# Heteronuclear Chains of Four Metal Atoms Including One Quadruply Bonded Dimetal Unit. Dichromium and Dimolybdenum Compounds with Appended Copper(I) Atoms

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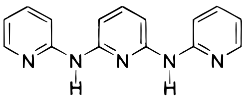
It is shown that the $M_2(DPhIP)_4$ molecules (M = Cr, Mo; HDPhIP = 2,6-di(phenylimino)piperidine) can each capture two $Cu^I$ atoms to form molecules with linear $Cu\cdots M\overset{4}{-}M\cdots Cu$ chains. In these chains the $Cu^I$ atoms have only weak interactions with the M atoms (Cr···Cu = 2.628 Å; Mo···Cu = 2.615 Å) even though their introduction causes marked decreases in the $M\overset{4}{-}M$ distances (from 2.265 to 1.906 Å for Cr and from 2.114 to 2.078 Å for Mo). These seemingly contradictory facts are explained by noting that in the $M_2(DPhIP)_4$ molecules there are strong destabilizing (to the $M\overset{4}{-}M$ bonds) donor interactions of the dangling nitrogen atoms with the $\pi^*$ orbitals. When these are eliminated by the introduction of the $Cu^I$ atoms, the $M\overset{4}{-}M$ bonds become stronger and shorter.

## Introduction

Several strategies exist for making molecules that have three or more metal atoms lined up in direct contact with one another. One of these is the all-in-one fell swoop (ofs) strategy whereby one simply combines several (commonly four) ligands with high enough denticity to hold *n* metal atoms in place with enough of a metal reagent to supply *n* metal atoms, and the derived $L_4M_nX_2$ type molecule is obtained directly. One example of this is the preparation of $Cr_5(tpda)_4Cl_2$[1] (eq 1), and even longer chains have been made in this way.[2]

$$4Li_2(tpda) + 5CrCl_2 \longrightarrow Cr_5(tpda)_4Cl_2 + 8LiCl \quad (1)$$

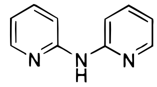
$H_2tpda$ =

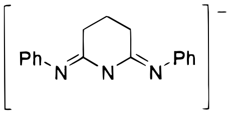


Another strategy is to employ ligands capable of binding *n* metal atoms with a source of <*n* metal atoms, thereby obtaining an isolable intermediate to which further metal atoms can later be added. This step-by-step (sbs) strategy has already been used (see, for example,[3] the conversion of $Cr_2(dpa)_4$ to $Cr_3(dpa)_4Cl_2$) to make homoatomic chains (eq 2)), but it has the potential to make mixed metal chains in a controlled way.[4,5] We are reporting here some examples of the latter type of chemistry. The ligand used in this work is the anion of 2,6-di(phenylimino)piperidine (**I**) for which we used the acronym DPhIP (pronounced deefip). The preparation of this ligand and the dichromium complex, $Cr_2(DPhIP)_4$ (**1**), has been reported earlier.[6] We now report the molybdenum homologue of **1**, $Mo_2(DPhIP)_4$ (**2**), and the reaction products of **1** and **2** with CuCl, namely, $[Cr_2Cu_2(DPhIP)_4(CH_3CN)](CuCl_2)_2\cdot 2CH_3CN$, $[\mathbf{3}(CH_3CN)]\cdot 2CH_3CN$, $[Mo_2Cu_2(DPhIP)_4(CH_3CN)](CuCl_2)_2\cdot 2CH_3CN$, and $[\mathbf{4}(CH_3CN)]\cdot 2CH_3CN$.

$$2CrCl_2 + 4Lidpa \longrightarrow Cr_2(dpa)_4 + 4LiCl$$
$$Cr_2(dpa)_4 + CrCl_2 \longrightarrow Cr_3(dpa)_4Cl_2 \quad (2)$$

Hdpa =





**I**

## Experimental Section

**General Procedures.** All syntheses and sample manipulations were carried out under an atmosphere of nitrogen with standard Schlenk and glovebox techniques. The compounds $Mo(CO)_6$ and anhydrous CuCl were purchased from Strem Chemicals and stored in a drybox under argon. H(DPhIP) and $Cr_2(DPhIP)_4$ were synthesized following known procedures.[5] Infrared spectra were recorded from KBr pellets on a Perkin-Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded on a Varian VXR-300 spectrometer. Elemental analyses were performed by Canadian Microanalytical Services Ltd.; they were satisfactory.

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**Preparation of $Mo_2(DPhIP)_4$, 2. (a) Method A.** The compound H(DPhIP) (0.53 g, 2.0 mmol) was dissolved in THF (20 mL) and deprotonated at −78 °C by methyllithium (1.0 M in THF, 2.0 mL). The pale-yellow solution obtained was transferred to a flask containing $Mo_2(O_2CCH_3)_4$ (0.216 g, 0.50 mmol), and the reaction mixture was heated at reflux temperature overnight. After filtration, the orange solution obtained was layered with hexanes. Red crystals of compound **2** and yellow crystals of $Mo_2(DPhIP)_2(O_2CCH_3)_2$ [7] were obtained after a week. This preparation was not optimized. IR (KBr, $cm^{-1}$) for $Mo_2(DPhIP)_2(O_2CCH_3)_2$: 1600 (s), 1498 (vs), 1477 (vs), 1450 (vs), 1437 (vs), 1423 (vs), 1345 (s), 1335 (s) 1316 (m), 1255 (m), 1215 (s), 1183 (s), 1152 (w), 1140 (w), 1108 (w), 1074 (w), 1057 (w), 1028 (w), 1001 (w), 980 (w), 921 (w), 861 (w), 805 (w), 782 (m), 762 (m), 715 (m), 695 (m), 671 (m), 630 (w), 593 (w), 516 (w).

**(b) Method B.** The solvent *o*-dichlorobenzene (25 mL) was degassed using two freeze−pump−thaw cycles and transferred to a 100 mL flask charged with $Mo(CO)_6$ (1.34 g, 5.1 mmol) and H(DPhIP) (4.0 g, 15 mmol); hexane (3 mL) was then added to the mixture in order to wash down $Mo(CO)_6$ that sublimed at the beginning of the reaction. The reaction mixture was heated overnight to 80 °C and then to reflux temperature for 24 h. The resulting dark-red suspension was concentrated to ca. 5 mL and mixed with diethyl ether (20 mL). The crude product was collected by filtration, washed with acetone (2 × 20 mL) and ethanol (2 × 20 mL), and dried under vacuum overnight. Yield: 1.93 g (61%). Crystals suitable for X-ray crystallographic study were grown from a $CH_2Cl_2$ solution of **2** layered with diethyl ether. $^1H$ NMR, $CD_2Cl_2$, $\delta$ (intensity, multiplicity, apparent *J*, assignment): 2.013 (8H, quintet, 10.2 Hz, piperidine); 2.533 (8H, t, 10.2 Hz, piperidine); 2.821 (8H, t, 10.2 Hz, piperidine); 5.420 (8H, d, 11.1 Hz, phenyl); 6.594−6.757 (16H, m, 11.2 Hz, phenyl); 6.859 (8H, t, 11.0 Hz, phenyl); 6.980 (8H, d, 11.7 Hz, phenyl). IR (KBr, $cm^{-1}$): 1623 (s), 1594 (m), 1542 (w), 1499 (vs), 1419 (m), 1330 (m), 1314 (m), 1257 (w), 1216 (s) 1186 (m), 1097 (w), 1069 (w), 1025 (w), 930 (w), 900 (w), 853 (w), 806 (w), 779 (m), 762 (w), 698 (s), 598 (w), 506 (w).

**Preparation of $[Cr_2Cu_2(DPhIP)_4](CuCl_2)_2$, 3.** The yellow crystalline $Cr_2(DPhIP)_4{\cdot}2THF$(0.32 g, 0.25 mmol) was dissolved in THF (20 mL), CuCl (0.10 g, 1.0 mmol) was added through a solids addition tube, and the mixture was heated at reflux temperature for 3 h. The resulting brown powder was collected, washed with THF (2 × 10 mL), and dried. Yield: 0.15 g (37%). The orange-yellow square-plate crystals of $[\mathbf{3}(CH_3CN)]{\cdot}2CH_3CN$ suitable for crystallographic study were grown by layering an acetonitrile solution of **3** with diethyl ether. $^1H$ NMR, $CD_3CN$, $\delta$ (intensity, multiplicity, assignment): 2.611 (8H, t, piperidine); 2.715 (8H, t, piperidine); 6.265 (8H, d, phenyl); 7.065−7.392 (32H, m, phenyl). IR (KBr, $cm^{-1}$): 1580 (m), 1560 (m), 1537 (vs), 1517 (vs), 1491 (w), 1449 (w), 1437 (s), 1420 (w), 1405 (s), 1371 (s), 1345 (w), 1329 (w), 1263 (w), 1223 (s), 1195 (s), 1156 (w), 1071 (w), 1028 (w), 1004 (w), 972 (w), 948 (w), 916 (w), 867 (w), 803 (m), 764 (m), 722 (m), 697 (m), 607 (w), 510 (w).

**Preparation of $[Mo_2Cu_2(DPhIP)_4](CuCl_2)_2$, 4.** Compound **2** (0.31 g, 0.25 mmol) was dissolved in $CH_2Cl_2$ (10 mL), and the dark-red solution was transferred to another flask containing a CuCl (0.10 g, 1.0 mmol) suspension in $CH_2Cl_2$ (10 mL). The mixture was heated at reflux temperature for 1 h to give an orange crystalline solid, **4**, which was collected by filtration, washed with $CH_2Cl_2$ (2 × 5 mL), and dried under vacuum. Yield: 0.36 g (84%). Orange-red crystals of $[\mathbf{4}(CH_3CN)]{\cdot}2CH_3CN$ were obtained from a solution of **4** in acetonitrile that was layered with diethyl ether. $^1H$ NMR, $CD_2Cl_2$, $\delta$ (intensity, multiplicity, apparent *J*, assignment): 2.095 ppm (8H, quintet, 6.6 Hz, piperidine); 2.789 (8H, t, 6.6 Hz, piperidine); 3.093 (8H, t, 6.3 Hz, piperidine); 6.240 (8H, d, 7.7 Hz, phenyl); 7.012 (4H, t, 7.4 Hz, phenyl); 7.096 (8H, t, 7.4 Hz, phenyl); 7.191 (4H, t, 7.4 Hz, phenyl); 7.291 (8H, t, 7.2 Hz, phenyl); 7.399 (8H, d, 7.7 Hz, phenyl). IR (KBr, $cm^{-1}$): 1591 (w), 1560 (w), 1549 (w), 1497 (vs), 1480 (s, sh), 1448 (m), 1389 (s), 1360 (s), 1342 (m), 1261 (w), 1218 (m), 1191 (s), 1155 (w), 1070 (w), 1026 (w), 1002 (w), 983 (w), 946 (w), 913 (w), 858 (w), 803 (m), 764 (m), 725 (m), 696 (m), 675 (w), 643 (w), 624 (w), 604 (w), 507 (w).

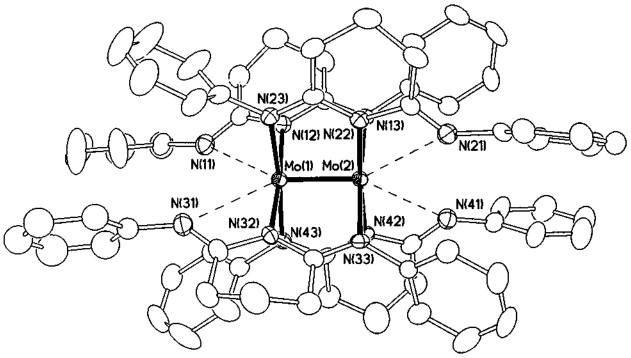

**Figure 1.** Drawing of the molecular structure of compound **2**, $Mo_2(DPhIP)_4$. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Axial $\pi^*$ interactions are indicated by broken lines.

**Crystallographic Studies.** Data collection for **2** and $[\mathbf{3}(CH_3CN)]{\cdot}2CH_3CN$ was carried out on a Nonius FAST area detector diffractometer with each crystal mounted on the tip of a glass fiber under a stream of nitrogen at −60 °C. Cell parameters were obtained by least-squares refinement of 250 reflections ranging in $2\theta$ from 18.1° to 41.6°. Laue groups and centering conditions were confirmed by axial images. Data were collected using 0.2° intervals in $\phi$ over the range $0 \leq \varphi \leq 220°$ and 0.2° intervals in $\omega$ for two different regions in the range $0 \leq \omega \leq 72°$; in this way, nearly a full sphere of data were collected. The highly redundant data sets were corrected for Lorentz and polarization effects and for absorption. Data collection for $[\mathbf{4}(CH_3CN)]{\cdot}2CH_3CN$ was performed on a Bruker Smart CCD diffractometer at −120 °C.

The positions of the metal atoms and sometimes the atoms of the first coordination sphere were located from a direct-methods E-map; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions.

A phenyl ring in **2**, an interstitial $CH_3CN$ molecule in $[\mathbf{3}(CH_3CN)]{\cdot}2CH_3CN$, and a $CuCl_2^-$ anion in $[\mathbf{4}(CH_3CN)]{\cdot}2CH_3CN$ are disordered. Each of them was modeled as having two orientations; the occupancy of each orientation was refined as an optimal fit determined by SHELXL.

Crystallographic data for **2**, $[\mathbf{3}(CH_3CN)]{\cdot}2CH_3CN$, and $[\mathbf{4}(CH_3CN)]{\cdot}2CH_3CN$ are given in Table 1; selected bond distances and angles for **2**, $[\mathbf{3}(CH_3CN)]{\cdot}2CH_3CN$, and $[\mathbf{4}(CH_3CN)]{\cdot}2CH_3CN$ are listed in Tables 2, 3 and 4, respectively. Drawings of molecular structures of compound **2** and the cation in **4** are given in Figures 1 and 2, respectively.

## Results and Discussion

**Syntheses.** A common approach to the preparation of dimolybdenum complexes is reaction of $Mo_2(O_2CCH_3)_4$ and the lithium salt of the corresponding ligand.[8] When this synthetic route was used for the DPhIP ligand, we found that a mixture of $Mo_2(DPhIP)_2(O_2CCH_3)_2$ and $Mo_2(DPhIP)_4$ formed. This was clearly visible by NMR. Even though we were able to separate a few crystals of each product, the yields were poor mainly because the solubilities of both of these compounds are quite similar in common organic solvents, making efficient separation difficult. Fortunately, compound **2** can be prepared in high purity and in good yield by an alternative route involving $Mo(CO)_6$

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(7) Crystal data for $Mo_2(DPhIP)_2(O_2CCH_3)_2$, $M = 834.62$. Triclinic, space group $P\bar{1}$, $a = 8.791(1)$ Å, $b = 9.939(2)$ Å, $c = 10.690(2)$ Å, $\alpha = 69.43(1)°$, $\beta = 85.65(1)°$, $\gamma = 88.90(2)°$, $V = 871.9(3)$ Å$^3$, $D_c = 1.590$ g/cm$^3$, $Z = 1$, $\mu = 7.69$ cm$^{-1}$. Data were collected at 213(2) K on a FAST area detector system. A total of 2737 unique reflections ($2\theta \leq 50°$) were measured. Full-matrix least-squares refinement on $F^2$ converges to $R1 = 0.039$, $wR2 = 0.099$ (all data). The structure corresponds to a typical paddlewheel with four bridging ligands; two DPhIP ions are trans to each other with a hanging arm at each end of the Mo−Mo bond. The Mo−Mo distance is 2.0888(7) Å.

(8) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993.

**Table 1.** Crystal Data and Structure Refinement

| complex | **2** | [**3**($CH_3CN$)]$\cdot$2$CH_3CN$ | [**4**($CH_3CN$)]$\cdot$2$CH_3CN$ |
|---|---|---|---|
| chemical formula | $C_{68}H_{64}N_{12}Mo_2$ | $C_{74}H_{73}N_{15}Cl_4Cu_4Cr_2$ | $C_{74}H_{73}N_{15}Cl_4Cu_4Mo_2$ |
| fw | 1341.19 | 1672.43 | 1760.31 |
| space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 14.405(4) | 16.956(8) | 17.0279(8) |
| $b$, Å | 12.45(3) | 17.409(3) | 17.4881(8) |
| $c$, Å | 32.786(8) | 24.674(5) | 24.672(1) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 93.04(5) | 100.52(2) | 100.780(1) |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 5872(12) | 7161(4) | 7217.3(6) |
| $Z$ | 4 | 4 | 4 |
| data collection instrument | Nonius FAST | Nonius FAST | Smart CCD |
| temp, K | 213(2) | 213(2) | 153(2) |
| radiation $\lambda$, Å | 0.710 73 | 0.710 73 | 0.710 73 |
| $\rho$(calcd), g cm$^{-3}$ | 1.404 | 1.551 | 1.620 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 4.81 | 16.64 | 16.97 |
| R1$^{a,b}$/R1$^{d}$ | 0.044/0.052 | 0.070/0.088 | 0.033/0.057 |
| wR2$^{b,c}$/wR2$^{d}$ | 0.103/0.113 | 0.172/0.193 | 0.084/0.094 |

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] Denotes values of the residuals considering only the reflections with $I > 2\sigma(I)$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. [d] Denotes value of the residual considering all the reflections.

**Table 2.** Selected Interatomic Distances (Å) and Torsional Angles (deg) for $Mo_2(DPhIP)_4$, **2**

| | | | |
|---|---|---|---|
| Mo(1)—Mo(2) | 2.114(1) | Mo(2)—N(22) | 2.157(5) |
| Mo(1)—N(32) | 2.144(4) | Mo(2)—N(42) | 2.168(5) |
| Mo(1)—N(12) | 2.157(4) | Mo(2)—N(33) | 2.179(3) |
| Mo(1)—N(43) | 2.199(5) | Mo(2)—N(13) | 2.196(4) |
| Mo(1)—N(23) | 2.124(3) | | |
| Mo(1)···N(11) | 2.989(5) | Mo(2)···N(21) | 2.932(5) |
| Mo(1)···N(31) | 2.998(5) | Mo(2)···N(41) | 3.085(5) |
| Mo(1)—N(12)—C(107)—N(11) | 7.3(4) | Mo(2)—N(22)—C(207)—N(21) | 3.4(4) |
| Mo(1)—N(32)—C(307)—N(31) | 3.0(4) | Mo(2)—N(42)—C(407)—N(41) | 4.1(4) |

**Table 3.** Selected Interatomic Distances (Å) and Bond Angles (deg) for [**3**($CH_3CN$)]$\cdot$2$CH_3CN$

| | | | |
|---|---|---|---|
| Cr(1)—Cr(2) | 1.906(2) | Cr(2)—N(11) | 2.054(5) |
| Cr(1)—N(2) | 2.052(5) | Cr(2)—N(5) | 2.058(5) |
| Cr(1)—N(8) | 2.053(5) | Cr(2)—N(9) | 2.077(5) |
| Cr(1)—N(12) | 2.072(5) | Cr(2)—N(3) | 2.090(5) |
| Cr(1)—N(6) | 2.085(5) | Cr(2)···Cu(2) | 2.689(2) |
| Cr(1)···Cu(1) | 2.628(2) | Cu(2)—N(4) | 1.906(5) |
| Cu(1)—N(1) | 1.873(5) | Cu(2)—N(10) | 1.885(6) |
| Cu(1)—N(7) | 1.868(5) | Cu(2)—N(1S) | 2.26(1) |
| N(7)—Cu(1)—N(1) | 177.6(2) | N(10)—Cu(2)—N(4) | 169.0(2) |
| N(10)—Cu(2)—N(1S) | 94.1(4) | N(4)—Cu(2)—N(1S) | 96.1(4) |
| N(1S)—Cu(2)—Cr(2) | 159.2(5) | | |

**Table 4.** Selected Interatomic Distances (Å) and Bond Angles (deg) for [**4**($CH_3CN$)]$\cdot$2$CH_3CN$

| | | | |
|---|---|---|---|
| Mo(1)—Mo(2) | 2.0778(3) | Mo(2)—N(22) | 2.135(2) |
| Mo(1)—N(32) | 2.132(2) | Mo(2)—N(42) | 2.141(2) |
| Mo(1)—N(12) | 2.133(2) | Mo(2)—N(33) | 2.199(2) |
| Mo(1)—N(43) | 2.178(2) | Mo(2)—N(13) | 2.192(2) |
| Mo(1)—N(23) | 2.181(2) | Mo(2)···Cu(2) | 2.7248(4) |
| Mo(1)···Cu(1) | 2.6149(4) | Cu(2)—N(41) | 1.978(2) |
| Cu(1)—N(11) | 1.904(2) | Cu(2)—N(21) | 1.980(2) |
| Cu(1)—N(31) | 1.906(2) | | |
| Cu(2)—N(51) | 2.139(3) | | |
| N(11)—Cu(1)—N(31) | 175.80(9) | N(41)—Cu(2)—N(21) | 161.73(9) |
| N(41)—Cu(2)—N(51) | 98.4(1) | N(21)—Cu(2)—N(51) | 98.81(9) |
| N(51)—Cu(2)—Mo(2) | 163.11(8) | | |

and the neutral H(DPhIP) compound in refluxing *o*-dichlorobenzene:

$$2Mo(CO)_6 + 2H(DPhIP)_4 \xrightarrow{o\text{-dichlorobenzene}} Mo_2(DPhIP)_4 + 2H_2 + 12CO$$

To ensure complete reaction, a slight excess of the ligand must be present in solution. The excess ligand can be easily removed from the resulting product by washing with acetone.

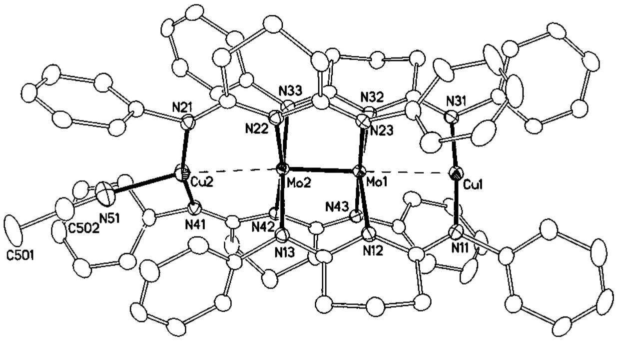

**Figure 2.** Molecular structure of the cation of compound **4** in [$Mo_2Cu_2(DPhIP)_4(CH_3CN)](CuCl_2)_2\cdot 2CH_3CN$. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity. Compound **3** is isostructural.

Reactions of **2** or its chromium analogue (**1**) with stoichiometric amounts of CuCl produce the corresponding [$M_2Cu_2(DPhIP)_4](CuCl_2)_2$ ionic species, M = Cr (**3**) or Mo (**4**), according to

$$M_2(DPhIP)_4 + 4CuCl \xrightarrow[\text{solvent}]{\Delta} [M_2Cu_2(DPhIP)_4](CuCl_2)_2$$

The choice of the reaction solvent is important. For the synthesis of **4**, $CH_2Cl_2$ gives better yields than THF; the solubility of the starting material **2** is significantly higher in $CH_2Cl_2$ than in THF. Compound **4** can be purified by washing with THF and is soluble in a variety of solvents such as $CH_3CN$, acetone, and $CH_2Cl_2$.

The synthesis of **3** cannot be carried out efficiently in an analogous way. Even though $CH_2Cl_2$ is a better solvent for the starting material, the product appears to react with this solvent at the reflux temperature necessary for the reaction to occur, and a "dirty-green" suspension of an uncharacterized material is obtained. Thus, THF is better as the reaction solvent, although because of solubility factors, the yield of the product is less than that of the molybdenum analogue, but the purity is excellent, as attested by the $^1$H NMR spectrum.

**Axial π* Coordination vs Metal—Metal Communication.** In the two compounds **1** and **2**, there are four DPhIP ligands surrounding the quadruply bonded dimetal unit; these alternate their directions around the M—M bond to form an $S_4$ type arrangement. Each ligand has a pendant arm, and the two pendant arms of two of the DPhIP's at each end of the molecule are opposite to each other, thus providing possible bites for two more metal atoms and the potential of forming a linear chain of four metal atoms. This is indeed possible by addition of CuCl. This raises the question as to whether there is any communication between the two axially placed metal atoms and the quadruply bonded dimetal unit in such heteronuclear tetrametal chains. A way to find out if this type of M—M communication exists is to use a dichromium unit in the middle of the tetrametal chain because Cr—Cr distances are known to be very sensitive to axial coordination. In different dichromium complexes, the Cr—Cr separations range from 2.689(3) Å [9] in compounds having strong axial coordination to 1.828(2) Å [10] in those without it. Even axial coordination from benzene molecules can lengthen a Cr—Cr bond significantly.[11] In our previous report,[6] four imino nitrogen lone pairs in compound **1** were found to donate electron density to the $\pi^*$ orbitals of a dichromium unit, giving a Cr—Cr distance of 2.265(1) Å. For direct comparison, the compound $Cr_2(PhIP)_4$ (PhIP is the anion of 2-(phenylimino)-piperidine), in which there are no pendant arms, was made and was found to have a significantly shorter Cr—Cr distance of 1.858(1) Å.

In compound **3**, two Cu atoms are incorporated into the chain where they occupy the two axial positions in **1**, forming a heteronuclear Cu···Cr—Cr···Cu chain. The four imino nitrogen lone pairs used to provide $\pi^*$ donation in compound **1** are no longer available because of Cu—N bond formation, and the Cr—Cr distance here is only 1.906(2) Å. This is much shorter than the Cr—Cr distance of 2.265(1) Å in **1**, and only 0.048(2) Å longer than that of $Cr_2(PhIP)_4$. These data seem to suggest that the Cu···Cr contacts of 2.628(2) and 2.689(2) Å found in **3** are too weak to affect significantly the Cr—Cr separation by axial coordination.

Compound **2** is the molybdenum analogue of compound **1**. The average distance from the four imino nitrogen atoms to the corresponding molybdenum atoms is 3.00 Å, and the average direction angle[6] (the Mo—N—C—N torsional angle, which should be close to 0° in order to have efficient overlap between the $\pi^*$ orbital and the nitrogen lone pair orbitals) is only 4.5°. The Mo—Mo bond length is 2.114(1) Å, which can be compared to the Mo—Mo bond length of 2.0812(5) Å in $Mo_2(DPhAP)_4$ [12] (DPhAP is the anion of 2,6-di(phenylamino)pyridine). The DPhAP ligand is structurally very similar to DPhIP except that the lone pair orbital is on an amino N and points away from the $\pi^*$ orbitals of the dimolybdenum unit. Thus, the bond lengthening by axial $\pi^*$ coordination in **2** is only 0.033(1) Å, which is insignificant compared to the 0.406(2) Å bond elongation in compound **1**. This is in accord with the well-known insensitivity of a Mo—Mo bond to axial coordination.

Compound **4**, which is the molybdenum analogue of **3**, has also been made and characterized by X-ray crystallography. In the Cu···Mo—Mo···Cu chain, the Cu atoms are 2.6149(4) and 2.7248(4) Å from the dimolybdenum unit and the Mo—Mo bond length is 2.0778(3) Å, which is almost the same Mo—Mo distance as that found in $Mo_2(DPhAP)_4$. This again is an indication of the removal of axial $\pi^*$ coordination and more importantly no significant Cu···Mo interaction.

**$CH_3CN$ Molecule at an Axial Position.** Since compounds **3** and **4** are isotypic, compound **4** will be used as a representative for the following discussion. In compound **4**, one axial $CH_3CN$ molecule is coordinated to one of the two Cu atoms. The $CH_3CN$-coordinated Cu has a T-shaped ligand arrangement, while the other Cu atom is linearly coordinated. The rod-shaped $CH_3CN$ molecule is not aligned along the metal—metal vector; the N(51)—Cu(2)—Mo(2) angle is 163.11(8)°. In contrast we have found that in compound $[Cr_3(DPhIP)_4(CH_3CN)](PF_6)_2$,[13] the $CH_3CN$ molecule is aligned with the three Cr atoms. The reason for this peculiar arrangement of the $CH_3CN$ ligand in [**4**($CH_3CN$)]·2$CH_3CN$ is the repulsion from the two opposite phenyl rings above and below the axial ligand. The axial coordination closes one end of the molecule but leaves the other one open. This has implications in the metal-to-ligand distances; i.e., the Mo(2)—N bond distances are longer than the Mo(1)—N separations (Table 4).

We have tentative crystallographic evidence that the axial $CH_3CN$ molecule in compound [**4**($CH_3CN$)]·2$CH_3CN$ can be removed by crystallizing **4** from $CH_2Cl_2$ or acetone, but in each case the molecules of **4** are highly disordered. They can be modeled as the superposition of two oppositely orientated molecules, but no satisfactory refinement of either structure[14] has yet been achieved.

For compounds **2** and **4**, we see a small decrease in the Mo—Mo distance (from 2.114 to 2.078 Å) for which the following explanation is proposed. In **2**, the Mo—Mo quadruple bond is slightly weakened by donation from the pendant nitrogen atoms into the $\pi^*$ orbitals. On addition of the $Cu^I$ atoms, these interactions are abolished, and since the copper atoms do not act as donors to the molybdenum atoms, the Mo—Mo bond length remains as short as one would expect for an unmolested quadruple bond.

For compounds **1** and **3**, we have a similar situation as with **2** and **4** except greatly exaggerated because the $\pi^*$ donation by the dangling nitrogen atoms in **1** is extensive, lengthening the Cr—Cr distance to 2.265 Å. When those interactions are abolished by the introduction of the $Cu^I$ atoms, which do not themselves have any significant donor function, the Cr—Cr bond contracts to 1.906 Å, which is appropriate for an unperturbed quadruple bond.

In conclusion it is pertinent to make a comparison of our results with those reported by Mashima et al.[4,5] These workers used the ligand 6-(diphenylphosphino)-2-pyridonate, pyphos. Insofar as the $Mo_2(pyphos)_4(PdCl_2)_2$, $Mo_2(pyphos)_4(PdBr_2)_2$, and $Mo_2(pyphos)_4(PtCl_2)_2$ compounds[4b] are concerned, the situation is quite similar to what we found for $[Mo_2(DPhIP)_4Cu_2]^{2+}$. The added metal atoms have very little interaction with the molybdenum atoms, and the Mo$\overset{4}{—}$Mo bond is left essentially unperturbed. Mashima et al. were able to reduce the $Pd^{II}$ and $Pt^{II}$ atoms to $Pd^I$ and $Pt^I$, giving $Mo_2(pyphos)_4(MX)_2$ molecules in which Mo—Pd and Mo—Pt bonds were postulated, although

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(14) Crystal data for **4** (crystallized from acetone): monoclinic, space group $C2/c$, $a = 21.263(3)$ Å, $b = 19.087(4)$ Å, $c = 20.132(3)$ Å, $\beta = 110.54(2)°$, $Z = 4$, $V = 7651(2)$ Å$^3$. Crystal data for **4** (crystallized from $CH_2Cl_2$): monoclinic, space group $C2/c$, $a = 27.301(4)$ Å, $b = 16.600(3)$ Å, $c = 16.903(2)$ Å, $\beta = 98.388(9)°$, $Z = 4$, $V = 7578(4)$ Å$^3$. Data were collected at 213(2) K on a FAST area detector system.

the Mo—Mo distances increase very slightly (by ca. 0.02 Å) while the Mo—Pd and Mo—Pt distances hardly change. With $[Mo_2(DPhIP)_4Cu_2]^{2+}$ no comparable experiment has been done.

In the case of $Cr_2(pyphos)_4(PtMe_2)_2$,[5] there is a marked contrast with our work. Here, there are $Pt^{II}$ atoms that interact strongly with the $Cr_2$ unit, increasing the Cr—Cr distance from 2.015 Å in $Cr_2(pyphos)_4$ to 2.389 Å, even though the Cr—Pt distances are relatively long, 2.81 Å. This is in contrast to the situation in $[Cr_2(DPhIP)_4Cu_2]^{2+}$ where the Cr—Cr distance is only 1.906 Å even though the Cr···Cu distance is 2.628 Å.

So far we do not have an entirely satisfactory explanation as to why the interactions of quadruply bonded species with a first-row closed-shell $d^{10}$ metal atom are so different from those of heavier $d^9$ metal atoms having the same oxidation state or why a $PtMe_2$ unit can be such a good electron donor.

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**Supporting Information Available:** Four figures showing thermal ellipsoids of **2**, **3**$(CH_3CN)\cdot 2CH_3CN$, $[Cu_2Mo_2(DPhIP)_4(CH_3CN)]^{2+}$, and $Mo_2(DPhIP)_2(OAc)_2$. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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