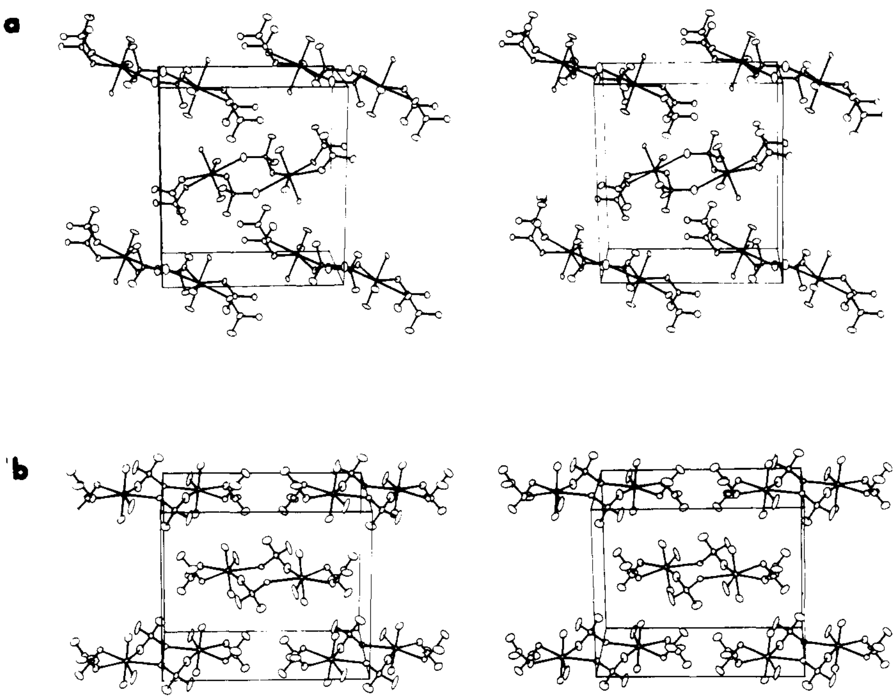

Figure 2. Stereoscopic drawings of the unit cell of (a) α-$UO_2SO_4 \cdot 2CO(NH_2)_2$ and (b) β-$UO_2SO_4 \cdot 2CO(NH_2)_2$ as viewed along the *a* axis. In the α form the *c* axis is running horizontally and the *b* axis vertically and in the β form the *b* axis is running horizontally and the *c* axis vertically. Hydrogen atoms are not included.

Table V. Possible Hydrogen Bond Distances (Å) and Angles (deg)

(A) α-$UO_2SO_4 \cdot 2CO(NH_2)_2$

atoms[a]	N···O	H-O	N-H-O
N(1)-H(1)···O(6)^{i}	3.061 (15)	2.10	157
-H(2)···O(7)^{ii}	3.201 (14)	2.21	173
N(2)-H(3)···O(4)^{iii}	3.294 (16)	2.39	152
-H(4)···O(2)	3.226 (17)	2.38	141
N(3)-H(5)···O(6)^{iv}	3.197 (14)	2.37	139
-H(5)···O(2)^{iv}	3.217 (14)	2.44	133
-H(6)···O(8)^{v}	3.043 (13)	2.17	145
N(4)-H(7)···O(4)^{vi}	3.295 (16)	2.39	148
-H(8)···O(6)	3.084 (16)	2.19	150

(B) β-$UO_2SO_4 \cdot 2CO(NH_2)_2$

atoms[b]	N···O	H-O	N-H-O
N(1)-H(1)···O(6)^{i}	3.079 (16)	2.35	128
-H(2)···O(8)^{ii}	3.081 (14)	2.12	162
N(2)-H(3)···O(4)^{i}	2.982 (11)	1.99	169
-H(4)···O(8)	3.209 (12)	2.42	135
N(3)-H(6)···O(7)^{iii}	3.105 (14)	2.23	147
N(4)-H(7)···O(6)^{iv}	2.853 (13)	1.86	165
-H(8)···O(7)	3.124 (12)	2.36	134

[a] Symmetry transformations: (i) $1 + x, {}^1/_2 - y, z - {}^1/_2$; (ii) $2 - x, 1 - y, -z$; (iii) $2 - x, y - {}^1/_2, {}^1/_2 - z$; (iv) $x, {}^1/_2 - y, z - {}^1/_2$; (v) $1 - x, 1 - y, -z$; (vi) $1 - x, y - {}^1/_2, {}^1/_2 - z$. [b] Symmetry transformations: (i) $2 - x, y - {}^1/_2, 1{}^1/_2 - z$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$; (iv) $x, {}^1/_2 - y, z - {}^1/_2$.

and are situated on the same side of it, whereas in the β form they are on opposite sides of the uranyl equatorial plane, forming angles of 48 and 59° with it. Table IV[17] gives the deviations of the atoms from the least-squares plane.

The urea molecules are involved in the hydrogen bonding within and between the chains. Table V lists the distances and angles for probable hydrogen bonds, which appear to be weak ones. In the α form there are hydrogen bonds N(2)-H(4)···O(2) and N(4)-H(8)···O(6) within the chain, while in the β form NH_2 groups and oxygen atoms O(7) and O(8) form a hydrogen-bonding network along the edges of the chains.

The main structural difference between the two forms lies in the packing of the chains. In spite of the roughly equal geometry of the unit cells the orientation of the chains is different, as seen in Figures 2 and 3.[17] In the α form the chains are propagated along the *a* axis in the *ac* plane, whereas in the β form they are in the *ab* plane. The shortest U-U distances within the chains are 5.89 and 6.04 Å and between the chains 7.52 and 6.05 Å, for the α and β forms, respectively. The packing efficiency is slightly greater in the α form as the unit cell volume is 2.3% smaller.

Acknowledgments. We are grateful to Magnus Fagerström, M.Sc. (Eng.), for preparing the crystals used in this study. We also thank Dr. Risto Laitinen for useful discussions.

Note Added in Proof. It has recently come to our attention that Soldatkina et al. have reported their work concerning the structure of $UO_2SO_4 \cdot 2CO(NH_2)_2$ (the α form in this work). For the original reference, see: Soldatkina, M. A.; Serezhkin, V. N.; Trunov, V. K. *Zh. Strukt. Khim.* **1981**, *22*, 146.

Registry No. $UO_2SO_4 \cdot 2CO(NH_2)_2$, 80315-67-9.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom coordinates, least-squares planes (Table IV), and observed and calculated structure factors and an illustration of the projections of the structures (Figure 3) (42 pages). Ordering information is given on any current masthead page.

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[17] Supplementary material.

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Metal-Metal Multiple Bonds. 12. Synthesis and Fluxional Behavior of $Cp_2MoW(CO)_4$[1]

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Received September 27, 1982

In contrast to the large number of heteronuclear dimers and clusters that contain metal-metal single bonds, there is a paucity of complexes that contain two different metal atoms multiply bonded to one another.[2] The first such compound to be synthesized, $MoW(O_2CCMe_3)_4I$, may be reduced to give the quadruply bonded dimer $MoW(O_2CCMe_3)_4$.[3] Garner and co-workers[4] have synthesized the quadruply bonded chromium–molybdenum dimer $CrMo(O_2CMe)_4$, and the molybdenum–tungsten dimer $MoW(hmp)_4$ (hmp = 2-hydroxy-6-methylpyridine) has been described by Cotton and Hanson.[5]

Chisholm et al.[6] failed to observe any mixed-metal dimers when dialkylamides were added to mixtures of $MoCl_5$ and WCl_6 (eq 1). The lack of heteronuclear formation was taken to mean that the L_3MML_3 complexes are not formed from the coupling of reactive ML_3 fragments. These workers also attempted to demonstrate the metathesis of metal–metal triple bonds by heating solutions of the homonuclear dimers (eq 2). When M = $Mo(CO)_2Cp$ and M′ = $W(CO_2)Cp$ (eq 2), some $Cp_2MoW(CO)_4$ was observed in the mass spectrum of the reaction products, but the compound was not isolated.[6]

$$WCl_6 + MoCl_5 + LiNMe_2 \rightarrow Mo_2(NMe_2)_6 + W_2(NMe_2)_6 \quad (1)$$

$$M{\equiv}M + M'{\equiv}M' \rightleftarrows 2M{\equiv}M' \quad (2)$$

However, it is known that the triply bonded complexes $Cp_2M_2(CO)_4$ (M = Mo, W) react rapidly with CO to form the *singly* bonded complexes $Cp_2M_2(CO)_6$ and that these dissociate readily to $CpM(CO)_3$ radicals, which may combine to give the observed small amounts of metathetical products.[7,8] Similarly, there was no observable metathesis between $Cp_2Cr_2(CO)_4$ and $Cp_2Mo_2(CO)_4$ when these complexes were subjected to prolonged reflux in toluene solution.[9]

$$Cp_2Cr_2(CO)_4 + Cp_2Mo_2(CO)_4 \nrightarrow 2Cp_2CrMo(CO)_4 \quad (3)$$

The above results suggest that metathesis of multiply bonded dimers does not occur to any appreciable extent[10] and other routes to mixed-metal, multiply bonded dimers must be employed. The proposed mechanism for the formation of $Cp_2M_2(CO)_4$ from $Cp_2M_2(CO)_6$ invokes the homolytic dissociation of the *singly* bonded dimers to $CpM(CO)_3$ radicals, which lose CO to form the 15-electron fragment $CpM(CO)_2$. These fragments then combine to form the triply bonded species.[7,8] Therefore, heating together the singly bonded hexacarbonyl dimers should lead to heteronuclear, multiply bonded dimers according to eq 4.

$$Cp_2M_2(CO)_6\ (Cp_2M'_2(CO)_6) \rightleftarrows CpM(CO)_3\ (CpM'(CO)_3) \xrightleftharpoons{-CO} CpM(CO)_2\ (CpM'(CO)_2) \rightarrow Cp_2M_2(CO)_4 + Cp_2MM'(CO)_4 + (CO)_4Cp_2M'_2 \quad (4)$$

This note describes the use of this route for the preparation of $Cp_2MoW(CO)_4$, its fluxional behavior, and improved syntheses of the homonuclear complexes $Cp_2M_2(CO)_4$ (M = Mo, W).

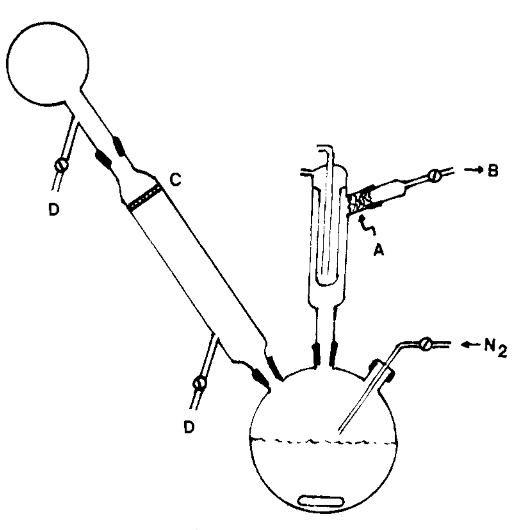

Figure 1. Diagram of the flask used in $Cp_2M_2(CO)_4$ preparations: (A) loose plug of glass wool to inhibit entrainment of solvent in the gas stream; (B) connection to oil bubbler; (C) medium-porosity, fritted-glass filter; (D) stopcocks for attachment to Schlenk line (N_2 or vacuum). An even more efficient aparatus has the fritted filter sealed directly onto the reaction flask.

Experimental Section

$Cp_2Mo_2(CO)_6$ was prepared according to the recipe of King[11] or by heating $Mo(MeCN)_3(CO)_3$[12] with neat, monomeric cyclopentadiene for 1–2 h. $Cp_2W_2(CO)_6$ was prepared by the thermolysis of solid $CpW(CO)_3CH_2Ph$ according to the directions of Ginley et al.[8]

$Cp_2M_2(CO)_4$ (M = Mo, W). A 1000-mL three-neck flask was fitted with a Friedricks condenser, a N_2 inlet which impinges *above* the liquid level, and a double-ended fritted-glass filter (see Figure 1). A large magnetic stir bar and 40 g of $Cp_2Mo_2(CO)_6$ were placed in the flask, which was then evacuated and backfilled with nitrogen. Diglyme (ca. 400 mL, previously distilled from sodium/benzophenone ketyl) was then transferred to the flask. The mixture was heated to reflux with a slow N_2 stream sweeping through the system. The rate of CO evolution was checked periodically by turning off the N_2 flow and observing the oil bubbler. Depending on the efficiency of the N_2 sweep, the reaction was complete in 1.5–3 h, and the color of the solution had changed from cherry red to brick red with an orange cast to it.

Workup was as follows. While the solution was still very hot, the condenser was replaced with a glass stopper (*caution*! diglyme vapors are extremely flammable) and the apparatus inverted. The hot solution was filtered through the frit into the Schlenk flask with a minimum pressure differential. The solution must be kept hot at all times (a heat gun is convenient), or the product will start to crystallize and clog the frit. After filtration, the solution was allowed to cool to ambient temerature and then cooled further in an ice–salt bath to obtain the product, $Cp_2Mo_2(CO)_4$, as deep maroon, needlelike crystals. A second crop may be obtained by reducing the volume of the filtrate on a rotary evaporator or by adding hexane to the filtrate. Yields ranged from 80 to 90%.

Using $Cp_2W_2(CO)_6$ in place of $Cp_2Mo_2(CO)_6$ gives high yields of pure $Cp_2W_2(CO)_4$. Anal. Calcd for $C_{14}H_{10}O_4W_2$: C, 27.57; H, 1.65; W, 60.29. Found: C, 27.40; H, 1.56; W, 60.44.

$Cp_2MoW(CO)_4$. One gram (2.0 mmol) of $Cp_2Mo_2(CO)_6$ and 1.33 g (2.0 mmol) of $Cp_2W_2(CO)_6$ were added to a 100-mL Schlenk flask fitted with a side-arm stopcock and a condenser connected to an oil bubbler. To the mixture was added 45 mL of dry diglyme. The solution was then heated to reflux while a slow stream of N_2 was passed through the system. After 3 h, the diglyme was distilled off under vaccum and the red-brown, solid residue was purified by column chromatography. The solid was placed on the top of a Florisil (100–200 mesh) column (70 × 2.5 cm), which had been evacuated for 12 h to remove oxygen. Methylene chloride/hexane (10:90 v/v) was used as the developer. After the bands had separated, the eluent was gradually enriched with CH_2Cl_2 to hasten the elution. Four fractions were obtained. In order of elution, they were $Cp_2MoW(CO)_6$,

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(10) The reason for this lack of metathetical activity is most probably steric in origin. Dissociative pathways are undoubtedly blocked by the high enthalpy of dissociation of the metal–metal multiple bonds,[2] and associative pathways[7] are precluded by the steric bulk of the ligands on the metal centers.

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Table I. Spectral Properties of $Cp_2MM'(CO)_4$ (M, M' = Mo, W)

M	M'	IR, ν_{CO}, cm^{-1}	^1H NMR, δ	^{13}C NMR, δ
Mo	Mo	1900, 1850	5.22[a], 4.65[b]	105.6, 195.9[b]
Mo	W	1950, 1890, 1835[d]	5.36, 5.30[a]	92.9, 92.1, 229.7[c] (231.7, 227.9 (J_{WC} = 218 Hz))[e]
W	W	1885, 1830	5.2[a]	92.6, 222.7[c]

[a] $CDCl_3$ solvent, ambient temperature (~30 °C). [b] C_6D_6 solvent, ambient temperature. [c] CD_2Cl_2 solvent, T = 30 °C. [d] KBr disk. [e] Toluene-d_8, T = −50 °C.

$Cp_2Mo_2(CO)_4$, $Cp_2MoW(CO)_4$, and $Cp_2W_2(CO)_4$. The identity of each fraction was confirmed by its mass spectrum. Recrystallization of the $Cp_2MoW(CO)_4$ from CH_2Cl_2/heptane gave pure material, yield ca. 30% (based on $Mo_2 + W_2 = 2MoW$). Anal. Calcd for $C_{14}H_{10}MoO_4W$: C, 32.2; H, 1.92. Found: C, 32.3; H, 2.05.

Results and Discussion

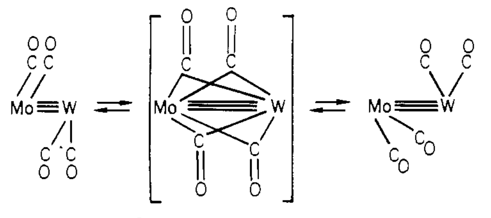
The use of the high-boiling ether, diglyme or bis(2-methoxyethyl) ether, in place of toluene[7] or xylene[8] as solvent for the thermal decarbonylation of $Cp_2M_2(CO)_6$ to $Cp_2M_2(CO)_4$ (M = Mo, W) shortens the requisite reaction time and gives purer product. With sufficient care to exclude oxygen, no recrystallizations are necessary to obtain analytically or spectroscopically (NMR) pure product. The pure solids may be handled in air for hours, but over a period of several weeks or months, progressive deterioration of the samples is evident. Solutions are rapidly attacked by oxygen, giving dark insoluble solids and $Cp_2M_2(CO)_6$, formed by the reaction of $Cp_2M_2(CO)_4$ with the CO liberated by the oxidation process.

The reaction shown in eq 5 must be nearly thermoneutral

$$\mathrm{Mo{\equiv}Mo + W{\equiv}W \rightleftarrows 2Mo{\equiv}W} \qquad (5)$$

since the yields of the Mo_2, MoW, and W_2 dimers were in an *approximate* 1:2:1 ratio (determined by ^1H NMR of the crude mixture), as expected for a statistical distribution. This result suggests that *at the reaction temperature*, the triply bonded species are all essentially at equilibrium with the CO in the system and hence are in equilibrium with each other and with the respective singly bonded dimers. As the CO is swept out of the system the equilibrium is gradually shifted to the triply bonded dimers.

At room temperature, the heteronuclear complex, $Cp_2MoW(CO)_4$, displays two resonances for the Cp groups in both the ^{13}C and ^1H NMR spectra (see Table I) as expected. However, only one resonance is observed for the carbonyl groups. In the solid state, $Cp_2Mo_2(CO)_4$ has disordered carbonyls that can be interpreted as a "stop-action" photograph of a fluxional process in which the carbonyls hop from one metal to another across the triple bond:[13,14]



(6)

Also, Jemmis et al.[15] have calculated that only a small energy difference exists between a tetrabridged structure (e.g., the proposed intermediate in eq 6) and the observed semibridging structures. The synthesis of the heteronuclear dimer, $Cp_2MoW(CO)_4$, has given us the first opportunity to study the process indicated in eq 6.

A variable-temperature NMR study of the MoW dimer showed that, below −10 °C, the carbonyl ^{13}C resonances split into two peaks. At −50 °C, the low-temperature limit has peaks at 231.7 and 227.9 ppm. The latter resonance is assigned to the carbonyls bonded to the tungsten atom due to its satellites (J_{WC} = 218 Hz). This coupling constant is considerably larger than the typical 130 Hz observed for many $W(CO)_5L$ complexes[16] and suggests that a higher fraction of s-character is present in the W–CO bonded of the multiply bonded dimer. One also notes that the carbonyl bonded to Mo in the MoW dimer is considerably deshielded with respect to the Mo_2 dimer (δ 231.7 vs. 195.9), whereas the shieldings of the carbonyls on W are more similar in the two compounds (δ227.9 and 222.7, respectively). Since *both* sets of resonances are shifted downfield, it is unlikely that the shifts are caused entirely by a polarity, e.g. $Mo^{\delta+}{\equiv}W^{\delta-}$, in the MoW bond (the electronegativity of W may be slightly higher than that of Mo due to the lanthanide contraction[17]). More likely, the cause of these shifts may be found in changes in the paramagnetic shift contributions, which depend on the energy differences between filled and empty orbitals in the complex.

The peak shapes corresponding to various temperatures were calculated as a function of exchange rate with the program DNMR-3A.[18] An Arrhenius plot was fitted by a least-squares procedure to give an activation energy of 10.4 ± 0.3 kcal/mol for the fluxional process. Jemmis et al.[15] calculated the energy surface interconnecting the semibridged and quadruply bridged structures to be relatively flat. Their EHMO method predicted the (μ-CO)$_4$ structure to be about 2 kcal *lower* in energy than the observed semibridged structure. However, they pointed out that the quadruply bridged structure has a near degeneracy that would tend to give an open-shell configuration subject to a second-order Jahn–Teller distortion. Consequently, deformations of the ground-state, semibridged structure to the quadruply bridged structure would be disfavored. Our value for the activation energy of the carbonyl exchange (eq 6) places an upper limit of ca. 10 kcal/mol on the energy difference between these two structures.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Amax Foundation for support of this research.

Registry No. $Cp_2Mo_2(CO)_6$, 12091-64-4; $Cp_2W_2(CO)_6$, 12091-65-5; $Cp_2Mo_2(CO)_4$, 56200-27-2; $Cp_2MoW(CO)_4$, 65995-85-9; $Cp_2W_2(CO)_4$, 62853-03-6; W, 7440-33-7; Mo, 7439-98-7.

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Synthesis, Characterization, and Properties of Stable Chromium(III) Aryl Isocyanide Complexes

David A. Bohling and Kent R. Mann*

Received August 9, 1982

The chemistry of homoleptic isocyanide complexes of chromium has been of interest[1-15] to organometallic chemists

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