Scheme I

1. Hydrolysis

$$\text{ImpA} + H_2O \xrightarrow{Zn^{2+}} \text{pA} + \text{ImH} \qquad (1a)$$

$$\text{ImpApA} + H_2O \xrightarrow{Zn^{2+}} \text{pApA} + \text{ImH} \qquad (1b)$$

2. Pyrophosphate bond formation

$$\text{ImpA} + \text{pA} \longrightarrow \text{AppA} + \text{ImH} \qquad (2)$$

3. Phosphodiester bond formation

$$\text{ImpA} + \text{ImpA} \xrightarrow{Zn^{2+}} \text{ImpApA} + \text{ImH} \qquad (3a)$$

$$\text{ImpAPA} + \text{ImpA} \xrightarrow{Zn^{2+}} \text{ImpApApA} + \text{ImH} \qquad (3b)$$

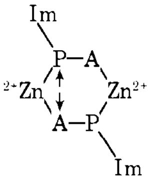
$$\text{ImpA} + \text{pA} \xrightarrow{Zn^{2+}} \text{pApA} + \text{ImH} \qquad (3a')$$

$$\text{ImpApA} + \text{pA} \xrightarrow{Zn^{2+}} \text{pApApA} + \text{ImH} \qquad (3b')$$

The pApA and pApApA formed in the reaction were analyzed by RNA'ase T_2 digestion,[4] and were found to contain 76-90% of unhydrolyzable 2'-5' phosphodiester bonds (Table I). The proportion of 2'-5' linkages and the efficiency of phosphodiester-bond formation were greater at lower reaction temperatures. Neither quantity was affected when $ZnCl_2$ was replaced by $Zn(NO_3)_2$.

When ImpU is used instead of ImpA in the Zn^{2+}-catalyzed reactions discussed above, the qualitative features of the reaction are unchanged. However, the yields of corresponding oligonucleotides are smaller with ImpU than with ImpA (Table II).

The explanation of our results at a mechanistic level is unclear. On the one hand, it is possible that two imidazolide molecules, bound in a single Zn^{2+} complex, react together to form an internucleotide bond; a 2:2 complex can be formulated in which the 2'-OH of an ImpA approaches the 5'-phosphate of another.[5] On the other hand, the reaction may occur between ImpA molecules attached to independent Zn^{2+} ions in the precipitate. In either case ImpA coordinates to Zn^{2+} ion and the internucleotide-bond formation takes place in the coordination sphere of Zn^{2+} ion.



A number of DNA and RNA polymerases have been shown to contain tightly bound Zn^{2+} ion[6] in the active site. It seems possible that the simple Zn^{2+} ion-catalyzed polymerization of activated nucleotides is the forerunner of nucleic acid synthesis. In this connection, it is interesting that the Mg^{2+} ion catalyzes the hydrolysis of ImpA and ImpU but does not enhance the formation of phosphodiester bonds. (Table I and Table II).

Acknowledgment. We wish to thank Dr. Jacques Ninio for his generous gift of authentic 3'-5' linked oligoadenylic acids (pApA, pApApA, pApApApA, and pApApApApA) and oligouridylic acids (pUpU and pUpUpU). This work was supported by NASA Grant NGR-05-067-001.

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(4) The enzymatic activity of venom phosphodiesterase (Worthington Biochemical) and RNase T_2 (Sankyo Co.) were checked by the assay using 3'-5' linked ApA, pApA, pApApA, and pUpU.
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Hiroaki Sawai, Leslie E. Orgel*
The Salk Institute for Biological Studies
San Diego, California 92112

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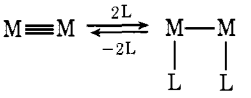
Reversible Addition of Carbon Monoxide to Tetracarbonylbis(η^5-pentamethylcyclopentadienyl)dimolybdenum(I)

Sir:

We wish to report the first example of a reversible addition of simple, two-electron donor ligands to metal triple bond of a coordination compound. The general reaction is shown in eq 1 where L is a two-electron donor ligand and M is a metal. This new reaction of metal-metal bonded complexes may have importance in catalysis and organometallic synthesis. Additionally, the work reported herein clarifies the uncertainties associated with previous studies[1-3] of tetracarbonylbis(η^5-pentamethylcyclopentadienyl)dimolybdenum(I), I.



$$\text{M}\equiv\text{M} \underset{-2\text{L}}{\overset{2\text{L}}{\rightleftharpoons}} \underset{\text{L}}{\text{M}}\text{—}\underset{\text{L}}{\text{M}} \qquad (1)$$

The complex I was prepared according to the literature procedure,[1,2] and as expected[2] the purest samples show only two CO stretching bands in the infrared. Purging isooctane solutions of I with CO at 25° leads to the complete and rapid decline of the two CO stretching bands characteristic of I and the growth of two new CO stretching absorptions both higher in energy than those in I. Accompanying these spectral changes are uv-visible spectral changes like those depicted in Figure 1. The spectral changes indicate a half-

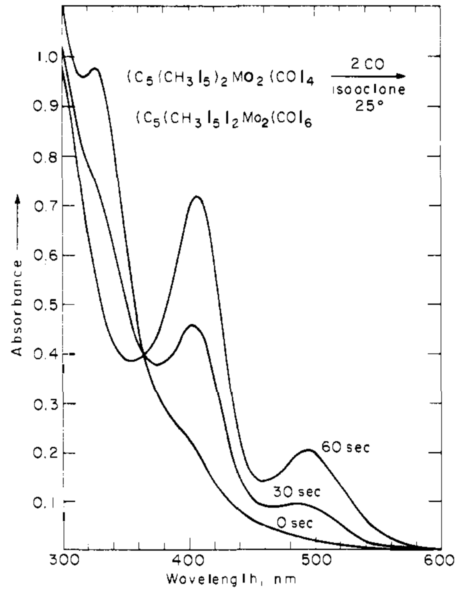


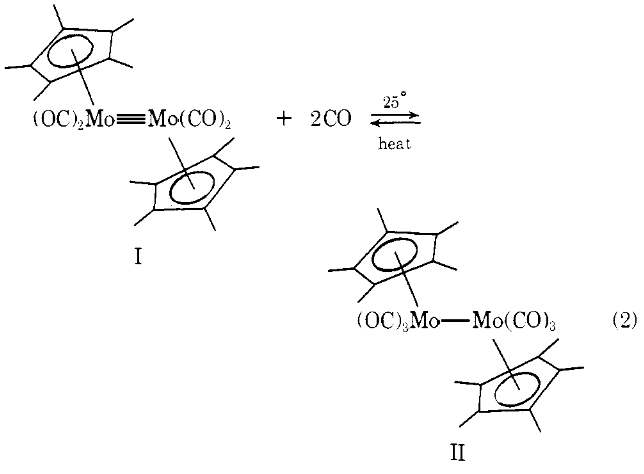
Figure 1. Uv-visible absorption spectral changes accompanying the conversion of I to II by purging an isooctane solution of I with CO at 25°. The band at 409 nm in II is the $\sigma_b \rightarrow \sigma^*$ transition analogous to that found at 388 nm in III.

Table I. Spectroscopic Data for Several Cyclopentadienyl Complexes

Complex	Infrared		Uv–visible	
	Solvent	Bands, cm^{-1}	Solvent	Bands, nm (ϵ)
$[(C_5(CH_3)_5)Cr(CO)_2]_2$	alkane	1876; 1857[a]		
$[(C_5H_4CH_3)Cr(CO)_2]_2$	CS_2	1897; 1875[b]		
$[(C_5H_5)Cr(CO)_2]_2$	CS_2	1904; 1881[b]		
$[(C_5(CH_3)_5)Mo(CO)_2]_2$	Cyclohexane	1874; 1846[a,c,d]	Isooctane[d]	395(sh); 326 (13,200); 280 (sh)
$[(C_5(CH_3)_5)Mo(CO)_3]_2$	Isooctane	1940; 1907[d]	Isooctane[d]	409 (9500); 495 (2500)
$[(C_5H_5)Mo(CO)_3]_2$	Isooctane	1960; 1915[d,e]	Isooctane[e]	388 (20,400); 512 (1720)
$[(C_5H_5)Mo(CO)_2]_2$	Isooctane	1889; 1859[d]	Isooctane[d]	380 (sh); 325 (13,700); 280 (sh)
$[(C_5H_5)W(CO)_3]_2$	Isooctane	1958; 1910[e]	CCl_4[e]	362 (20,200); 493 (2450)
$(C_5(CH_3)_5)Mo(CO)_3I$	Benzene	2028; 1945(br)[d]		
$(C_5(CH_3)_5)Mo(CO)_3Cl$	CCl_4	2030; 1960; 1925[d]		
$(C_5H_5)Mo(CO)_3Cl$	CCl_4	2055; 1983[e]		
$(C_5H_5)W(CO)_3Cl$	CCl_4	2053; 1968; 1947[e]		

[a] Reference 2. [b] Reference 7. [c] Reference 1. [d] This work. [e] Reference 6.

time for the reaction of the order of a minute. The reaction associated with these spectral changes is the quantitative generation of hexacarbonylbis(η^5-pentamethylcyclopentadienyl)dimolybdenum(I), II.[4] The heretofore unknown complex II has been identified spectroscopically by ir, ^{1}H NMR, and uv-visible as compared to the well-known[5] structural analog, hexacarbonylbis(η^5-cyclopentadienyl)dimolybdenum(I), III. Spectroscopic data for several pertinent compounds are summarized in Table I. The key spectroscopic features in II are (1) the presence of the intense electronic absorption band near 400 nm which is associated with a $\sigma_b \rightarrow \sigma^*$ electronic transition[6] characteristic of a Mo–Mo or W–W chromophore, (2) the two CO stretching bands and their position in the ir, and (3) a singlet ^{1}H NMR signal at τ 8.03 in $CDCl_3$. Additionally, the ^{1}H NMR of II has been measured in CD_2Cl_2 in the temperature range −90 to 35° and in toluene-d_8 in the temperature range 35–110°. In every case the ^{1}H NMR signal remains a sharp singlet near τ 8.0 associated with the 30 equivalent protons. Ir measurements in CH_2Cl_2 also show no evidence for the presence of a significant amount of a "gauche" conformation which has been observed for III in CH_2Cl_2.[5c,d] Thus, it appears that the solution structure of II is restricted to the "anti" conformation possibly due to the steric interactions of the methyl groups in a "gauche" conformation. The elemental analysis for II is satisfactory, particularly for the oxygen analysis. Anal. Calcd for C, 49.5; H, 4.8; O, 15.2. Found: C, 49.39; H, 4.80; O, 15.09. At room temperature and in the dark II is air stable as a solid or in solution. However, upon refluxing an N_2 purged toluene solution of II in the dark for several hours complex I is essentially quantitatively regenerated. Also, vacuum sublimination of II at ~150° results in the generation of a substantial amount of I in the sublimed material. Thus, eq 2 obtains. Alternatively, we have found that visible light irradiation of II in N_2 purged benzene or isooctane solutions at 25° results in the regeneration of I.



The conversion of II to I has precedence in that the Cr analog of III has been shown to undergo loss of two CO's yielding a Cr to Cr triple bonded complex.[7] This Cr result[7] and our discovery of the reactions (eq 2) prompted us to attempt to generate tetracarbonylbis(η^5-cyclopentadienyl)-dimolybdenum(I), IV,[8] by heating III. Refluxing III for several hours in N_2-purged m-xylene does lead to the decline of the two CO stretching bands associated with III and the concomitant growth of the two new bands at lower energy that we associate with IV.[9] Addition of CO at 25° to solutions containing IV, within seconds, regenerates III. Species IV is air sensitive in solution at 25° and obtaining pure samples has proved difficult, but samples of IV containing essentially no III have been isolated.

The formulation of I and IV as containing a Mo to Mo triple bond is appropriate based on a valence electron count, the short Cr to Cr bond in the Cr analog to I,[10] and the short Mo to Mo distance in IV[9] compared to III.[5a] Thus, the interconversions I $\rightleftarrows$ II and III $\rightleftarrows$ IV represent the first phenomenological examples of eq 1. The mechanisms of both the forward and reverse reactions are currently under study in these laboratories. The photochemical II → I conversion that we find suggests that this conversion can occur by Mo–Mo bond cleavage. This statement is supported by the additional observation that photolysis of II in CCl_4 efficiently yields $(\eta^5\text{-}C_5(CH_3)_5)Mo(CO)_3Cl$ in analogy to the photochemistry of III which has been shown[6] to only undergo Mo–Mo bond cleavage upon visible or near-ultraviolet irradiations. Regarding the synthesis[1] and the chemistry of I,[3] we have shown that simple ligand addition is possible and yields a stable, characterizable product, and it is likely that the two extra infrared bands in the CO stretching region generally found in impure samples of I,[1,2] and ascribed to "decomposition",[2] are in fact due to the presence of II. Finally, the work in ref 7 and now with III[8,9] shows that simple cyclopentadienyl complexes can also exist as multiple metal-metal bonded complexes just as with the pentamethylcyclopentadienyl species.

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(4) Complex II is purified by column chromatography on grade no. 1 alumina eluting with isooctane. The red-purple solid is isolated by simply removing the solvent at room temperature by rotary evaporation. As II is light sensitive in solution all manipulations should be carried out in darkened rooms.

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(9) The compound we obtain has the ir spectroscopic features reported[8] for IV and the uv-visible spectrum is similar to I. The synthesis of IV by heating III has been independently studied, and an X-ray structure confirms its formulation as an analog to I: R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, following paper.

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David S. Ginley, Mark S. Wrighton*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Synthesis, Reactivity, and Molecular Structure of Cyclopentadienylmolybdenum Dicarbonyl Dimer. The Molybdenum-Molybdenum Triple Bond

Sir:

We wish to report the thermal conversion of $Cp_2Mo_2(CO)_6$ to the triply bonded $Cp_2Mo_2(CO)_4$ as well as the molecular structure and reactivity of the latter. In an attempt to prepare diolefin complexes of $Cp_2Mo_2(CO)_6$, we have refluxed the hexacarbonyl dimer in various olefins and observed the formation of $Cp_2Mo_2(CO)_4$ analogous to the recently reported $Cp_2Cr_2(CO)_4$.[1]

In refluxing 1-octene or toluene, the thermal decomposition of $Cp_2Mo_2(CO)_6$ to $Cp_2Mo_2(CO)_4$ is erratic, with yields varying from about 0 to 90%. This observation, coupled with the results of Ginley and Wrighton[2] which suggest a Mo-Mo bond scission in the photolytic formation of $Cp_2Mo_2(CO)_4$ from $Cp_4Mo_2(CO)_6$, raises the possibility that the thermal reaction also proceeds via a free radical pathway.

Only recently has any precedent been reported for such a mechanism in organometallic reactions. Byers and Brown[3] have observed that carbonyl substitution reactions of $HRe(CO)_5$ proceed via a radical chain path and that in the absence of added chain initiators the reactions are very erratic. Similarly, Osborne et al. and Lappert and Lednor have shown that oxidative additions of low valent complexes may proceed via radical pathways.[4,5]

$Cp_2Mo_2(CO)_4$, prepared as described above, has physical properties identical with those reported earlier.[6,7] The chemical properties of the tetracarbonyl dimer are remarkably different from those of the permethylated analog, $(C_5Me_5)_2Mo_2(CO)_4$, as reported by King et al.[8,9] These authors were unable to find any addition reactions involving the Mo≡Mo triple bond that did not completely cleave the dimer. In contrast, $Cp_2Mo_2(CO)_4$ readily adds soft nucleophiles, e.g., phosphines and phosphites, to give addition products in which the metal-metal π-bonds have been displaced:

$$Cp_2Mo_2(CO)_4 + 2L \longrightarrow Cp(CO)_2LMo\text{—}MoL(CO)_2Cp$$

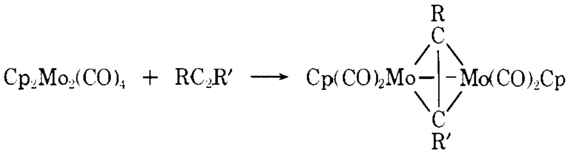
$$\text{Ia, } L = Ph_3P$$
$$\text{Ib, } L = (MeO)_3P$$

Compounds Ia and Ib are identical with those prepared by CO displacement from $Cp_2Mo_2(CO)_6$.[10,11] No monosubstitution is observed when a molar equivalent of ligand is allowed to react with $Cp_2Mo_2(CO)_4$. The observed products are equimolar mixtures of disubstituted Ia or Ib and unreacted tetracarbonyl dimer. This behavior is in keeping with the maintenance of the 18-electron count around each molybdenum.

$$Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp + L \xrightarrow{\text{slow}} Cp(CO)_2Mo\text{—}MoL(CO)_2Cp$$

$$Cp(CO)_2Mo\text{—}MoL(CO)_2Cp + L \xrightarrow{\text{fast}} Cp(CO)_2LMo\text{—}MoL(CO)_2Cp$$

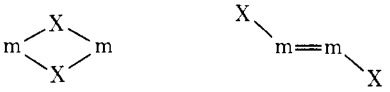
$Cp_2Mo_2(CO)_4$ also reacts with acetylenes to give addition products, $Cp_2Mo_2(CO)_4(RC_2R')$. On the basis of their ir and NMR spectra, these complexes are assigned a tetrahedrane structure.



IIa, R = R' = H
IIb, R = Ph; R' = H

Both IIa and IIb are red crystalline solids and melt at 147-149 and 134-136°, respectively. IIa has carbonyl stretches at 2000, 1920, and 1850 cm^{-1} and its NMR spectrum shows two singlets at τ 4.67 (Cp) and 5.17 (H). The corresponding data for IIb are: 2000, 1930, and 1850 cm^{-1}; 2.96 (Ph), τ 4.65 (H), and 4.78 (Cp).

Unlike the permethylated analog $Cp_2Mo_2(CO)_4$ reacts with I_2 to give the violet, *dimeric* iodide, $Cp_2Mo_2(CO)_4I_2$, III, mp 129-130°. This complex shows carbonyl bands at 1950 sh, 1940, and 1860 cm^{-1}, and the NMR consists of a singlet at τ 5.18. In solution, the iodide decomposes by a second-order process to give $CpMo(CO)_3I$ among other products. Possibly related compounds are formed when $Cp_2Mo_2(CO)_4$ is allowed to react with organic disulfides. These compounds may be formulated with no formal Mo-Mo bond, or a double bond, depending on whether or not the structure is bridged.



m = $Cp(CO)_2Mo$; X = I, SR

Tetracyanoethylene and HCl also form addition products with $Cp_2Mo_2(CO)_4$, but these are not yet adequately characterized. The chemistry and fluxional behavior of these adducts are currently under study.

The structure of $Cp_2Mo_2(CO)_4$ has been determined by X-ray diffraction methods.[12] The compound crystallizes in the orthorhombic system: a = 6.485 (2), b = 18.465 (2), c = 11.639 (3) Å; V = 1401.2 (5) $Å^3$; Z = 4; ρ (obsd) = 2.04, ρ (calcd) = 2.06 g cm^{-3}. While the systematic extinctions are compatible with several space groups, the structure has been refined in *Pbcm* (no. 57, $D_{2h}{}^{11}$). The data set consisted of 2388 unique reflections collected by automated diffractometer out to 2θ = 60°. Reflections (871) with $F > 3\sigma(F)$ were used in the refinement and the current discrepancy indices are R_1 = 0.043 and R_2 = 0.054.[12]