nm, which occurs in all three complexes, has been assigned[5] to a metal-based transition ($b_2(yz) \rightarrow a_1(z^2)$).

As far as we can tell, the IR spectra of our complexes of the type $[Mo(CNR)_7](PF_6)_2$ and of $[Mo(CNCH_3)_7](BF_4)_2$ are in accord with comparable data reported by Lippard[5] for $[Mo(CNCMe_3)_7](PF_6)_2$. In addition to the characteristic anion bands,[14] nujol mull spectra reveal an intense, split ν ($N{\equiv}C$) absorption centered at ~2160 (R = Me) or ~2140 cm^{-1} (R = CMe_3 or C_6H_{11}). The position of this band is little changed upon dissolution of the complexes in dichloromethane but sharpens with loss of the solid-state splittings.

In $CDCl_3$ or acetone-d_6, the proton NMR spectra of $[Mo(CNR)_7]^{2+}$, where R = CH_3 or CMe_3, consist of a single

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Mo(CNCH_3)_7][BF_4]_2$[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Mo	0.16853(8)	0.14649(5)	0.11641(4)	2.75(4)	3.28(4)	2.82(4)	−0.24(4)	−0.19(4)	0.12(4)
F(1)	0.333(1)	0.3931(7)	−0.0010(5)	11.1(3)					
F(2)	0.142(1)	0.3857(7)	−0.0195(5)	10.6(3)					
F(3)	0.269(1)	0.4122(9)	−0.0852(7)	14.3(5)					
F(4)	0.263(1)	0.3074(10)	−0.0506(7)	14.4(5)					
F(5)	0.414(1)	0.9797(8)	0.2339(6)	12.2(4)					
F(6)	0.523(3)	0.8858(13)	0.2222(11)	25.4(11)					
F(7)	0.408(2)	0.2837(8)	0.2454(8)	14.5(5)					
F(8)	0.502(3)	0.3754(11)	0.2238(10)	22.8(9)					
N(1)	0.4298(9)	0.1359(6)	0.1608(4)	3.0(4)	6.5(6)	4.2(5)	0.4(4)	−0.7(4)	1.6(4)
N(2)	0.0418(10)	0.2202(5)	0.0015(5)	5.1(5)	4.1(5)	4.4(5)	0.1(5)	−2.0(4)	0.3(4)
N(3)	0.1667(9)	0.0584(6)	0.2382(4)	4.4(5)	7.2(6)	3.8(4)	−0.9(5)	−0.5(4)	1.6(4)
N(4)	−0.0635(9)	0.2128(6)	0.1793(5)	3.1(4)	5.1(5)	4.7(5)	−0.5(4)	0.9(4)	−0.2(4)
N(5)	0.0208(9)	0.0034(5)	0.0851(4)	4.1(5)	3.7(4)	4.0(4)	−1.1(4)	0.3(4)	−0.2(4)
N(6)	0.3187(10)	0.0925(8)	0.0068(5)	3.6(5)	10.1(8)	5.8(6)	−0.7(6)	−1.1(5)	−2.0(6)
N(7)	0.2310(9)	0.3141(6)	0.1337(4)	4.4(5)	4.3(5)	4.3(5)	−0.5(4)	−0.0(4)	−0.4(4)
C(1)	0.334(1)	0.1401(6)	0.1456(5)	4.8(6)	3.8(5)	3.2(5)	−0.2(6)	0.2(5)	0.2(4)
C(2)	0.087(1)	0.1949(7)	0.0414(6)	4.6(6)	3.8(6)	4.2(6)	−0.6(5)	−0.5(5)	−0.0(5)
C(3)	0.170(1)	0.0898(6)	0.1964(5)	3.4(5)	4.0(5)	3.2(5)	−0.3(5)	−0.8(4)	−0.3(4)
C(4)	0.018(1)	0.1882(6)	0.1599(5)	4.7(6)	3.8(5)	4.1(5)	−0.6(5)	0.2(5)	0.1(5)
C(5)	0.076(1)	0.0515(6)	0.0950(5)	4.4(6)	3.9(5)	2.1(4)	1.0(5)	−0.1(4)	−0.1(4)
C(6)	0.268(1)	0.1113(8)	0.0459(5)	3.2(5)	7.2(8)	2.8(5)	−0.0(6)	0.4(4)	−1.2(5)
C(7)	0.216(1)	0.2532(6)	0.1292(5)	3.1(5)	4.1(5)	3.1(5)	−0.7(5)	0.3(4)	−0.3(4)
C(11)	0.550(1)	0.1284(9)	0.1791(6)	2.0(5)	8.9(9)	5.2(6)	−0.4(6)	0.0(5)	1.8(6)
C(21)	−0.020(1)	0.2527(8)	−0.0469(7)	9.5(9)	4.6(7)	7.4(8)	0.9(7)	−4.3(7)	1.8(6)
C(31)	0.165(1)	0.0129(8)	0.2922(6)	7.1(9)	6.5(7)	4.6(6)	−0.6(8)	−0.1(6)	2.3(5)
C(41)	−0.163(1)	0.2468(9)	0.2003(7)	3.9(6)	7.2(8)	6.9(8)	1.4(7)	1.6(6)	0.5(7)
C(51)	−0.054(1)	−0.0565(8)	0.0701(7)	5.9(7)	4.5(6)	7.3(8)	−1.5(6)	−0.1(6)	−2.0(6)
C(61)	0.391(1)	0.0722(14)	−0.0468(7)	5.0(8)	21(2)	6.7(8)	−0(1)	2.3(6)	−6.6(9)
C(71)	0.247(2)	0.3917(8)	0.1398(8)	9(1)	2.9(6)	10(1)	−0.9(7)	1.1(9)	−1.0(7)
B(1)	0.250(2)	0.379(1)	−0.0361(9)	6.5(5)					
B(2)	0.500(0)	0.937(2)	0.2500(0)	9.4(9)					
B(3)	0.500(0)	0.320(2)	0.2500(0)	7.5(7)					

[a] The form of the anisotropic thermal parameter is: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

sharp resonance with δ 3.72 ppm for R = CH_3 and δ 1.65 ppm for R = CMe_3 (the latter value agrees well with δ 1.62 ppm reported by Lippard[5]). The much more complex ^1H NMR of $[Mo(CNC_6H_{11})_7](PF_6)_2$ reveals multiplets at δ ca. 1.55, 1.93, and 4.36 ppm. The diamagnetism of these complexes, which is implied by their normal ^1H NMR spectra, is supported by magnetic susceptibility measurements on $[Mo(CNCH_3)_7](PF_6)_2$ ($\chi_g = -0.13 \times 10^{-6}$ cgs units at 25 °C) and the absence of discernible resonances in the EPR spectra of the methyl and *tert*-butyl isocyanide derivatives (as CH_2Cl_2 glasses at −160 °C).

The X-ray photoelectron spectra (XPS) of the three derivatives of the type $[Mo(CNR)_7](PF_6)_2$, are essentially identical. These complexes possess Mo $3d_{3/2,5/2}$ binding energies ($3d_{3/2}$ at 232.2 ± 0.1 eV and $3d_{5/2}$ at 229.1 ± 0.1 eV) which are similar to those of other molybdenum(II) species, including halide[15-17] and allyl[18] derivatives. The Mo 3d peaks are narrow (fwhm values of 1.2–1.3 eV) and, furthermore, the spectra reveal the absence of any molybdenum containing contaminants. Other binding energies of note are N 1s = 399.9 (± 0.1) eV (fwhm of 1.5–1.7 eV), P 2p = 136.1 (± 0.1) eV and a complex C 1s spectrum, an analysis of which will be reported elsewhere.

Structure. The $[Mo(CNCH_3)_7]^{2+}$ ions occupy the general eightfold position and have no imposed crystallographic symmetry. Figure 1 presents two drawings of the cation with different orientations (for convenience in later discussion) in each of which the numbering scheme is defined. The 16 BF_4^- ions in the cell occupy one general eightfold position (B(1), F(1)–F(4)) and two fourfold positions, each of type o, y, ¼ on the crystallographic C_2 axis. The bond distances are listed in Table II and bond angles in Table III. The seven-coordinate cation is the main feature of interest and will be discussed in detail below.

The BF_4^- ions are poorly defined. The one on a general position behaves tolerably, giving B–F bond lengths that range from 1.27 to 1.38 Å with an average of 1.32 ± 0.04 Å and F–B–F angles ranging from 105 to 121° with an average of 109 ± 5°. Since the F atoms in this ion show isotropic thermal parameters ranging from 11.6 to 14.4 Å^2, the average dimensions and the variation of individual values therefrom seem reasonable on the assumption that there are librational motions of very large amplitude about the central boron atom. Insofar as the fluorine atoms can be considered to be moving on the surface of a sphere centered at the position of the boron atom, the centroids of their electron density will appear closer to the boron atom than the actual B–F bond length. In this way the apparent shortening of the B–F bonds, compared with an expected length of about 1.40 Å, can be understood. The two other BF_4^- ions that lie on special positions refined very badly. In each case, the boron atom and one pair of fluorine atoms behaved tolerably with thermal parameters of 12.2 and 14.5 Å^3, B–F distances of 1.34 (2) and 1.27 (1) Å and FBF angles of 106 (2) and 116 (2)°. The other pair of fluorine atoms in each case behave quite unreasonably giving extremely high thermal parameters (22.8 and 25.4 Å^2), bond lengths of 1.17 and 1.20 Å and, worst of all, FBF angles of 59 and 71°. Attempts to constrain these fluorine atoms to reasonable positions failed; their thermal parameters exploded. If they were set at reasonable positions but not constrained to remain there, they

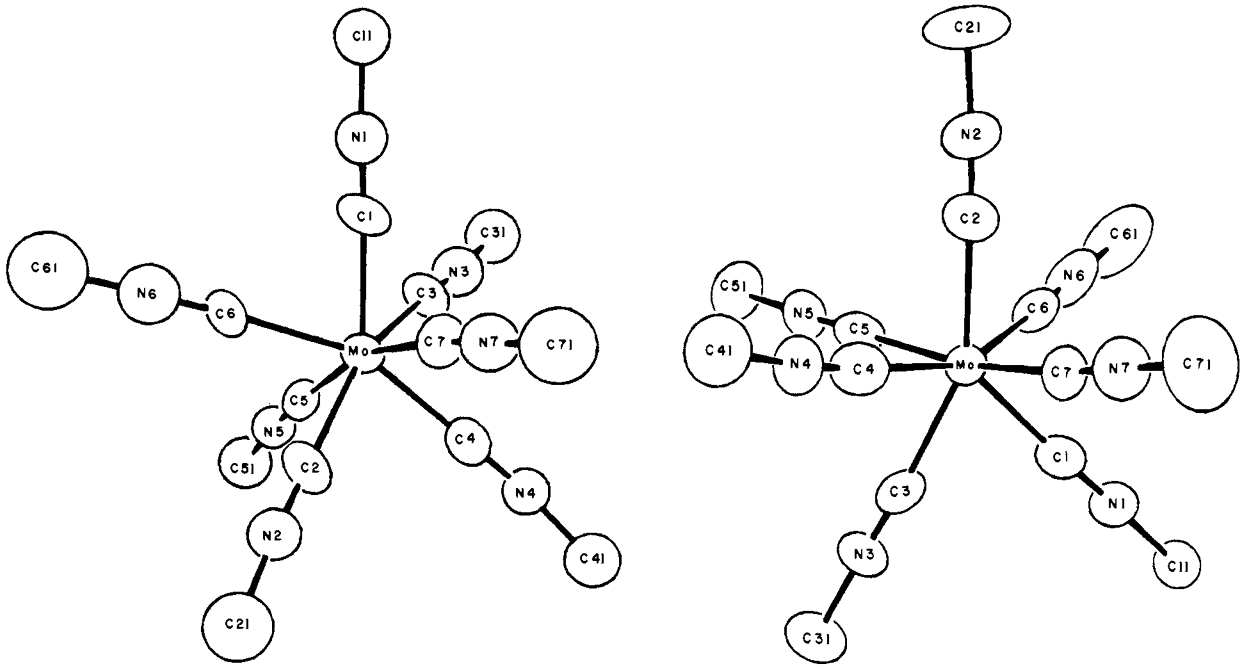

Figure 1. The $[Mo(CNCH_3)_7]^{2+}$ ion in two orientations. (Left) With the approximate C_3 axis that coincides with Mo-C(1)-N(1)-C(11) vertical. (Right) With the approximate C_2 axis that coincides with Mo-C(2)-N(2)-C(21) vertical. The atomic numbering scheme is shown for each one.

Table II. Bond Distances (Å), for $[Mo(CNCH_3)_7][BF_4]_2$

Mo-C(1)	2.038(9)	C(1)-N(1)	1.18(1)
C(2)	2.145(9)	C(2)-N(2)	1.15(1)
C(3)	2.098(8)	C(3)-N(3)	1.114(9)
C(4)	2.16(1)	C(4)-N(4)	1.14(1)
C(5)	2.137(9)	C(5)-N(5)	1.129(9)
C(6)	2.075(9)	C(6)-N(6)	1.12(1)
C(7)	2.095(8)	C(7)-N(7)	1.16(1)
N(1)-C(11)	1.47(1)	B(1)-F(1)	1.27(1)
N(2)-C(21)	1.44(1)	F(2)	1.32(1)
N(3)-C(31)	1.49(1)	F(3)	1.29(1)
N(4)-C(41)	1.41(1)	F(4)	1.38(2)
N(5)-C(51)	1.46(1)	B(2)-F(5)	1.34(2)
N(6)-C(61)	1.52(1)	F(6)	1.17(2)
N(7)-C(71)	1.47(1)	B(3)-F(7)	1.27(1)
		F(8)	1.20(2)

Table III. Bond Angles (deg) for $[Mo(CNCH_3)_7][BF_4]_2$

C(1)-Mo-C(2)	134.4(3)	Mo-C(7)-N(7)	172.8(7)
C(3)	71.5(3)		
C(4)	130.0(3)	C(1)-N(1)-C(11)	178.3(9)
C(5)	120.2(3)	C(2)-N(2)-C(21)	177(1)
C(6)	72.9(3)	C(3)-N(3)-C(31)	177(1)
C(7)	76.2(3)	C(4)-N(4)-C(41)	176.1(9)
C(2)-Mo-C(3)	154.1(3)	C(5)-N(5)-C(51)	177.0(8)
C(4)	81.1(3)	C(6)-N(6)-C(61)	176(1)
C(5)	87.0(3)	C(7)-N(7)-C(71)	178.7(9)
C(6)	76.9(3)		
C(7)	79.8(3)	F(1)-B(1)-F(2)	121(1)
C(3)-Mo-C(4)	78.3(3)	F(3)	108(1)
C(5)	77.2(3)	F(4)	106(1)
C(6)	119.7(3)	F(2)-B(1)-F(3)	111(1)
C(7)	111.2(3)	F(4)	105(1)
C(4)-Mo-C(5)	89.5(3)	F(3)-B(1)-F(4)	104(1)
C(6)	156.5(3)	F(5)-B(2)-F(5)′	106(2)
C(7)	78.9(3)	F(6)	121(1)
C(5)-Mo-C(6)	81.0(3)	F(6)′	117(1)
C(7)	163.6(3)	F(6)-B(2)-F(6)′	71(2)
C(6)-Mo-C(7)	105.2(3)	F(7)-B(3)-F(7)′	116(2)
Mo-C(1)-N(1)	178.0(7)	F(8)	116(1)
Mo-C(2)-N(2)	179.0(8)	F(8)′	119(1)
Mo-C(3)-N(3)	177.1(7)	F(8)-B(3)-F(8)′	59(2)
Mo-C(4)-N(4)	175.2(7)		
Mo-C(5)-N(5)	175.6(7)		
Mo-C(6)-N(6)	178.2(8)		

simply moved back to the positions given in Table I. We have examined electron density maps and difference maps in this region and can find no disordered model that fits. Thus, faute de mieux, we report the highly distorted BF_4^- ions.

Discussion

The Synthesis of $[Mo(CNR)_7]^{2+}$. One of our original objectives in reacting $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_3$ with alkyl isocyanides was to ascertain whether the dimers $[Mo_2(CNR)_x]^{n+}$, where $x = 8$, 9, or 10, could be isolated. Although reaction occurs very readily, we have been unable to isolate these dimeric species either through varying the reaction stoichiometry or the reaction temperature. The facile cleavage of the Mo-Mo quadruple bond by RNC, to produce $[Mo(CNR)_7]^{2+}$, contrasts with the lack of reactivity of dichloromethane solutions of the molybdenum(II) dimers $Mo_2Cl_4(PR_3)_4$ (and their rhenium analogues $Re_2Cl_6(PR_3)_2$) toward CO.[4,19] However, these reactivity differences may in fact be more a reflection of differences in solubility of these reagents in the reaction media (CO is much less soluble than RNC) than of any inherent differences in the reactivity of these molybdenum dimers toward isoelectronic RNC and CO.[20]

While the cleavage of M-M *quadruple* bonds occasionally occurs upon reaction with certain σ donors, it seems that such a reaction course may be quite normal with π-acceptor ligands. In the two studies of the latter type which have been carried out to date, namely, the reactions between $Mo_2X_4(PR_3)_4$ and NO[19] and those between $Mo_2(O_2CCH_3)_4$ (or $K_4Mo_2Cl_8$) and RNC, the "18-electron" monomers $Mo(NO)_2X_2(PR_3)_2$ and $[Mo(CNR)_7]^{2+}$ are the primary reaction products.

Structure of the $[Mo(CNCH_3)_7]^{2+}$ Ion. The fact that the coordination number is as high as seven is not surprising when the existence of the $[Mo(CNCMe_3)_7]^{2+}$ cation[6] is noted. Indeed, from a strictly steric point of view an eight-coordinate ion would seem possible. It may be that electronic factors for a d^4 ion lead to a preference for 7-coordination, but in spite of the extensive studies available on 7-coordination[21] and 8-coordination,[22] as individual categories, it does not appear feasible to decide on theoretical grounds whether electronic factors alone might favor one or other of these coordination numbers.[23]

Given the experimental fact that we have the seven-coordinate cation, its structure is interesting for the reasons previously stated by Lewis and Lippard,[6] namely, because ML_7 species with identical unidentate ligands "permit an analysis of the factors influencing the choice of geometry for a seven-coordinate complex in the absence of stereochemical constraints imposed by multidentate, chelating ligands" and because relatively few such ML_7 species have so far been structurally characterized by X-ray crystallography. According to Drew[21] only nine such structures have been reported, two of which contain the same complex, $[Mo(CN)_7]^{5-}$, in different salts. Of the eight chemically distinct entities, six were found to have pentagonal bipyramidal (PB) structures, with varying degrees of distortion and two to have a capped trigonal prismatic (CTP) structure. There are no examples of the capped octahedron (CO) or the 4:3 structure among the homoleptic ML_7 species listed by Drew.

The comparison of $[Mo(CNCH_3)_7]^{2+}$ with $[Mo(CNCMe_3)_7]^{2+}$ is of particular interest because for the first time one can compare two species that contain ligands of nearly identical electronic properties, but appreciably different steric properties. It must, of course, be kept in mind that the $[Mo(CNCH_3)_7]^{2+}$ and $[Mo(CNCMe_3)_7]^{2+}$ ions are in different environments in their crystals and that this, too, may be an important though subtle factor in determining their structures.

The procedure we used to search for the most suitable idealized coordination geometry from among the four mentioned above, viz., PB, CO, CTP, and 4:3, consisted of the following steps. (1) Visual examination of an accurate scale model of the molybdenum atom and the seven appended carbon atoms. It was thus seen unequivocally that the PB arrangement is out of the question. (2) Continuing with visual examination of the model, it was clear that there is only one orientation that might allow the assignment of a 4:3 structure, namely, with C(2) C(4), and C(7) constituting the set of three. (3) It was seen that there are two orientations that might possibly allow assignment of a CTP structure, namely, those with C(2) or C(4) as capping atoms. (4) Lastly, it was seen that there is one orientation that might allow the assignment of a CO structure, namely, with C(1) as the capping atom. These four possibilities were then each subjected to more quantitative evaluation.

The 4:3 Structure. This is tenable on the basis of conformity of C–Mo–C angles with those required in the ideal structure. This type of structure requires a set of four atoms to be coplanar and this is indeed the case for C(1), C(3), C(5), and C(6), all which deviate insignificantly from a common plane. This plane is then only 3.5° from being parallel to the plane of the three carbon atoms forming the triangle. However, the 4:3 structure is not attractive when the Mo–C bond lengths are considered. The bond lengths, which range from 2.04 to 2.16 Å, do *not* group themselves according to the 4:3 pattern. In the set of three, we have Mo–C bond lengths of 2.16, 2.14_5, and 2.09 Å, while in the set of four the distances are 2.14, 2.10, 2.08, and 2.04 Å.

The CTP Structures. In an ideal structure of this kind, there must be two sets of four ligand atoms each defining a plane and having two atoms in common that define the intersection between the two planes. For each of the two possible CTP structures already mentioned, one such plane is defined by C(1), C(3), C(5), and C(6), which is the same group of atoms making up the set of four in the 4:3 structure just discussed. As noted, these four atoms are coplanar within the errors and define a rectangle that is almost a perfect square. However, for neither of the possible choices of capping atom does the other set of four atoms approach very closely to planarity. If the capping atom is C(2), as shown in Figure 1, right, then the other set must be C(1), C(3), C(4), and C(7) and these have deviations of −0.14, +0.16, +0.14, and −0.15 Å, respectively, from their best common plane. Moreover, the symmetry of the CTP requires that M–L distances should fall into sets of 1, 4, and 2, within which last two the distances should be equal. In fact, with C(2) as capping atom this requirement is very poorly met. The sets of 1, 4, and 2 are as follows: 2.14; 2.08, 2.09, 2.14, 2.16; 2.04, 2.09 Å.

With C(4) as capping atom we again have one perfectly coplanar set of four atoms, but for the other, C(1), C(2), C(6), C(7), the deviations are in excess of ±0.20 Å. Moreover, the M–L distances also fail to group themselves satisfactorily into the appropriate sets of 1, 4, and 2 as the following figures show: 2.16; 2.10, 2.10, 2.14, 2.15; 2.04, 2.08 Å.

The CO Structure. As shown in Figure 1, left, this can be recognized with C(1) as the capping atom. The C–Mo–C angles within the set C(3), C(6), C(7) are 120, 111, and 105°, while those in the set C(2), C(4), C(5) are 81, 87, and 90°, whereas in the ideal CO structure those within each set should be equal. The planes defined by these two sets should be parallel: in fact, there is only a small angle, 5.6°, between them. On the basis of these considerations one could not argue conclusively that the CO structure is preferable to the other three previously considered, although it is certainly not inferior. However, when the pattern of M–L distances is considered, this structure shows its clear superiority. For the 1, 3, 3 grouping we have the following sets of Mo–C distances: 2.04; 2.08, 2.09, 2.09; 2.14, 2.14, 2.16 Å. The required equality within each of the two sets of three is fully satisfied within the experimental uncertainties.

Still another criterion of the symmetry required for the CO structure is that the angles from the capping atom to the other six atoms should form two sets within each of which the three angles are equal. One such set consists of the angles 72, 73, and 76°, while the other contains 130, 134, and 120°. The discordant angle in the last set is C(1)–Mo–C(5) and indeed practically all of the distortion of this structure from the ideal C_{3v} symmetry of the CO arrangement can be attributed to this ca. 12° deviation of this angle from the mean value of the other two in the same set. If this angle were increased by 12°, the two planes of three atoms would become perfectly parallel within experimental error and the C(2)–Mo–C(4) angle of 81° would increase to 88°.

In summary, while this structure is qualitatively recognizable as a distorted 4:3 structure or, in either of two ways as a CTP structure, it is much more satisfactorily considered as a slightly distorted capped octahedron. According to Drew's table,[21] it must be regarded as the first example of such an ML_7 arrangement. Whether the difference from the CTP structure of the $[Mo(CNCMe_3)_7]^{2+}$ ion is best understood in terms of a significant difference in internal repulsive forces or merely reflects the fact that there is so little difference between the internal energy of the two arrangements that packing forces are responsible for the different arrangements is a question we are not prepared to answer.

Acknowledgments. We are grateful to the National Science Foundation for support of this research and to Mr. James Corning for experimental assistance.

Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Arylmetal-1B, Aryllithium, and Arylmetal-1B-Lithium Clusters $Ar_4M_2Li_2$ (M = Cu, Ag, or Au). Detection of Rotation of Three-Center Two-Electron Bonded Aryl Groups around the C(1)–C(4) Axis[1a]

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Abstract: Arylmetal-1B, aryllithium, and arylmetal-1B-lithium compounds have polynuclear structures consisting of a metal core to which each of the aryl groups is bound via C(1) to two metals by a three-center two-electron (3c–2e) bond. When the metals are unlike and aryl is dissymmetrically substituted C(1) is a center of chirality. Rotation of the aryl group around the C(1)$\cdots$C(4) axis causes a continuous inversion of configuration at C(1). Dynamic ^1H and ^{13}C NMR studies revealed that the prochiral methylene group in 2-$(Me_2NCH_2)C_6H_4$–metal compounds $Ar_4M_2Li_2$ (M = Cu, Ag, or Au) is an excellent probe for the monitoring of the configuration at C(1) in each of the 2-$(Me_2NCH_2)C_6H_4MLi$ units. In this way the rotation of 3c–2e bonded aryl groups around the C(1)$\cdots$C(4) axis has been established for the first time. Introduction of a second center of chirality of which the configuration cannot invert allows the detection of the stereochemistry of the $Ar_4M_2Li_2$ aggregates. The use of the chiral 2-$Me_2NCH(Me)$ rather than the prochiral 2-Me_2NCH_2 group as a built-in ligand provided unambiguous proof for the occurrence of Cu–N coordination in the Ar_4Cu_4 compounds at low temperature. Formation of Cu–N coordination bonds in the Ar_4Cu_4 cluster having C_2 symmetry constitutes a second element of chirality which in combination with the chirality at the benzylic C atoms gives rise to two distinguishable stereoisomers of Ar_4Cu_4. Li–N coordination in [5-Me-2-$(Me_2NCH_2)C_6H_4]_4Li_4$, which likewise constitutes an element of chirality, could be detected by ^1H and ^{13}C NMR. The novel results concerning the dynamics of 3c–2e bonded aryl groups at the same time provide a rationale for the kinetic stability order of the ortho-substituted arylmetal-1B clusters: 2-$Me_2NC(Z)HC_6H_4$ (Z = H or Me) $\approx$ 2-$Me_2CHCH_2C_6H_4$ $\approx$ 2-$Me_2NC_6H_4$ $\approx$ 2,6-$(MeO)_2C_6H_3$ $\approx$ 2,6-$Me_2C_6H_3$ > 2-MeC_6H_4 > 4-MeC_6H_4 $\approx$ unsubstituted phenyl–M cluster.

Introduction

Considerable information concerning the structure of homo- and heteronuclear arylcopper, -silver, and -gold compounds has recently become available (see ref 6–9). The presence of a central metal core to which aryl groups are bonded via 3c–2e bonds appears to be a persistent structural feature for these compounds. In the simple arylcopper tetramers, e.g., 4-$tolyl_4Cu_4$,[7] the aryl groups bridge the Cu_2 edges of an arrangement of four Cu atoms, which, as a result of linear hybridization at Cu (cf. the structure of $(Me_3SiCH_2)_4Cu_4$),[10] has a planar configuration. In the presence of built-in ligands (cf. the structure of $(5\text{-Me-}Me_2NCH_2C_6H_3)_4Cu_4$), the Cu_4 core has a butterfly-type configuration which is a consequence of the almost planar trigonal coordination geometry of the Cu atoms[11,12] The X-ray analysis further revealed a dihedral angle of about 80° between the aryl nucleus and the plane through the bridged metals and the bridging atom.

In this paper we present a qualitative study of the dynamic behavior in solution of 3c–2e bonded aryl groups present in polynuclear aryllithium, arylmetal-1B, and arylmetal-1B-lithium compounds. This study is related to the problem of stabilization of the configuration of chiral centers by intramolecular coordination. Recently, we have studied the latter problem using $(2\text{-}Me_2NCH(Z)C_6H_4)PhMeSnBr$ (Z = H or (*S*)-Me) as model compounds.[13]

Outline of the Dynamic Process

Bonding of Ar in Ar_4M_4 and $Ar_4M_2Li_2$. The proposed bonding in arylmetal-1B clusters[9,12] is schematically shown in Figure 1. The molecular orbital, which is lowest in energy, results from overlap of hybrids of s and p orbitals on copper (depending on the coordination symmetry, sp or sp^2) and a carbon sp^2 orbital. The second molecular orbital involves overlap of a carbon p_z orbital with an antisymmetric combination of Cu orbitals.

In the solid the aryl nucleus occupies a position almost perpendicular to the Cu–Cu vector.[9,12] Taking into account the bonding scheme in Figure 1, rotation of the aryl nucleus

0002-7863/79/1501-6593$01.00/0