디카르보닐테트라키스 몰리브데늄(0)과 텅스텐(0) 착물들에 대한
합성과 전자적 성질에 관한 연구

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Synthesis and Electronic Properties of Dicarbonyltetrakis(triphenylphosphine) Complexes of Molybdenum(0) and Tungsten(0)

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ABSTRACT. The chemical behavior for Mo(0) and W(0) complexes, $[M(CO)_2(PPh_3)_4]$ (M=Mo and W), has been investigated by UV-vis spectroscopic, magnetic, and electrochemical methods. Three absorption bands are observed in the UV-spectra. The crystal-field-splitting energy, spin-pairing energy, and bond strengths were deduced from the spectra. The metal *d* electrons in both complexes seemed to be delocalized in low-spin state. Metal ligand correlation appeared to strongly depend on bond strengths and diamagnetic properties. In electrochemical processes, both complexes exhibit an irreversible reduction wave.

INTRODUCTION

There are many biologically interesting ligands that form various complexes with molybdenum and tungsten.[1,2] A few important complexes may deserve mentioning. For example, the purple-brown, air-sensitive solid $Mo(acac)_3$ was obtained by heating $Mo(CO)_6$ or K_3MoCl_6 with acetylacetonate($CH_3COCHCOCH_3$, acac). Pyrazolyborate complexes of the type $(Hbpz_3)MCl_3$ were obtained from molybdenum compounds, and their oxidation to a variety of mixed oxochloro species was carried out.[3,4] Dinitrogen complexes have been studied extensively with a view to understanding natural nitrogen-fixing systems.[5] The bis(dinitrogen) complexes are generally prepared by the reactions of higher-valent halogen complexes already containing the phosphine ligands with strong reducing agents (e.g., Na/Hg) in the presence of N_2 gas.[6] Of the ligands that form various complexes with both Mo and W, the dithiocarbamato ligand is the most important.[7]

Molybdenum and tungsten complexes frequently exhibit similarities in various aspects of their chemistry, although there are some differences that are not easy to explain. Thus, some compounds of the same type differ noticeably in their reactivity toward various reagents; for example, $Mo(CO)_6$ and $W(CO)_6$ do not react with acetic acid to give the same type of the compounds, quadruply bonded dimetal tetraacetate. For the heavier elements, the higher oxidation states are more common and more stable against reduction than the lighter ones. Molybdenum is one of the biologically active transition elements.[8] It is intimately involved in the functioning of enzymes called nitrogenases, which cause atmospheric N_2 to be reduced to NH_3. In this paper, we report the electronic properties, magnetic properties, and electrochemical behavior of complexes of the type $M(CO)_2(PPh_3)_2$ (M=Mo and W).

EXPERIMENTAL SECTION

Materials and instrumentation. All reagents and sol-

vents were purified according to the conventional proce-
dures. Dimethylsulfoxide(DMSO) used in electrochemic-
al measurements was distilled twice over P_2O_5 and then
once over CaH_2 under nitrogen. Tris(acetylacetonato)
molybdenum(III) and -tungsten(III) compounds, [M(acac)$_3$]
(M=Mo, W; acac=$CH_3COCHCOCH_3$) were prepared by
the literature method.[9]

UV-visible spectra were obtained with a Beckmann
DU-68. Elemental analyses were performed with Perkin-
Elmer Model 240C Elemental Analyzer, and conduc-
tance was measured with an ORION 142. The magnetic
susceptibilities were measured with a PARC Model 155
Vibrating Sample Magnetometer(V.S.M). Cyclic Volta-
mmetry(CV) was carried out with a PARC Model-303A
static mercury dropping electrode(SMDE) and PARC
264A polarographic analyzer equipped with a PARC
Model KE-0089 XY recorder. A three-electrode cell
consisting of a working electrode, a platinum-wire coun-
ter electrode, and a Ag/AgCl reference electrode, was
used. Lithium perchlorate(LiClO$_4$) was used as a sup-
porting electrolyte.

Preparation. Unless otherwise stated, all the reactions
have been performed with standard Schlenk line and
cannula techniques under argon or nitrogen. The title
compounds, cis-M(CO)$_2$(PPh$_3$)$_4$ (M=Mo and W) were
synthesized by the same method reported for related
Mo(0) and W(0) compounds.[10]

To a stirred solution of 0.723 g(1.84 mmol) of [Mo
(acac)$_3$] and 4.840 g (11.1 mmol) of PPh$_3$ in 35 ml of tol-
uene was added 2.2 g(11.1 mmol) of tri(isobutyl)alumi-
num at −40 °C. The temperature was gradually raised to
room temperature, and the CO gas was bubbled into the
reaction mixture for 30 min. Addition of 30 ml of n-hex-
ane to the solution gave cis-Mo(CO)$_2$(PPh$_3$)$_4$ (1) as brown-
yellow crystals. In the same way, cis-W(CO)$_2$ (PPh$_3$)$_4$ (2)
was obtained as dark brown crystals, respectively. Com-
pounds 1 and 2 were recrystallized from n-hexane. Anal.
calcd for $C_{74}H_{60}O_2P_4Mo$: C, 74.00; H, 5.04; O, 2.66. Found:
C, 73.50; H, 5.05; O, 2.57. $C_{74}H_{60}O_2P_4W$: C, 68.93; H 4.69;
O, 2.48. Found: C, 68.88; H, 4.65; O, 2.50.

RESULTS AND DISCUSSION

UV-vis spectroscopy. The UV-visible spectra of [Mo
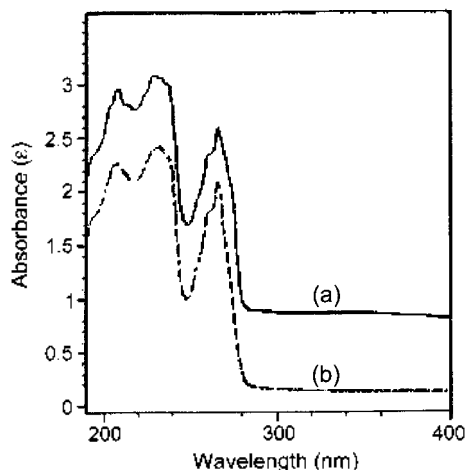(CO)$_2$(PPh$_3$)$_4$] (1) and [W(CO)$_2$(PPh$_3$)$_4$] (2) are shown in

Fig. 1. UV visible absorption spectra of [Mo(CO)$_2$(pph$_3$)$_4$]
(a) and [W(CO)$_2$(pph$_3$)$_4$](b) complexes in dimethylsulfoxide
solutions.

Fig. 1, which shows distinctive three absorption bands
for each compound. Compound 1 exhibits one band at
18870.17 cm^{-1} that can be assigned as a d-d transition, in
addition to two intense bands ($\varepsilon=10^4$-10^5) at 20708.03
and 23881.47 cm^{-1} that can be assigned as charge-trans-
fer or intraligand transitions.[11] In a similar manner, com-
pound 2 exhibits one band at 18904.43 cm^{-1}(a d-d
transition) and two bands at 20874.87 and 23881.47 cm^{-1}.

Table 1 lists absorption data for compounds 1 and 2.
Because the coordination sphere of the Mo(0) and W(0)
metals in both compounds is octahedral, the absorption
bands expected for these compounds should be spin-
allowed, but Laporte-forbidden, d-d transitions, although
weak in intensity.

The spin state of the central metal (high- or low-spin)
depends on the relative magnitudes of crystal-filed-split-
ting energy (Δ_o) and spin-pairing energy (P). The mag-
nitude of Δ_o can be determined by investigating the
energy difference between the two bands at v_2 and v_3 in
the free metal ion and those in its complex.[12] On the
basis of the values in Table 1, the Δ_o value for compound
1 can be calculated as 3173.43 cm^{-1}, and its P value as
650.74 cm^{-1}. In the same manner, the Δ_o value for com-
pound 2 can be calculated as 3006.60 cm^{-1}, and its P
value as 149.65 cm^{-1}. These values indicate that the
mean Δ_o value is greater than the mean P value, and
therefore both compounds are expected to be in the low-

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Table 1. Parameters for crystal field splitting of Mo(VI) and W(VI) complexes

Parameters Complexes	P(cm^{-1})	Q(cm^{-1})	μ_{eff}'(B.M)	E^a(KJ/mol)	B^b(cm^{-1})	Observed spin
Mo(CO)$_2$(L)$_4$	37908.78 37258.04 36036.03	23881.47 (1.147) 20708.03 (1.377) 18870.17 (1.147)	0.34	453.14	2138.42	low-spin
W(CO)$_2$(L)$_4$	38759.68 38610.03 36231.88	23881.47 (0.490) 20874.87 (0.465) 18904.43 (0.464)	0.28	453.14	2124.34	low-spin

L: Tetrakis-Triphenylphosphine, P: Free ion Frequency (cm^{-1}), Q: Complex Frequency (cm^{-1}), μ_{eff}: Magnetic susceptibility, a: Strength of Bonding, b: Electronic Repulision Parameter, (ε): (logεM^{-1}) (Absorption Ratio)

spin state. It is well known that, with increasing crystalfiled strength, the electrons will preferentially occupy the more stable t_{2g} orbitals.[13]

Three d-d transitions are observed in these systems: at 18870.17, 20708.03, and 23881.47 cm^{-1} for compound 1; 18904.43, 20874.87, and 23881.47 cm^{-1} for compound 2. These transitions can be assigned to the transitions $^1A_{1g}(F) \rightarrow {}^3T_{1g}(F)$, $^1A_{1g}(F) \rightarrow {}^1T_{1g}(F)$, and $^1A_{1g}(F) \rightarrow {}^1T_{2g}(P)$. From the equations proposed by Dou[14] and from the energies of the bands at ν_2 and ν_3, the band expected for the third, high energy, spin-allowed d-d transition ($^1A_{1g}(F) \rightarrow {}^1T_{2g}(P)$) should occur at ν_3. This band can be overlapped by the stronger charge-transfer or ligand-centered bands appearing near at ν_3. The calculated Racah parameter is 211.56 cm^{-1} for 1 and that is 200.440 cm^{-1} for 2.

The electronic structure of these complexes might be predicted on the basis of electron configuration of metals. According to the calculations (Δ_o), the lowest energyband might be assigned as a d$_{xy}$, d$_{yz}$, d$_{xz}$ (nonbonding)$\rightarrow$ e$_g^*$(antibonding π^*) transition, that is, a metal-centered d-d transition. The t_{2g} and e_g^* orbitals can accommodate all the necessary metal d-electrons. In addition, both octahedral complexes are expected to be in d^{2}sp^3 hybridization with low-spin states.

Magnetic Measurements. Magnetic susceptibilities were measured with a vibrating sample magnetometer. The susceptibilities were calculated from the eq 1.

$$\mu_{\text{eff}}' = 2.84\ (\chi_M^{\text{corr}} \times T) \quad (1)$$

From eq 1, the dipole moments (μ_{eff}') for compounds 1 and 2 can easily be calculated from the measured susceptibilities (χ_M). The calculated values of χ_M, as shown

in *Table* 1, suggest a very similar diamagnetic behavior for both compounds. On the basis of the experimental values, we speculate that empty metal d orbitals can receive electron density arising from the metal-centered d-d transition.

Crystal-field strength. From the absorption maximums in *Fig.* 1 and eq 2, the spin-paring energy can be calculated, and *Table* 1 shows the results.

$$E = 1.20 \times 10^5/\lambda \quad (2)$$

The E term in eq 2 has the unit of kJ/mol, and the λ term has the unit of nm. As mentioned earlier, the value of E for compound 1 is 453.14 kJ/mol, and that for 2 is 453.14 kJ/mol. The crystal-field splitting (Δ_o) values in our study are comparable to the values obtained by Basolo and co-workers.[15]

The large Δ_o values suggest compounds 1 and 2 to be ionic in the strong field.[15] Thus both molecular orbital theory and crystal field theory account for magnetic and spectral properties in terms of Δ_o, which is greater than the spin-pairing energy (P) for compound 1 and 2. The calculated spin-pairing energies are greater than 400 kJ/mol, suggesting that both compounds are ionic with lowspin state.[16]

The value of B (the interelectronic repulsion parameter) for $^1A_{1g}(F) \rightarrow {}^1T_{1g}(P)$ transition can be calculated by using following eq 3.

$$15B = \nu_3 + \nu_2 - 3\nu_1 \quad (3)$$

The states of a free metal ion in a crystal field are usually denoted by the symbols introduced by Mülliken based on group theory, and the states are shown in *Fig.* 3 and 4 (Tanabe Sugano diagrams). The Jahn Teller effect
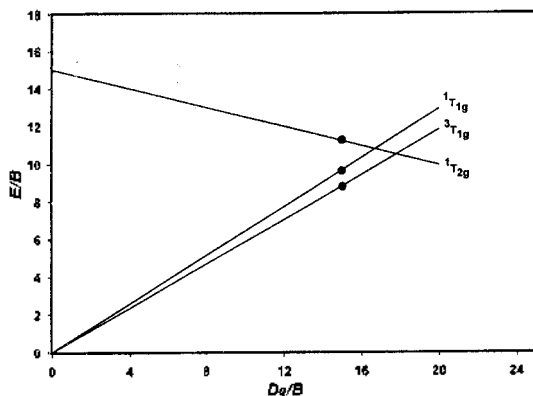
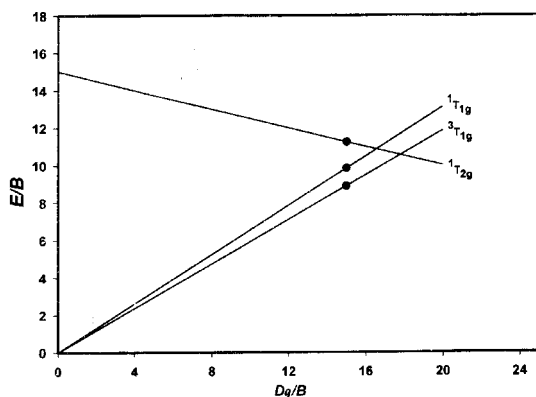*Fig.* 2. Energy diagram for spin allowed transitions [Mo(CO)₂(pph₃)₄] complex.

Fig. 3. Energy diagram for spin allowed transitions [Mo(CO)₂(pph₃)₄].

Fig. 4. Cyclic voltamogram on the [Mo(CO)₂(pph₃)₄] reduction in dimethylsulfoxide solution with 0.1 M·LiClO₄ supporting electrolyte (scan rate: ① 50 mV/s, ② 100 mV/s, ③ 200 mV/s, ④ 500 mV/s).

on aan octahedral complex of a d^6 ion is expected to cause E_g and T_{2g} states to split further in such a manner, as shown in *Fig.* 3 and 4. As expected, the ground state of the free metal ion is split field into a T_{2g} ground state and an E_F excited state.

Fig. 2 and 3 are plotted as a function of 10 Dq/B against E/B. The intersection points of the vertical line at Dq/B=15.04 and the lines for the $^1T_{1g}(F)$ and $^1T_{2g}(P)$
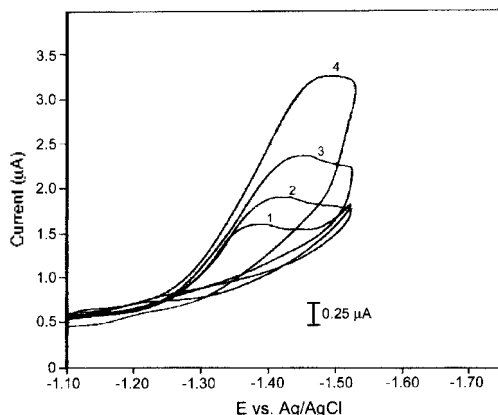
terms in *Fig.* 2 correspond to the values of E/B to be 11.20, 9.68, and 8.83. In addition, we obtained the value of Dq/B to be 15.00 and the values of E/B to be 11.24, 9.83, and 8.90 in *Fig.* 3. From the above results, compound **2** turns out to have B=2138.42 cm^{-1} and 10 Dq=3173.43 cm^{-1}, and compound **3** B=2124.34 cm^{-1} and 10 Dq=3006.60 cm^{-1}.

There are very weak bands arising from the F and P terms in *Fig.* 1. The stronger band is due to spin-allowed (but Laporte-forbidden) transition originating from the $^3T_{1g}(^1A_g)$ ground term. The other band, also very weak, seems to arise from the spin-forbidden (and Laporte-forbidden) transition. These assignments reasonably agree with observed bands, and the calculated values (E/B and 10 Dq/B) suggest the spin-orbital coupling effects. These values for two complexes are listed in *Table* 2.

The interelectron-pair repulsive terms, F and P, (in *Fig.* 2 and 3) are greater than 10,000 cm^{-1}.[16] The decrease in the interelectronic repulsions between the d-electrons of the metal ion on complex formation (*Tables* 1 and 2)

Table 2. Parameter for Mo(VI) and W(VI) metal complexes

Parameters Complexes	Racah[a] Constant	β[b]	Dq/B[c]	Localization Type	Λ$_M$
Mo(CO)₂(L)₄	211.56	0.36	15.04	delocalize	48.00
W(CO)₂(L)₄	200.44	0.38	15.00	delocalize	43.00

a: Energy gaps between excited terms of spin orbital F and P; b: Nephelauxetic ratio of B[Complex]/B'(free ion); c: Crystal field strength (Dq: frequency difference (P-F); B: Racah parameter); Λ$_M$: Molar Coductance
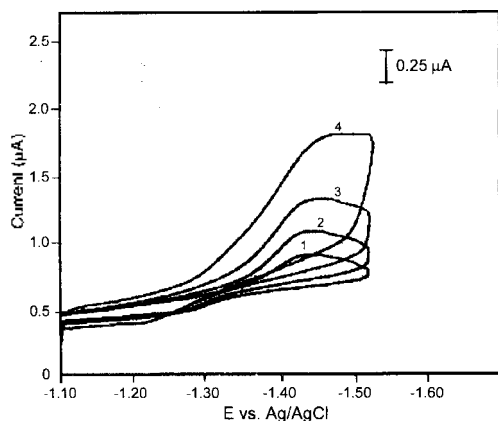
Fig. 5. Cyclic voltamogram on the [W(CO)₂(pph₃)₄] reduction in dimethylsulfoxide solution with 0.1M-LiClO₄ supporting electrolyte (scan rate: ①50 mV/s, ②100 mV/s, ③ 200 mV/s, ④ 500 mV/s).

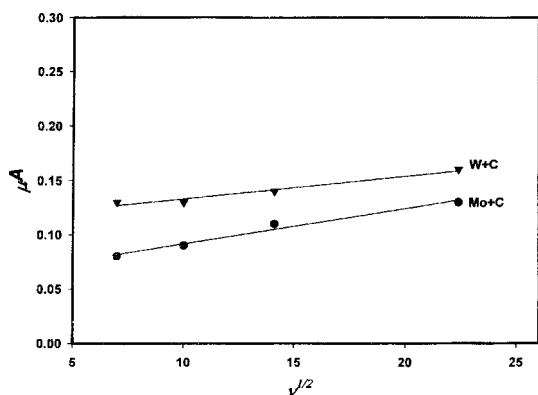*Fig.* 6. Plot of the peak current vs the square root of the scan rate; cyclic voltamogram for the reduction processes of 1mM Mo(VI) and W(VI) complex in DMF(0.1 M TEAP supporting electrolyte) at 20±0.1 °C).

might be explained on the basis of the delocalization of the metal *d*-electrons over the ligands. The extent of this delocalization can be expressed in terms of the β value, where β=*B*[complex]·*B*[free ion] ----- (4), *B* being the interelectronic repulsion parameter. The decrease in β value is known to correspond to a greater delocalization of the metal *d*-electrons.[18] The calculated β values in our experiment are 0.36 (for **1**) and 0.38 (for **2**). Therefore, the degree of delocalization (or covalence) between the metal and ligands for compounds **1** and **2** seems to be large, as indicated by these relatively values.[17]

Electrochemical properties. The electrochemical properties of the complexes were investigated by cyclic voltammogram (CV) in 0.1 M LiClO₄-DMSO solutions at the scan rate of 50-500 mVs⁻¹. All electrochemical measurements were carried out under nitrogen, and the results are shown in *Fig.* 4 and 5 and in *Table* 3. Compounds **1** and **2** exhibit a reduction wave, but the corresponding oxidation wave is not observed.

CONCLUSION

The crystal-field strength (Δ₀) for [M(CO)₂(PPh₃)₄] (M=Mo (**1**) and W (**2**)) are greater than the spin-pairing energy (*P*), from which both metals are expected to have d²sp³ hybrdization. Both complexes have the magnetic dipole moments of 0.34 and 0.28 B.M, which suggests diamagnetism. These results suggest that both complexes are ionic in a strong field. Interelectron-pair repulsions of *F* and *P* terms appear to arise from spin-orbital coupling. Compounds **1** and **2** exhibit an irre-

Table 3. Electrochemical data for [Mo(CO)₂L₄] and [W(CO)₂L₄] complexes in dimethylformamide

Complex	Sweep rate (mV/s)	E_Pc	E_1/2	I_Pc	I_Pc/√v
		-E(V)		(μA)	μA/(mV/sec)^{1/2}
Mo(CO)₂(L)₄	50	1.43	0.71	0.90	0.08
	100	1.44	0.72	1.08	0.09
	200	1.45	0.73	1.33	0.11
	500	1.48	0.74	1.83	0.13
W(CO)₂(L)₄	50	1.38	0.69	1.10	0.12
	100	1.41	0.71	1.40	0.13
	200	1.44	0.72	1.88	0.14
	500	1.49	0.75	2.77	0.16

L: Tetrakis-Triphenylphosphine:(pph₃)₄

versible reduction wave.

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