Crystal Structure and Bonding in the Dinuclear Complexes $(\pi\text{-}C_5H_5)_2W(SPh)_2M(CO)_4$ (M = Cr, Mo, and W) and $(\pi\text{-}C_5H_5)_2Ti(SMe)_2Mo(CO)_4$

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Summary The crystal structures of the title compounds (I, IIa) provide evidence for metal–metal bonding specific to the titanium–molybdenum complex: spectroscopic data support this conclusion.

THE crystal structures of the title compounds have been determined. All four complexes have similar geometry, with a planar $M^1(S)_2M^2$ ring. There are, however, significant differences in the dimensions of these rings.

Compounds (I) are isomorphous, with near-equal metal–metal distances of *ca.* 400 pm, and M^1SM^2 angles around 105°. In (IIa),[1] the metal–metal distance is shorter (332 pm) and the M^1SM^2 angle is acute. Acute bridging angles are also found in $Et_3P(OC)_3Mo(PMe_2)_2Mo(CO)_3PEt_3$[2] and $[Fe(NO)_2I]_2$,[3] and are generally ascribed to metal–metal bonding.

The spectra of the Cr,W analogues of (II) are similar to those of (IIa) and (IIb), but the conformation of the solids is uncertain for R = Ph.

TABLE 2

Selected spectroscopic data

Compound	ν(CO) (cm^{-1})	Low-energy electronic transitions (cm^{-1}) (log ϵ)
(Ib)	2010, 1898, 1870, 1850, 1842sh, 1817[a]	
(IIa)[b]	2071, 2016, 1918, 1903	18,800(3·6) 16,500(3·7)[c]
(II)[b]	2018, 1930, 1912, 1899	18,600(3·6) 16,000(3·7)[c]
$MeSC_2H_4SMeMo(CO)_4$[d]	2030, 1919, 1905, 1868	None
$PhSC_2H_4SPhMo(CO)_4$[b]	2027, 1905br, 1868	None
$(\pi\text{-}C_5H_5)_2Ti(SMe)_2$[b]	—	18,800(3·6)
$(\pi\text{-}C_5H_5)_2Ti(SPh)_2$[b]	—	18,600(3·6)

[a] Nujol mull.[4]
[b] In $CHCl_3$.[5]
[c] Resolved component peaks.[5]
[d] See H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 1962, 4454.

Spectroscopic data for compounds (IIa)[4] and (IIb)[5] support these conclusions, and demonstrate the nature of the bond (Tables 2,3). The similarity in properties between (IIa) and (IIb) shows that the difference between (IIa) and compounds (I) is not due to the change in the organothio-bridge, but rather to the replacement of W by Ti. We attribute the low CO stretching frequencies in compounds (I), as compared with bis(organothio)metal tetracarbonyls, to the low electronegativity of the $\pi\text{-}(C_5H_5)_2W(SPh)_2$ group, acting as a normal bidentate ligand. In (II), however, the frequencies are anomalously higher. Furthermore, the increase in τ values of the cyclopentadienyl protons in (II) relative to the free ligand would indicate a paradoxical increase in electron density on Ti. Compounds (II) show an intense low-energy charge transfer bond overlapping but distinguishable from the lowest energy bond in $(\pi\text{-}C_5H_5)_2Ti(SR)_2$, and responsible for the apparent

TABLE 1

Molecular dimensions for $\pi\text{-}(C_5H_5)_2M^2(SR)_2M^1(CO)_4$

	W–W	W–Mo	W–Cr	Ti–Mo[a]
M^2–M^1 (pm)	401	406	393	332
M^2–S	248	250	249	246
S–M^1	258	262	249	256
C_5H_5–M^2	199	200	199	207
S–S	294	294	293	377
$\angle C_5H_5$–M^1–C_5H_5	132·5°	134·5°	131·5°	128·7°
$\angle$S–M^2–S	72·8°	72·6°	72·1°	99·9°
$\angle$S–M^1–S	69·4°	69·0°	72·0°	94·6°
$\angle M^1$–S–M^2	104·9°	105·0°	104·2°	82·8°

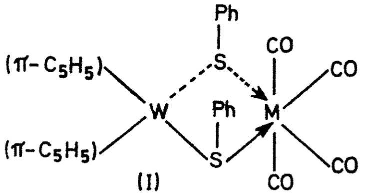
[a] From ref. 1.

TABLE 3

^{1}H *n.m.r. data* (τ *values in chlorobenzene*)[5]

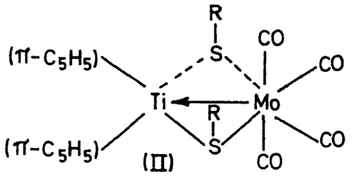
	C_5H_5	Me
(IIa)	4·80[a]	7·48
(IIb)	4·82[b]	—
$(\pi\text{-}C_5H_5)_2Ti(SMe)_2$	4·24	7·43
$(\pi\text{-}C_5H_5)_2Ti(SPh)_2$	4·24	—

[a] Time-averaged spectrum (+50°).
[b] Time-averaged spectrum (+25°).



(I)

a; M = Cr
b; M = Mo
c; M = W



(II)

a; R = Me
b; R = Ph

bathochromic shift[6] in this bond. Compounds (I) are yellow to red.

These data indicate that the two electrons present in (I), but absent in (II), and formally placed on the cyclopentadienyl metal, occupy an orbital with some metal–metal antibonding character. This would appear, from the M^{1}SM^2 angles, to correspond to Alcock's[7] ψ_y orbital, rather than to the more centrally localised orbital ψ_0 of Ballhausen and Dahl.[8] In the compounds (II), these electrons being absent, overlap of the carbonyl metal $d(x^2 - y^2)$ with the vacated orbital on Ti leads to a relative attraction between the metals and to the movement of charge indicated by the spectra.

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