STUDIES ON THE DICYCLOPENTADIENYL HYDRIDES OF RHENIUM AND TUNGSTEN

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The hydrides $(\pi\text{-}C_5H_5)_2ReH$, (I)[1], and $(\pi\text{-}C_5H_5)_2WH_2$, (II)[2], exhibit properties atypical of the M–H system in that they are basic and do not add M–H to diazomethane or tetrafluoroethylene as do many other hydrides[3]. Since $[(\pi\text{-}C_5H_5)_2Re]^-$ is isoelectronic with $(\pi\text{-}C_5H_5)_2Os$, and in view of the basic properties of the hydride (I), the formation of the first anionic dicyclopentadienyl complex might have been expected by abstraction of a proton from complex (I) using *n*-butyllithium. We have found, however, that the reaction leads to metallation of the cyclopentadienyl rings whilst the metal-hydrogen system is unaffected.

RESULTS

Treatment of an ethereal solution of the complex (I) with *n*-butyllithium initially leads to a darkening of the yellow colour but the solution finally lightens to a pale yellow. This ethereal solution is much more readily oxidised than that of the pure hydride (I), and removal of the ether leaves an involatile white solid (III), (no sublimate after 4 h at 150°/10^{-3} mm Hg) which is very readily hydrolysed and which turns purple immediately on contact with air. Similarly, treatment of an ethereal solution of the complex (II) with *n*-butyllithium gives a precipitate of golden crystals IV) which are insoluble in or decomposed by all common organic solvents. When dry the crystals are spontaneously inflamable in air; purification of both lithiated products was not achieved but analysis of the washed precipitate obtained from the dihydride II) gave a Li/W ratio of ~ 2:1.

Because of the difficulty in handling these lithiated derivatives they were characterized by a spectroscopic study of the products of their hydrolysis and deuterolysis.

Hydrolysis and deuterolysis of the lithiated species

Treatment of the involatile white lithiated salt (III) with water, followed by ublimation of the dried products, recovers $(\pi\text{-}C_5H_5)_2ReH$, (I), in very high yield. Similarly hydrolysis of the lithiated salt (IV) affords the parent hydride (II). The deuterated isomers, (V) and (VI), prepared by treatment of the lithiated species (III) and (IV) with deuterium oxide, have also been studied. The infra-red spectra of the complexes

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TABLE 1

INFRA-RED SPECTRA

$(C_5H_5)_2ReH$[a]	$(C_5H_5)_2WH_2$[b]	$(C_5H_4HgCl)_2$-ReH[b]	$[(C_5H_4HgCl)_2ReH_2]^+$-Cl^-[b]	$(C_5H_5)(CH_3C_5H_5)$-$Re(CH_3)_2$[a]
3100 w[c]	3060 w[c]	3100 w[c]	3070 w[c]	3100 m[c]
				3040 s[f]
				2930 s[g]
				2900 s[g]
				2817 m[g]
	(2310 w)[d]			2000 vw
2025 w[e]	1918 ms[e]			
			1560 vw	
		1415 m	1420 m	1452 s
1400 m	1410 w	1400 m	1403 m	1420 s
1345 w	1360 w		1365 vw	1380 m
		1255 vw		1357 s
				1327 s
1262 m	1252 w			1242 m, sh
				1226 s
1183 vw				1202 m
1099 s	1085 w	1100 vw[h]	1105 vw[h]	1108 s
				1090 m
1063 w, b				1065 m
1023 w, sh				1044 m
1005 s	1000 sh	1000 vw[h]	1008 vw[h]	1006 vs
992 s	980 m	940 vw	985 vw	898 s, sh
845 m	895 sh	920 w	948 vw	840 vs
837 m	870 w	850 m	920 vw	795 vs
807 s	813 m	826 w	875 vw	735 w
790 s	772 m		850 m	
			825 w	

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[a] Measured in carbon disulphide solution. [b] Measured in nujol and hexachlorobutadiene mulls. [c] C–H stretch of π-C_5H_5. [d] This band is present only in the spectrum of the deuterated complex (VI) and is assigned to a C–D stretch. [e] M–H stretch. [f] Olefinic C–H stretch. [g] C–H stretch of methyl group, measured in CCl_4 solution. [h] Extremely weak bands.

(I) and (II) are given in Table 1; the proton magnetic resonance data for benzene solutions of the complexes (I), (II), (V) and (VI) is given in Table 2. Comparing the proton magnetic resonance spectrum of the rhenium complex (I) with that of its deuterated isomer (V) shows that the high-field resonance due to the M–H system (23.3 τ) in the complex (I) is essentially unchanged in the spectrum of the complex (V) but that the doublet assigned to the cyclopentadienyl protons in the spectrum of the complex (I) has changed to a broad singlet in the spectrum of the complex (V). The infra-red spectrum of the complex (V) confirms the presence of the Re–H system ($\nu = 2025$ cm^{-1}) but no band at ~ 2300 cm^{-1} expected for the C–D stretching mode of a deuterated cyclopentadienyl ring is observed. Comparison of the proton magnetic resonance spectrum of the tungsten complex (II) with that of its deuterated isomer (VI) shows that the W–H system is unchanged and that the triplet due to the cyclopentadienyl ring protons in the complex (II) has changed to a broad singlet in the spectrum of the complex (VI). The infra-red spectrum of the complex (VI) confirms the presence of the W–H system ($\nu = 1915$ cm^{-1}) and a band at 2310 cm^{-1}, absent from the spectrum of the complex (II), is assigned to the C–D stretching mode.

E 2

AR MAGNETIC RESONANCE DATA

und	Band pos. (τ)	Rel. intensity	Multiplicity	Separation (cps)	Assignment
$)_2$ReH	6.10	10	Doublet	1.0	π-C_5H_5
H_6	23.3	1	—	—	Re–H
rated					
D$)_2$ReH	5.95	9	Not detected	—	π-C_5H_4D
H_6 and CS_2	23.3	1	—	—	Re–H
$)_2WH_2$	5.70	~ 5	Triplet	0.7	π-C_5H_5
H_6	22.4	1	—	—	W–H
rated					
D$)_2WH_2$	5.72	~ 5	Not detected	—	π-C_5H_4D
	22.4	1	—	—	W–H
$)(CH_3C_5H_5)$-	5.75	5	1	—	π-C_5H_5
$CH_3)_2$	Centre 6.15	2	Complex band (6 components)	—	H_2 and H_5 or H_3 and H_4
	Centre 7.31	3	Complex band (9 components)	—	H_1, H_2 and H_5 or H_1, H_3 and H_4
	9.50	3	2	5.8	CH_3 group of $C_5H_5CH_3$
	9.66	6	1	—	CH_3 groups bonded to Re

er reactions of the lithiated species

i) With mercuric chloride. Treatment of an ethereal solution of the complex (III) mercuric chloride in tetrahydrofuran affords a yellow precipitate which is in- le in all the common organic solvents; it may, however, be purified by reprecipi- n from dimethyl sulphoxide. Analysis indicates the empirical stoichiometry $_9$ReHg$_2$Cl$_2$ (VII). The proton magnetic resonance spectrum obtained from a e but saturated solution of the complex (VII) in dimethyl sulphoxide shows a netrical doublet at 4.50 τ (separation = 3.2 cps) but no resonance peak was ob- d to the high-field side of tetramethylsilane. The infrared spectrum of the com- (VII) (Table 1) shows bands typical of π-C_5H_5 species but bands at 1100 and cm^{-1} are unusually weak.

The complex (VII) dissolves slightly in hot concentrated hydrochloric acid and ng precipitates yellow crystals for which analyses indicate the formulation $_{10}$ReHg$_2$Cl$_3$ (VIII). Both the mercury derivatives (VII) and (VIII) are stable r for several weeks and are very insoluble. Very dilute, saturated solutions of the plex (VIII) in concentrated hydrochloric acid showed no proton resonance of the plex; it was also difficult to obtain satisfactory mulls for infra-red studies on the plexes (VII) and (VIII).

Treatment of the lithiated complex (III) with mercuric cyanide in tetrahydro- n gives a disubstituted derivative which was not fully characterized due to ulty in purification. Treatment of this "cyano-mercury" derivative with dilute ncentrated hydrochloric acid yields the complexes (VII) and (VIII) respectively.

ii) With methyl iodide. Treatment of an ethereal solution of the lithiated com- (III) with a large excess of methyl iodide affords yellow crystals for which yses and molecular weight data indicate the formulation $C_{13}H_{19}Re$ (IX). The plex (IX) is stable in the absence of air but decomposes on sublimation at 60° *acuo*; it is readily soluble in all the common organic solvents but decomposes fairly rapidly in carbon tetrachloride. The infra-red and proton magnetic resonance spectra are given in Tables 1 and 2.

The lithiated tungsten complex (IV) did not give a similar complex when treated with excess methyl iodide, but only a small yield of green crystals of the *diiodide* $(\pi\text{-}C_5H_5)_2WI_2$[4].

DISCUSSION

The ready hydrolysis of the lithiated derivatives (III) and (IV) and the high recovery yields thereby of the parent hydrides (I) and (II) show that the cyclopentadienyl-metal system is not destroyed by *n*-butyllithium.

The proton magnetic resonance and infra-red spectra of the hydrides (I) and (II) and of the hydrolysis and deuterolysis products of the complexes (III) and (IV) show that the M–H systems are unaffected by the metallation reaction, but in the proton magnetic resonance spectra of the deuterolysis products there is a broadening of the band at ~ 6 τ assigned to the protons of the cyclopentadienyl ring. In addition the fine structure present in this band in the spectra of the pure hydrides (I) and (II) which arises from coupling with the M-hydrogens is absent from the spectra of the deuterated products. The broadening of the band and the absence of fine structure may be explained by the presence of deuterium in the π-cyclopentadienyl ring. The

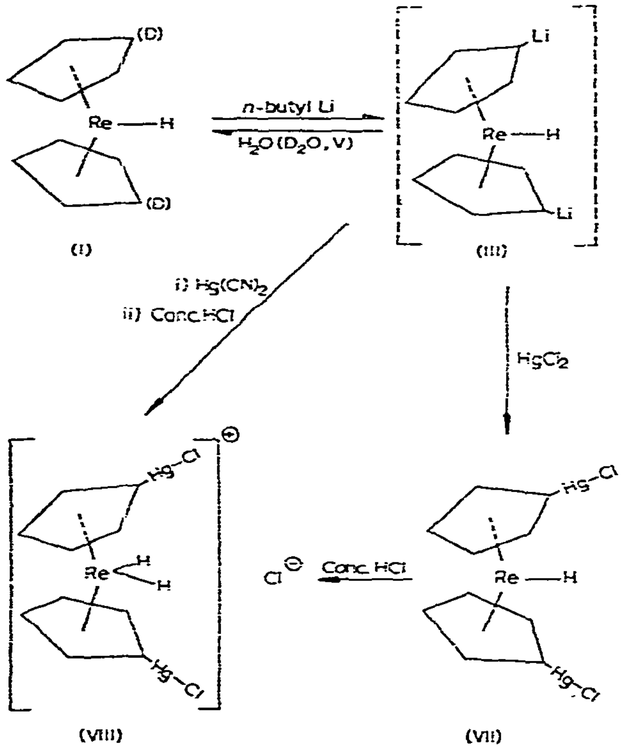


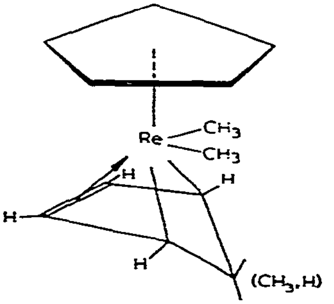
Fig. 1.

infra-red spectrum of the deuterated tungsten complex (VI) shows a C–D stretch at 2310 cm^{-1} in support of this suggestion and the absence of the corresponding C–D stretch in the spectrum of the deuterated rhenium complex (V) may be due to the low intensity of the band. Thus the Li/W ratio of 2:1 found for the complex (IV) and the stoichiometry of the mercury derivatives (VII) and (VIII) indicate that the pure hydrides (I) and (II) undergo dilithiation when treated with *n*-butyllithium. It remains to decide whether the substitution of the two lithium atoms is homo- or hetero-annular. The marked reduction in the relative intensity of bands at ~ 1000 and 1100 cm^{-1} in the spectra of complexes (VII) and (VIII) is consistent with substitution of both π-C_5H_5 rings[5]; also it has been shown that for other dicyclopentadienyl complexes electrophilic monosubstitution enhances hetero-annular disubstitution and for ferrocene affords 1,1'-disubstituted products[6]. It seems reasonable, therefore, that lithiation of the complexes (I) and (II) gives 1,1'-dilithiated derivatives (see also Fig. 1).

Although the Re–H proton resonance is not observed in the spectrum of the complex (VII) due to low solubility, the splitting of the band assigned to π-C_5H_4HgCl at 4.50 τ indicates coupling with an Re–H hydrogen; the separation between the components of 3.2 cps is of the same order of magnitude as that observed for the pure hydride (I)[1]. By analogy with the chemistry of the pure hydride (I)[1], the complex (VIII) is formulated as the dihydride cation (see Fig. 1). Again low solubility prevented determination of the proton magnetic resonance spectrum; no Re–H band could be observed.

Structure of the complex (IX)

The stoichiometry of the complex (IX) is shown to be $C_{13}H_{19}Re$. The infra-red spectrum and the *singlet* band at 5.75 τ in the proton magnetic resonance spectrum confirm the presence of a π-cyclopentadienyl ring and the absence of coupling with an Re–H hydrogen; in support of this, no bands assignable to Re–H hydrogen were observed in the region 10–40 τ. The hydrogen resonance band at relatively high fields (9.66 τ) of intensity 6 is assigned to two methyl groups attached to the rhenium. The remainder of the proton magnetic resonance spectrum shows a marked resemblance to that of the methylcyclopentadiene system found in π-$C_5H_5CoC_5H_5CH_3$[7] and is assigned to the same system. The infra-red spectrum of the complex (IX) is consistent with



(IX)

Fig. 2.

the above assignment, and we formulate the complex (IX) as π-cyclopentadieny dimethylrhenium methylcyclopentadiene (see Fig. 2). It may be noted that th infra-red spectrum of the complex (IX) shows no band assignable to C–H_α However, the factors which cause the anomalous C–H_α band and whether H_α is i the *endo*- or *exo*-position are not yet clear[7,8], and we are unable, therefore, to decid between an *endo*- or *exo*-position for the methyl group of the methylcyclopentadien ligand.*

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory, Lensfield Road Cambridge. All preparations, reactions and purifications were performed under nitrogen or in a vacuum unless otherwise stated; solvents and reagent solutions wer degassed before use. Filtered solutions of *n*-butyllithium were standardized using Gilman's benzyl chloride method immediately before use.

Reaction of di-π-cyclopentadienylrhenium hydride with n-butyllithium

A rapidly stirred solution of di-π-cyclopentadienylrhenium hydride (1.27 g, 4.0 × 10^{-3} moles) in ether (100 ml) was treated with *n*-butyllithium (10^{-2} moles). During the addition of *n*-butyllithium the colour of the solution changed from pale yellow to dark orange (0.5 mole-equivalents of *n*-butyllithium) and later lightened to pale yellow (2 mole-equivalents of *n*-butyllithium). The ether was evaporated from thi solution to give a white involatile solid which was extremely unstable in air. Thi white solid was divided into two portions: the first portion was treated with wate (5 ml) and the product extracted into ether; separation of the ether layer, followed by evaporation of the ether and sublimation (120°, 10^{-3} mm Hg) of the yellow solid produced, afforded di-π-cyclopentadienylrhenium hydride which was identified by its proton magnetic resonance and infra-red spectra. The second portion of white solid was treated with deuterium oxide (5 ml) and the products isolated as above affording the complex (V), whose identification is described in the text.

Reaction of di-π-cyclopentadienyltungsten dihydride with n-butyllithium

A rapidly stirred solution of di-π-cyclopentadienyltungsten dihydride (1.0 g, 3. × 10^{-3} mole) in ether (200 ml) was treated with excess (3 mole-equivalents) of *n*-butyllithium. The pale yellow solution deepened in colour during the addition and afte half the *n*-butyllithium had been added fine yellow crystals began to separate. The solution was stirred for a further 1 h and then filtered. The buff-yellow crystalline precipitate was washed thoroughly with ether and light petroleum. [Found: C, 30.9 H, 2.9, Li/W ratio (average of three analyses), 1.85:1. $C_{10}H_{10}Li_2W$ calcd.: C, 36.6 H, 3.05%, Li/W ratio, 2:1.] Hydrolyses were performed on this compound as described above.

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* *Note added in proof*. By three-dimensional X-ray analysis Dr. N. W. ALCOCK of Cambridge has confirmed the structure proposed for the complex (IX), and has shown that the ring-substituted methyl group is in the *exo*-position. The infra-red spectrum of the complex (IX) shows no anomalous C–H_α stretch, in contrast with the spectrum of the *exo*-methylcyclopentadiene complex π-$C_5H_5CoC_5H_5CH_3$[7]. This difference may be due to a greater bending away of the >CHCH system from the metal atom, as shown for the complex π-$C_5H_5CoC_5H_5$-*exo*-C_6H_5[8].

Reaction of the lithiated rhenium complex

i) With mercuric chloride. A fresh solution of the lithiated rhenium compound (III), prepared as described above from 0.62 g of the rhenium hydride, was treated with a solution of mercuric chloride (1.10 g) in tetrahydrofuran (25 ml). Immediately a yellow precipitate was formed; this was filtered, washed thoroughly with tetrahydrofuran and finally dried *in vacuo*. This crude product was purified by reprecipitation with ether from a saturated solution in dimethyl sulphoxide affording a pale yellow powder. (Found: C, 15.9; H, 0.93. $C_{10}H_9Cl_2Hg_2Re$ calcd.: C, 15.3; H, 1.16%.)

The crude dichloride (0.25 g) was dissolved in hot concentrated hydrochloric acid (30 ml) and the solution filtered. On cooling fine yellow crystals separated which were filtered, washed with water, alcohol and ether and finally dried *in vacuo*. Yield 0.05 g. (Found: C, 14.5; H, 1.08. $C_{10}H_{10}Cl_3Hg_2Re$ calcd.: C, 14.6; H, 1.23%.)

Treatment of the lithiated rhenium complex with mercuric cyanide afforded a yellow powder which could not be purified. Analysis of the thoroughly washed product showed a Re/Hg ratio of 1:2.2. Treatment of this "cyano–mercury" complex with hot concentrated hydrochloric acid afforded on cooling a yellow crystalline solid. (Found: C, 15.1; H, 1.42; Cl, 12.9; Re, 21.1. $C_{10}H_{10}Cl_3Hg_2Re$ calcd.: C, 14.6; H, 1.23; Cl, 12.9; Re, 22.6%.)

ii) With methyl iodide. Di-π-cyclopentadienylrhenium hydride (0.65 g) in ether was treated with a large excess of *n*-butyllithium (34.8×10^{-3} moles). Methyl iodide (15 ml) was added to the solution which was then stirred for 20 min. The solvent was removed *in vacuo* and the residue extracted with light petroleum (100 ml) and water (50 ml). The yellow petrol layer was separated and filtered and the solvent removed *in vacuo*.

The orange residue was dissolved in petrol (5 ml) and chromatographed on an alumina column made up in light petroleum. Elution with a 10% ether/light petroleum mixture gave a yellow band which was collected and evaporated. The yellow residue was finally recrystallised thrice from light petroleum at —50°, giving large yellow needles, m.p. 73–74°. (Found: C, 43.4; H, 5.17; Re, 51.0; mol. wt. cryoscopic in dioxane, 362. $C_{13}H_{19}Re$ calcd.: C, 43.2; H, 5.31; Re, 51.5%; mol. wt. 362.) The pure compound decomposed in air: the surface of the crystals turned purple-black after 4 h.

High-resolution nuclear magnetic resonance spectra

Measurements were made on a Perkin-Elmer spectrometer at 40 Mc/sec. The data and conditions of measurement are given in Table 2.

Infra-red spectra

Measurements were made with a Perkin-Elmer model 21 spectrometer. The data and conditions of measurement are given in Table 1.

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SUMMARY

The hydrides $(C_5H_5)_2ReH$ and $(C_5H_5)_2WH_2$ have been treated with *n*-butyllithium affording dilithiated species. Nuclear magnetic resonance and infra-red studies on the products of hydrolysis, deuterolysis and mercuration of these dilithiated species indicate their formulation as 1,1'-dilithiodicyclopentadienyl complexes. The complexes $(C_5H_4HgCl)_2ReH$ and $[(C_5H_4HgCl)_2ReH_2]^+Cl^-$ are described.

The reaction between the lithiated rhenium complex and methyl iodide affords a complex which, on the basis of analyses, nuclear magnetic resonance and infra-red data, is formulated as π-cyclopentadienyldimethylrhenium methylcyclopentadiene.

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