955. *The Di-π-cyclopentadienyl Hydrides of Tantalum, Molybdenum, and Tungsten.*

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The di-π-cyclopentadienyl hydrides of tantalum, molybdenum, and tungsten have been prepared. High-resolution nuclear magnetic resonance spectra of these compounds and of the trihydride cations of molybdenum and tungsten have been measured. For the trihydride species of tantalum and tungsten the patterns of the high-field lines show that there are two equivalent hydrogen atoms in an A_2B grouping. This observation is discussed with reference to the base character and structure of di-π-cyclopentadienylmetal hydrides.

In a previous note[1] infrared and high-resolution nuclear magnetic resonance spectra of di-π-cyclopentadienylrhenium hydride were reported; it was also shown that the compound behaves as a base and can be protonated to give the cation $(\pi\text{-}C_5H_5)_2ReH_2^+$. Analogous di-π-cyclopentadienyl hydrides of molybdenum, tungsten,[2,3] and tantalum[4] have been briefly described and we here present further details of our work together with a discussion of the structure of this series of complexes on the basis of evidence gained principally from high-resolution nuclear magnetic resonance spectra.

Preparations and Chemical Properties.—The hydride complexes are prepared in high yields by the interaction of the anhydrous metal chlorides ($MoCl_5$, WCl_6, or $TaCl_5$) with a solution of sodium cyclopentadienide in tetrahydrofuran containing an excess of sodium borohydride. Without addition of borohydride to the sodium cyclopentadienide solution only low yields of the hydrides can be obtained since the hydride ion required must come from the solvent or from traces of excess of cyclopentadiene or cyclopentene present in the reaction mixture.

The tantalum hydride, $(\pi\text{-}C_5H_5)_2TaH_3$, is a white crystalline compound which is very sensitive to air; the molybdenum and tungsten hydrides, $(\pi\text{-}C_5H_5)_2MH_2$, form yellow crystals, the former being more sensitive to air than the latter, which can be handled briefly in air. The tantalum compound is sparingly soluble in light petroleum but it is moderately soluble in benzene; the other hydrides are soluble in light petroleum as well as in other common solvents. Solutions of all three compounds decompose rapidly when exposed to air. The compounds are soluble in halogenated solvents and in carbon disulphide but react with them quite rapidly, the order of reactivity being Ta $>$ Mo $>$ W; dichloromethane reacts much more slowly than carbon tetrachloride.

Like $(\pi\text{-}C_5H_5)_2ReH$, the molybdenum and tungsten compounds behave as bases and are soluble in dilute aqueous acids[3] and in trifluoroacetic acid, to give the ions $(\pi\text{-}C_5H_5)_2MH_3^+$; with gaseous hydrogen chloride or bromide the white deliquescent halide salts are formed. The tantalum hydride does not appear to behave as a base, even in trifluoroacetic acid, and is decomposed by aqueous acids.

Spectroscopic Studies.—The most significant information bearing on the structure of these hydrides comes from high-resolution nuclear magnetic resonance studies. The data are presented in the Table, and the high-field region for $(\pi\text{-}C_5H_5)_2TaH_3$ and $(\pi\text{-}C_5H_5)_2WH_3^+$ is shown in Fig. 1. The spectra of all of the species are similar to those of $(\pi\text{-}C_5H_5)_2ReH$ and $(\pi\text{-}C_5H_5)_2ReH_2^+$ and also to those of the ferrocenonium ion, $(\pi\text{-}C_5H_5)_2FeH^+$, and its ruthenium and osmium analogues which were reported[5] (during the course of our work) to be formed when the neutral molecules $(\pi\text{-}C_5H_5)_2M$ are dissolved in boron trifluoride

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[1] Green, Pratt, and Wilkinson, *J.*, 1958, 3916.
[2] Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, **14**b, 738.
[3] Fischer and Hristidu, *Z. Naturforsch.*, 1960, **15**b, 135.
[4] McCleverty and Wilkinson, *Chem. and Ind.*, 1961, 288.
[5] Curphey, Santer, Rosenblum, and Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5249.

hydrate. In all these cases there are two main groups of resonance lines, one at low and one at high fields relative to tetramethylsilane. The low-field line of relative intensity 10

High-resolution proton magnetic resonance spectra (at 56·45 Mc./sec.).

	Hydride line			π-C_5H_5 line	
		Splitting (cycles/sec.)			
Compound	τ	by other hydride protons	by π-C_5H_5	τ	Splitting (cycles/sec.) by hydride protons
$(\pi\text{-}C_5H_5)_2TaH_3$ [a] ...	11·63 (B) 13·02 (A_2)	9·6 [d]		5·24	
$(\pi\text{-}C_5H_5)_2MoH_2$ [a] ...	18·76	—	Not resolved Line width 1·6 cycles/sec.	5·64 (triplet)	0·96
$(\pi\text{-}C_5H_5)_2MoH_3^+$ [b] ...	16·08	—	Not resolved Line width 1·4 cycles/sec.	4·38	
$(\pi\text{-}C_5H_5)_2WH_2$ [a] ...	22·28 [e] (" septuplet ")	—	$0{\cdot}7_5$	5·76 (triplet)	$0{\cdot}7_5$
$(\pi\text{-}C_5H_5)_2WH_3^+$ [c] ...	16·08 (B) 16·44 (A_2)	8·5	Not resolved Line widths $\leqslant$2·1 cycle/sec.	4·39	Not resolved Line width 1·4 cycle/sec.

[a] In benzene. [b] In trifluoroacetic acid. [c] In concentrated hydrochloric acid, reference $Me_3C{\cdot}OH$, for which $\tau = 8{\cdot}69$. [d] Calculated by using data tabulated by Corio (*Chem. Rev.*, 1960, **60**, 363). [e] The hydride lines of the tungsten compounds show weak satellite doublets from those molecules containing the isotope ^{183}W with spin ½ (abundance 14·3%). The tungsten-proton splitting is 36·6 cycles/sec. for the dihydride and 47·8 cycles/sec. for the A_2 protons in the trihydride cation.

is due to the ten equivalent protons of the π-C_5H_5 groups. The bands from molybdenum and tungsten dihydride show fine structure due to electron-coupled spin–spin interaction with the hydrogen atoms bound to the metal; this splitting is of the same order, *ca.* 1 cycle/sec., as that in $(\pi\text{-}C_5H_5)_2ReH$ and $(\pi\text{-}C_5H_5)_2FeH^+$. The high-field lines occur in the region characteristic for hydrogen atoms bound to transition-metal atoms and the areas, relative to the low-field lines, taken as 10, confirm the stoicheiometries of the various species.

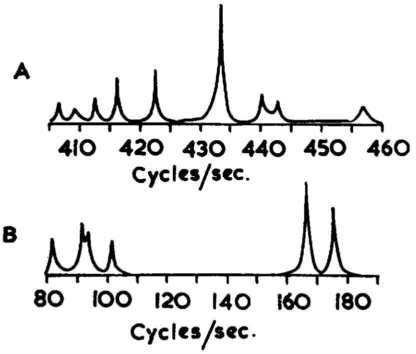

FIG. 1. High-resolution nuclear magnetic resonance spectrum in the high-field region of (A) $(\pi\text{-}C_5H_5)_2WH_3^+$ and (B) $(\pi\text{-}C_5H_5)_2TaH_3$.

For the dihydride species of rhenium, molybdenum, and tungsten there is only one high-field proton resonance line, as in $(\pi\text{-}C_5H_5)_2ReH$ and the ferrocenonium ion. For the rhenium and tungsten compounds, the fine structure on these lines is due to coupling with the π-C_5H_5 ring protons although all the expected components (eleven) cannot be resolved. It thus appears that the two hydrogen atoms in $(\pi\text{-}C_5H_5)_2MH_2$ are in equivalent environments. This is not true, however, of the three hydrogen atoms in $(\pi\text{-}C_5H_5)_2TaH_3$ and $(\pi\text{-}C_5H_5)_2WH_3^+$ since in these cases the high-field line patterns (Fig. 1) are characteristic of A_2B groupings [6] with two equivalent protons and one non-equivalent one. The cation

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[6] See Jackman, " Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959.

$(\pi\text{-}C_5H_5)_2MoH_3^+$ in water or in trifluoroacetic acid shows only a single line of relative intensity 3, which suggests that in this case there is a slow exchange with the protons of the solvent; this exchange also occurs in benzene–trifluoroacetic acid mixtures. A solution of $(\pi\text{-}C_5H_5)_2WH_2$ in D_2O—DCl mixtures shows no high field line, again indicating a slow exchange with the solvent which is complete within a few minutes. In neither the molybdenum or tungsten case is the exchange rate fast enough to make the solvent and hydridic proton lines coalesce.

The infrared spectra of the neutral hydrides have been measured down to 750 cm.$^{-1}$, and measurements below 750 cm.$^{-1}$ are given elsewhere.[7] The metal-to-hydrogen bond stretching frequencies occur in the region around 2000 cm.$^{-1}$; the band in $(\pi\text{-}C_5H_5)_2TaH_3$ is exceptionally intense, presumably owing to the greater ionic character in the metal-to-hydrogen bond. Even under the highest available resolution on a grating instrument only one symmetrical band is found for the M–H absorption in molybdenum and tungsten dihydrides, but for $(\pi\text{-}C_5H_5)_2TaH_3$ this band has weak shoulders.

Discussion.—We have discussed previously[1] the high-resolution nuclear magnetic resonance spectra of $(\pi\text{-}C_5H_5)_2ReH(D)$ and $(\pi\text{-}C_5H_5)_2ReH_2(D_2)^+$ and have shown that the structure with the hydrogen atom(s) lying between the metal atom and the $\pi\text{-}C_5H_5$ rings which had been proposed[8] for these compounds (and which has recently been suggested[5] as a possibility for the ferrocenonium ion) is unlikely. The main unsettled question in this work was whether the metal-to-ring axes are linear, as in ferrocene, or are angular. This problem has also been considered by others[7] in the light of dipole moment and far-infrared data on the rhenium, molybdenum, and tungsten species. Our present observations of the non-equivalence of the hydrogen atoms bound to the metal in the tantalum and tungsten trihydrides, and the ability of the neutral di-π-cyclopentadienyls or hydrides of Mo, W, Re, Fe, Ru, and Os to take up a proton, suggest a structural interpretation of the properties of this class of compounds.

The experimental results suggest that in the complexes $(\pi\text{-}C_5H_5)_2MH_x$ ($x = 1, 2,$ or 3) there are, in addition to the hybrid orbitals involved in metal-to-ring bonding, three bonding orbitals, two of which are equivalent. These three orbitals can be occupied by hydrogen atoms exclusively, as in $(\pi\text{-}C_5H_5)_2TaH_3$, or by hydrogen atoms and lone pairs of electrons—thus $(\pi\text{-}C_5H_5)_2ReH$ will have two lone pairs. In view of the steric effects of lone pairs in the compounds of transition and non-transition elements which have lone pairs present on the central atom,[9] it would be remarkable if the lone pairs in the present series of compounds did not have the same steric consequences and occupy bond positions. Hence we could consider the $(\pi\text{-}C_5H_5)_2MH_x$ species as 5-co-ordinate, probably with a configuration approximately trigonal bipyramidal, in which case the non-equivalence of the three hydrogen atoms in the trihydrides implies that the metal-to-ring axes are non-linear. In ferrocene, ruthenocene, and, presumably, osmocene, the metal-to-ring axes are certainly linear. While sterically active lone pairs are therefore presumably absent, there must nevertheless be primarily non-bonding (*versus* the rings) electrons on the metal atom. The addition of a proton to such a linear di-π-cyclopentadienyl compound would be expected to distort the rings as in the above cases. The greatly reduced basicity (protonation of ferrocene occurs in BF_3,H_2O,[5] but we find no high-field line in trifluoroacetic or concentrated sulphuric acid), compared with, say, $(\pi\text{-}C_5H_5)_2ReH$, is consistent with involvement of the non-bonding electrons in subsidiary metal-to-ring bonding. We have so far found no evidence in any case for the uptake of more than one proton, but it is only to be expected on electrostatic grounds that the second base constant would be very small. Even in BF_3,H_2O the ratio of the low and high field lines for the rhenium compound is 10 : 2.

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[7] Fritz, Hristidu, Hummel, and Schneider, *Z. Naturforsch.*, 1959, **15**b, 419.

[8] Liehr, *Naturwiss.*, 1957, **44**, 61.

[9] See Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339; "Progress in Stereochemistry," Butterworths, London, 1958, Vol. II; Nyholm, *op. cit.*, Vol. I, 1954.

In extending these ideas, it now seems likely that all di-π-cyclopentadienyl metal compounds of the general type $(\pi\text{-}C_5H_5)_2MX_n$ will have non-linear metal-to-ring axes. Non-linearity has indeed been confirmed for $(\pi\text{-}C_5H_5)_2TiCl_2Al(C_2H_5)_2$.[10] It also follows that some compounds such as $(\pi\text{-}C_5H_5)_2TiX_2$ should have a vacant orbital, and again there is evidence that this is so from the existence [11] of $[(\pi\text{-}C_5H_5)_2TiPh_3]^-$.

The above qualitative views of the nature of the hydride species have received mathematical support within the framework of molecular-orbital theory. Ballhausen and Dahl [12] have shown that the metal-to-π-C_5H_5-ring bonding, as made evident by orbital overlaps, is very little reduced even if the metal-to-ring axes are at angles down to 135°; even further distortion can doubtless occur with a sacrifice in metal to ring bonding energy. Further, with angular bonds, it follows immediately that there will remain on the metal atom three strongly space-directed orbitals (cf. Fig. 2): ψ_0 (an sp hybrid), ψ_{-y}, and ψ_y ($spd_{x^2-y^2},d_{z^2}$ hybrids), two of which are equivalent (ψ_{-y}, ψ_y), of precisely the character required. When ferrocene is protonated distortion to the angular form will occur with the hydrogen atom probably located in ψ_0, so that the electron pairs in the other two orbitals could take part in subsidiary metal-to-ring bonding. In $(\pi\text{-}C_5H_5)_2ReH$ the proton could be similarly located, but in $(\pi\text{-}C_5H_5)_2ReH_2^+$ the nuclear magnetic resonance spectra show equivalence of the protons, as is the case for the molybdenum and tungsten dihydrides, so that presumably ψ_{-y} and ψ_y are now occupied.

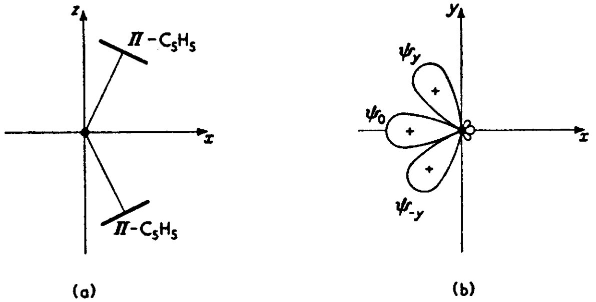

FIG. 2. Diagram showing disposition of $(\pi\text{-}C_5H_5)$ rings and non-bonding orbitals in $(\pi\text{-}C_5H_5)_2MH_n$ compounds.

The dipole-moment [7] and infrared data are consistent with non-linearity of the metal-to-ring axes, but provide little conclusive evidence either for or against them. Thus it might have been expected (cf. ref. 1) that, if the H–M–H bonds in the dihydride species are at an angle, both the symmetric and the asymmetric stretching modes would have been evident in the infrared region. This is not so. However, it is not necessarily surprising, since with the very heavy central metal atoms, together with the fact that if the H–M–H angle is about 90° as the molecular-orbital picture suggests, the coupling could be very small. A similar case occurs for the dialkyl- and aryl-tin dihydrides, where the H–Sn–H group is certainly angular, in which only one Sn–H stretching frequency can be observed.[13] It is also possible, in principle, to decide on structures with parallel or twisted rings in $(\pi\text{-}C_5H_5)_2M$ compounds by infrared studies, as discussed, for example, for dicyclopentadienyl-tin and -lead.[14,15] For the species $(\pi\text{-}C_5H_5)_2ReH$, $(\pi\text{-}C_5H_5)_2Mo(W)H_2$, and $(\pi\text{-}C_5H_5)_2Mo(W)H_3^+$ there are indeed differences in the number of bands observed [7] in the 400—600 cm.$^{-1}$ region associated with metal-to-ring stretching frequencies. However, only three or four of the predicted 7—9 bands appear. Further, the measurements were made in mulls where crystal lattice effects provide unknown and often large variables, so that such small differences among weak bands cannot be taken as providing substantial

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[10] Natta, Corradini, and Bassi, *J. Amer. Chem. Soc.*, 1955, **77**, 3604.
[11] Summers, Uloth, and Holmes, *J. Amer. Chem. Soc.*, 1955, **77**, 3604.
[12] Ballhausen and Dahl, *Acta Chem. Scand.*, in the press.
[13] Potter and Wilkinson, unpublished work.
[14] Dave, Evans, and Wilkinson, *J.*, 1959, 3684.
[15] Fritz and Fischer, *J.*, 1961, 547.

evidence for or against an angular configuration. (A similar conclusion was reached[14] for the tin and lead compounds, even from solution spectra where the spectra were independent of the nature of the solvent.) It may be noted also that the reliability of intercomparisons of the spectra of the hydride species may be suspect because there are differences in the structure of the species—neutral compounds and salts, different numbers of hydrogen atoms, and valency of the metal atom—all of which could well complicate the interpretation of solid-state spectra.

EXPERIMENTAL

Microanalyses are by the Microanalytical Laboratory of this College. Preparations and operations were carried out under oxygen-free nitrogen or in a vacuum.

Di-π-cyclopentadienyltantalum Trihydride.—Anhydrous, freshly sublimed tantalum pentachloride (36 g., 0·1 mole) was slowly added to an ice-cooled solution of sodium cyclopentadienide (0·7—0·8 mole) in tetrahydrofuran (250 ml.) containing sodium borohydride (10 g.). The mixture was stirred for 4 hr. under reflux. After removal of the solvent in a vacuum the product was sublimed from the residue (*ca.* 120°/10^{-2} mm.) and purified by resublimation at 100° as white crystals, m. p. 187—189° (decomp.) (Found: C, 37·0; H, 4·0. $C_{10}H_{13}Ta$ requires C, 38·2; H, 4·2%). The preparation does not always succeed, but the reasons for failure are not clear; on occasion we have experienced yields of the order of 60% based on tantalum metal.

Di-π-cyclopentadienylmolybdenum Dihydride.—The reaction was carried out as above, but with molybdenum pentachloride (27 g.), sodium cyclopentadienide (0·5 mole), and sodium borohydride (10 g.). The product was sublimed from the residue and crystallised from diethyl ether–light petroleum (b. p. 40—60°) at −78°. An alternative method of isolation is that used for the rhenium hydride[1] where the dry residue is treated with 3N-hydrochloric acid. After filtering, the solution is neutralised with 2N-sodium hydroxide, and the liberated hydride extracted with ether. The product was purified by vacuum-sublimation at 50°, to give yellow crystals (*ca.* 50% based on molybdenum), m. p. 183—185° (Found: C, 51·0; H, 5·3. $C_{10}H_{12}Mo$ requires C, 52·7; H, 5·3%).

Di-π-cyclopentadienyltungsten Dihydride.—A similar procedure but with tungsten hexachloride (40 g.), sodium cyclopentadienide (0·6 mole), and sodium borohydride (10 g.) led to yellow crystals (*ca.* 65% based on tungsten), subliming in a vacuum at 80° and having m. p. 163—165° (Found: C, 38·2; H, 3·9. $C_{10}H_{12}W$ requires C, 38·0; H, 3·8%). The tungsten compound is moderately stable in air and after about 15 min. in air about half of the material can be recovered.

Di-π-cyclopentadienylmolybdenum and Tungsten Trihydride Salts.—The dihydrides were treated with gaseous hydrogen bromide at room temperature as for the rhenium compound.[1] The yellow crystals rapidly disintegrated, leaving white, very hygroscopic solids. In presence of excess of hydrogen bromide, the solids are pink [cf. $(\pi\text{-}C_5H_5)_2ReH_2Br$].

Aqueous solutions of the cations are obtained by dissolving the bromides in water or by dissolving the dihydrides in aqueous acid. The aqueous solutions are similar to those of $(\pi\text{-}C_5H_5)_2ReH_2^+$ [1] and give precipitates with large anions. On addition of base, the dihydrides are liberated quantitatively. The dihydrides readily dissolve in pure trifluoroacetic acid to solutions containing the trihydride ions; the molybdenum solution is green and the tungsten olive green.

The dideuterides and trideuteride ions can be obtained by the previous procedure,[1] by dissolution of the dihydrides in 2N-deuterium chloride, followed by neutralisation with sodium deuteroxide in deuterium oxide.

Infrared Spectra.—Measurements were made with a Perkin-Elmer model 21 spectrophotometer with sodium chloride optics and a Grubb-Parsons grating spectrophotometer in the region of the M–H stretching frequencies. The molybdenum and tungsten dihydrides were measured in CS_2 solutions and in Nujol mulls; mull spectra only were obtained for the tantalum trihydride.

$(\pi\text{-}C_5H_5)_2MoH_2$: 3060 (w), 1847 ± 2 (Mo–H str., ms), 1415m, 1369m, 1267m, 1121ms, 1064ms, 1055ms, 869w, 813m, 763s.

$(\pi\text{-}C_5H_5)_2WH_2$: 3050 (w), 1896 ± 2 (W–H str., ms), 1410m, 1257m, 1088m, 998m, 885w, 799m, 769m.

$(\pi\text{-}C_5H_5)_2TaH_3$: 3090 (w), 1735 ± 2 (Ta–H str., vs), 1425m, 1358w, 1265w, 1117w, 1072w, 1020s, 1005s, 905m, 870s, 858m, 848m, 825s, 795s, 720w.

High-resolution Nuclear Magnetic Resonance Spectra.—Measurements were made on a Varian Associates model 4300B spectrometer at 56·4 Mc./sec. and 22° ± 2°. The neutral hydrides were studied in strong solutions in benzene while the trihydride cationic species were measured in water and also in trifluoroacetic acid, tetramethylsilane then being added as an internal reference. Line positions were determined by conventional side-band techniques.

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