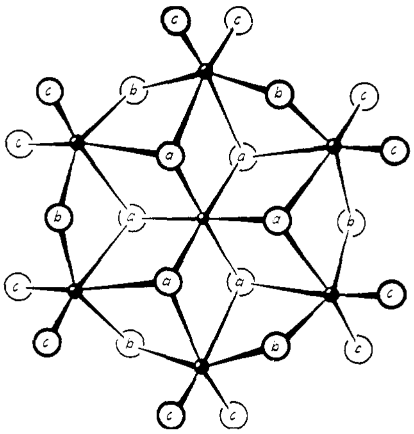


Figure 2. The hexamolybdotellurate complex ion $[TeMo_6O_{24}]^{6-}$, viewed along the trigonal axis through Te at the center. Atoms are labeled according to the ideal $\bar{3}m2$ symmetry (mirror planes viewed on edge pass through O_b–O_a–Te–O_a–O_b, and twofold axes pass through Mo–Te–Mo).

crystals $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$ and $K_6[TeMo_6O_{24}]\cdot 7H_2O$. Again only the heavy metal atoms were located directly and were found to be consistent with a flat structure containing seven octahedra, first proposed by Anderson.[5] A complete resolution has now been obtained of this complex ion as it occurs in the monoclinic compound $(NH_4)_6[TeMo_6O_{24}]\cdot Te(OH)_6\cdot 7H_2O$, in which it forms a crystal complex with telluric acid. The unit cell of the crystal conforms to the space group A2/a (or Aa) and has a = 21.353 Å, b = 9.950 Å, c = 18.757 Å, and β = 115° 37′; 5050 independent reflection data were collected for this crystal by visual estimate of intensities on multiple-film Weissenberg patterns made with Mo Kα radiation. The location of the Te atoms on symmetry centers in the space group A2/a made the structure analysis a trivial matter. A total of 114 parameters were varied in the full-matrix, least-squares analysis, and the final reliability factor is R = 0.100. The configuration of the hexamolybdotellurate ion previously proposed was fully confirmed, and individual bond lengths were determined with a standard error of 0.01 Å. The symmetry of the hexamolybdotellurate molecule ion conforms closely to $\bar{3}m$ (D_{3d}), which presumably represents the true symmetry of the free ion in solution. The complex ion is shown in Figure 2 as seen along the trigonal axis. The bond lengths averaged over the ideal symmetry are given in Table II.

Table II. Bond Lengths in the Hexamolybdotellurate Complex Ion $[TeMo_6O_{24}]^{6-}$, Averaged over the Ideal Molecular Symmetry $\bar{3}m$ (see Figure 2)

Bonded atoms	No. of bonds in molecule	Max var in crystal, Å	Av bond length, Å
Te–O_a	6	0.005	1.938
Mo–O_a	12	0.032	2.299
Mo–O_b	12	0.046	1.943
Mo–O_c	12	0.029	1.714
Te–Mo	6	0.016	3.299
Mo–Mo	6	0.040	3.299

In the crystal, the complex ion is joined to the telluric acid molecule only through hydrogen bonds. The telluric acid molecule $Te(OH)_6$ is a nearly regular octahedron, with an average Te–OH bond length of 1.910 Å.

Recently Perloff[6] completed a very precise crystal structure analysis of the triclinic compound $Na_3[H_6CrMo_6O_{24}]\cdot 8H_2O$, using counter-measured, three-dimensional data taken with Mo Kα radiation. He found that the hexahydrogen hexamolybdochromate(III) molecule ion has the same configuration as the hexamolybdotellurate ion. Furthermore, the corresponding averaged Mo–O bond lengths in the two complex ions are in agreement within 0.007 Å, although the central Cr–O bond length (1.975 Å) was found to be slightly longer than the Te–O bond.

---

[5] J. S. Anderson, *Nature*, **140**, 850 (1937).

[6] A. Perloff, Doctoral Dissertation, Georgetown University, Washington, D. C., 1966.

Howard T. Evans, Jr.
U. S. Geological Survey
Washington, D. C. 20242

Received January 22, 1968

Transition Metal Bonding through a Donor–Acceptor Interaction. $(C_5H_5)_2MoH_2\cdot Mo(CO)_5$ and Related Derivatives[1]

Sir:

We wish to report the synthesis and spectroscopic studies of a series of compounds containing metal-to-metal bonds formed through a donor–acceptor interaction.

The cyclopentadienyl hydrides Cp_2MoH_2 (Cp = C_5H_5) and Cp_2WH_2[2] have previously been shown to possess donor properties through a nonbonding electron pair on the metal atom to acceptor moieties such as the proton,[2] the boron halides,[3] and some group III alkyls.[4] We have now demonstrated that this donor property can also lead to strong interactions with transition metals that, in their complexes, exhibit *acceptor* power. The cyclopentadienyl hydrides can function as ligand, L, in complexes of the general formula $LM(CO)_5$ (M = Cr, Mo, W), which adducts are formed by displacement of tetrahydrofuran (THF) from the intermediate $(THF)M(CO)_5$.

To a solution of $(THF)M(CO)_5$ (M = Cr, Mo, or W)[5] is added 3 mmoles of $Cp_2M'H_2$ (M′ = Mo or W) in 20 ml of THF. After stirring at 50° for 15 min, the solvent is slowly stripped off and volatile residues are removed by sublimation under high vacuum at 50° for 10 hr. The remainder is dissolved in ether–hexane (1:1) and filtered, and the new compounds crystallize slowly at 0°, yield 25–40% based on $Cp_2M'H_2$.

Anal. Calcd for $C_{15}H_{12}Mo_2O_5$: C, 38.82; H, 2.61; Mo, 41.34; O, 17.24. Found: C, 38.93; H, 2.72; Mo, 41.46; O, 17.15.[6]

---

[1] Research supported by U. S. Public Health Service Grant GM-14336.

[2] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

[3] M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, **88**, 301 (1966).

[4] H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **1**, 125 (1965).

[5] Prepared by mercury lamp irradiation of 10 mmoles of $M(CO)_6$ in 70 ml of boiling THF until about 80% of the calculated volume of CO is evolved; see similar preparations of $LM(CO)_5$: W. Stohmeier, *Angew. Chem.*, **76**, 873 (1964), and references cited therein such as D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, **1**, 434 (1962).

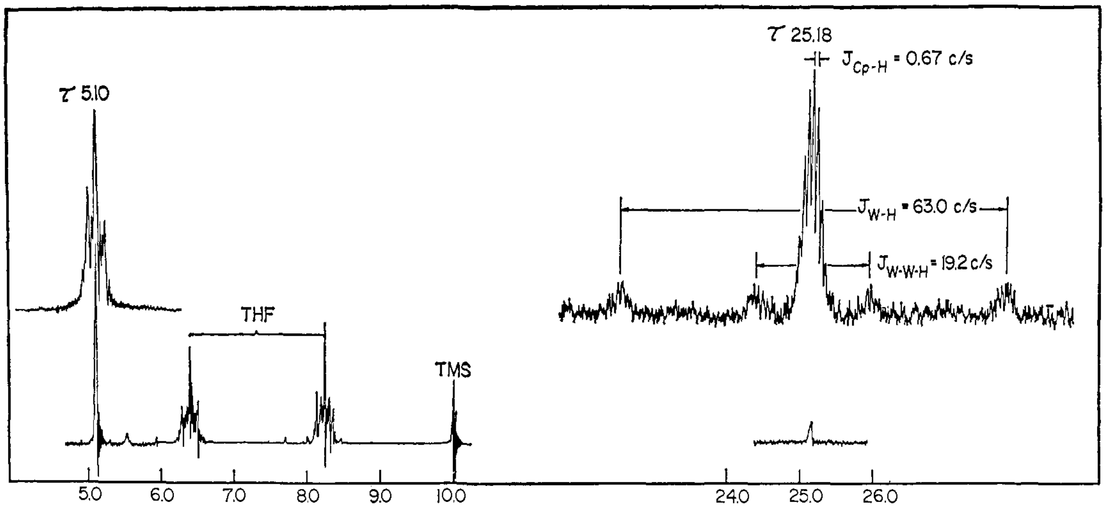
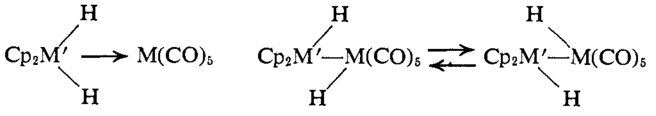


Figure 1. Proton magnetic resonance spectra for $(C_5H_5)_2WH_2 \cdot W(CO)_5$, tetrahydrofuran solution, tetramethylsilane internal standard. The lower traces were obtained at spectrum amplitude 2.5 and sweep width 500 cps, for which the given scale represents ppm (τ). The upper trace for the peak at τ 5.10 was scanned at spectrum amplitude 2.5 and sweep width 50 cps. The upper trace for the τ-25.18 peak and its satellites was scanned at spectrum amplitude of 40 and sweep width 100 cps; Varian A60 spectrometer equipped with 2000-cps sweep offset accessory.

The complexes are stable as solids varying in color from dark red, or brown to orange-red. In solution all exhibit slow, irreversible decomposition to $Cp_2M'H_2$ and insoluble residues. All the new complexes exhibit a three-band pattern in the CO stretching region of their ir spectra typical of $LM(CO)_5$ derivatives[7] (for M = M′ = Mo: 2066 (w), 1937 (s), and 1914 (m) cm^{-1}, in cyclohexane solution).

Two proton resonances are exhibited by the new complexes: a triplet in the cyclopentadienyl region (*ca.* τ 5.1, relative intensity 5) and a multiplet approximating 11 lines in the metal–H region (*ca.* τ 22–28, relative intensity = 1). The $C_5\mathit{H}_5$ resonances appear at *lower* magnetic fields and the $M'\mathit{H}_2$ resonances at *higher* fields than the corresponding resonances in the free cyclopentadienyl hydrides ($C_5\mathit{H}_5$, *ca.* τ 5.5; $M'\mathit{H}_2$, *ca.* τ 19–22).[2] The observation of a single principal resonance for $M'H_2$ is consistent with either a static structure I or a set of rapidly tautomerizing structures IIa and IIb. In compounds containing tungsten, spin-coupling satellites due to splitting of proton resonances by ^{183}W ($I = ^1/_2$, relative abundance = 14.3%) permit a clear choice between the isomeric forms I and II. The spectrum of $Cp_2WH_2W(CO)_5$ is shown in Figure 1. Two sets of satellites are clearly seen around the WH_2 resonance representing a strong coupling, 63.0 cps, and a weak coupling, 19.2 cps.[8] In the derivatives $Cp_2WH_2 \cdot M(CO)_5$ (M = Cr or Mo), only the *strongly* coupled satellites (64.5 and 65.8 cps, respectively) are observed, while in the derivative $Cp_2MoH_2 \cdot W(CO)_5$ only the *weakly* coupled satellites (19.6 cps) are observed. This observation is consistent only with the static structure I for all of these, which also requires that a donor–acceptor interaction is present between the $Cp_2M'H_2$ and $M(CO)_5$ moieties. (From the positions of the CO stretching frequencies, the $Cp_2M'H_2$ groups appear to have effects on the $M(CO)_5$ group similar to ligands such as pyridine or triphenylphosphine in their corresponding $LM(CO)_5$ derivatives.[9])


I IIa IIb

No infrared bands characteristic of a terminal M–H (*ca.* 1800–2200 cm^{-1}) or M–D (*ca.* 1300–1500 cm^{-1}) stretching frequency[8] were identified in the spectra of the new complexes or their metal-deuterated species. This could be due to masking of the former by CO stretching modes and the latter by C–H deformation frequencies.[8] Another possible explanation is that the hydrogen atoms bonded to M′ in $Cp_2M'H_2 \cdot M(CO)_5$ are affected by the electrons in the π regions of the $M(CO)_5$ moiety to the extent that their vibrational properties resemble bridging environment which would shift the absorptions to lower energies and also broaden them.[10]

Strong donors like the phosphines, R_3P, cause cleavage of the donor–acceptor bond slowly to produce $R_3P\text{–}M(CO)_5$ and free $Cp_2M'H_2$. We are at present attempting hydrogenolysis to give products such as $Cp_2M'H_2$ and $H_2M(CO)_5$, and also are looking for the possibility of H_2 abstraction to produce a multiple bonded species $Cp_2M'{=}M(CO)_5$.

Acknowledgment. We are grateful to Dr. J. R. Holmes for valuable suggestions and discussions.

Bernward Deubzer, Herbert D. Kaesz
Contribution No. 2238, Department of Chemistry
University of California, Los Angeles, California 90024

Received March 29, 1968

---

[6] Analysis by A. Bernhardt, Mulheim (Ruhr); satisfactory C and H analyses were obtained for the other members of the series, for which we thank Miss Heather King of the UCLA laboratories.

[7] See H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967), and references cited therein.

[8] In Cp_2WH_2 $J(^{183}WH_2)$ = 73.2 cps; see A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963), which value we confirm. The earlier report of this coupling constant in ref 2 is in error.

[9] See discussion by (a) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964); or more recently, (b) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

[10] A similar problem is encountered in $H_3Re_3(CO)_{12}$ (D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964)), in which only a broad absorption near 1000 cm^{-1} could be attributed to hydrogen stretching modes; see J. M. Smith, W. Fellmann, and L. H. Jones, *Inorg. Chem.*, **4**, 1361 (1965).