209. *Spectroscopic Studies on Alkyl and Hydrido Transition Metal Carbonyls and π-Cyclopentadienyl Carbonyls.*

By A. Davison, J. A. McCleverty, and G. Wilkinson.

High-resolution nuclear magnetic resonance spectra of hydrido, methyl, and ethyl derivatives of transition metal carbonyl and π-cyclopentadienyl carbonyl complexes have been measured, and the data compared with those for non-transition-metal compounds. Infrared spectra of some hydrides and corresponding deuterides are given. An improved preparation of decacarbonyldirhenium is given and the new complexes π-$C_5H_5Ru(CO)_2X$ ($X = H, D, I, CH_3$, and C_2H_5) are described.

High-resolution proton magnetic resonance studies of CH_3X and C_2H_5X compounds of the main-group elements have shown certain regularities and there have been attempts to correlate chemical shifts with the electronegativity of the X residue.[1] The spectra of some transition-metal complex alkyls which have π-bonding ligands, *e.g.*, π-$C_5H_5W(CO)_3C_2H_5$, were noted in an earlier study[2] and it seemed desirable to confirm and extend these results in the hope that it might be possible to determine the electronegativities of the transition metal in these low-valent complexes. In addition we also report some high-resolution proton magnetic resonance and infrared spectra of the allied hydride complexes.

Cavanaugh and Dailey, following Shoolery,[1] in a study of the proton resonance spectra of a series of CH_3X and C_2H_5X compounds, have demonstrated that there is a linear relation between the internal chemical shift, δ, of an ethyl group ($\delta = \tau_{CH_3} - \tau_{CH_2}$) and the electronegativity, ε, of the group X:

$$\varepsilon = 0{\cdot}684\delta + 1{\cdot}78. \qquad (1)$$

Using the values of ε calculated from eqn. (1) they derived an empirical relation between the "methyl shift," *m*, which is the separation, from methane, in cycles/sec. of the resonance of the methyl group at 60 Mc./sec.:

$$m = 100\varepsilon - 151. \qquad (2)$$

They found that both *m* and ε varied linearly with electronegativity but that the positions of neither the α- nor the β-proton resonance did. The lack of correlation of the α- and β-proton resonance with electronegativity was accounted for by the presence of a contribution from a "C–C bond shift." The magnitude of this shift would depend upon X and would affect both the α- and the β-protons equally. The difference between the α-shifts in methyl and ethyl compounds was taken as a measure of this "C–C bond shift"; the subtraction of this value from the β-resonance left a residual β-shift of 41 cycles/sec.

It appears that equations (1) and (2) hold only for those groups in which no large "neighbour anisotropy" effect is expected,[3-6] and it is expected that the use of equations (1) and (2) would give calculated methyl shifts higher than those which are observed in the CH_3X compounds when X is a highly diamagnetically anisotropic group.[7]

The apparent validity of equation (1) in compounds in which X should have a large "neighbour anisotropy" effect, *e.g.*, C_2H_5I, may arise because the contributions to the shielding at the α- and β-protons will be in the same direction and of comparable magnitude[7] so that the difference between their respective shifts, δ, is cancelled. The net effect is a move down-field of both the α- and the β-protons.

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[1] Cavanaugh and Dailey, *J. Chem. Phys.*, 1961, **34**, 1099; Shoolery, *ibid.*, 1953, **21**, 1899.
[2] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.
[3] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.
[4] Narasimhan and Rogers, *J. Amer. Chem. Soc.*, 1960, **82**, 5983.
[5] Narasimhan and Rogers, *J. Chem. Phys.*, 1961, **34**, 1049.
[6] Slomp, *J. Amer. Chem. Soc.*, 1962, **84**, 673.
[7] Spiesecke and Schneider, *J. Chem. Phys.*, 1961, **35**, 1.

The chemical shifts of protons bonded directly to transition metals in groups such as $Mn(CO)_5$- and π-$C_5H_5Fe(CO)_2$-, etc. (Table 1), when compared with the shifts of hydrogen atoms bonded to main-group elements of low electronegativity (*e.g.*, Sn; SnH_4, τ = 6·11),[8] show that they are highly diamagnetically shielded by the transition metal. If the shielding of the transition-metal hydrides can be regarded as the result of a large " neighbour anisotropy " effect of the transition metal atom, a large contribution from this might be expected to be present in the alkyl derivatives. The proton resonance spectra of these compounds (Tables 1 and 2) show clearly that: (*a*) there is no correlation between ε calculated from equation (1) and the position of the methyl resonances; (*b*) the subtraction of the difference between the shifts of the α-protons in CH_3X and C_2H_5X compounds from the β-shift of the ethyl protons does not leave a residual β-shift of 41 cycles/sec.; and (*c*) the methyl-shifts calculated by using equation (2) [except for $Re(CO)_5CH_3$] are 0·25—0·85

TABLE 1.

Proton resonance spectra of the transition-metal hydrides, alkyls and propionyls at 56·46 Mc./sec.

($SiMe_4$ used as internal reference in all cases.)

Compound	Solvent	C_5H_5	M–H	CH_2	CH_3	δ (c./sec.)	J (c./sec.)	J/δ
$Mn(CO)_5H$			17·50 *					
$Mn(CO)_5CH_3$	CCl_4				10·11			
$Mn(CO)_5C_2H_5$	C_6H_6			8·96	8·55	−22·9	8·02	−0·35
$Mn(CO)_5CO{\cdot}C_2H_5$	CH_2Cl_2			7·04	9·08	+82·5	7·22	+0·09
$Re(CO)_5H$	C_4H_8O		15·66					
$Re(CO)_5CH_3$	CCl_4				10·23			
$Re(CO)_5C_2H_5$	C_6H_6			9·00	8·23	−43·35	7·81	−0·18
$Re(CO)_5COC_2H_5$	C_6H_6			7·53	9·12	+86·40	7·26	+0·08
π-$C_5H_5Fe(CO)_2H$	C_6H_{12}	5·26	21·91					
π-$C_5H_5Fe(CO)_2CH_3$ †	CCl_4	5·30			9·89			
π-$C_5H_5Fe(CO)_2C_2H_5$ † ‡	C_6H_6	5·40		8·45	8·75	+16·96	7·63	+0·45
π-$C_5H_5Ru(CO)_2H$	C_6H_{12}	4·84	20·92					
π-$C_5H_5Ru(CO)_2CH_3$	CCl_4	4·76			9·71			
π-$C_5H_5Ru(CO)_2C_2H_5$	C_6H_6	5·31		8·67	9·03	+21·35	7·69	+0·36
π-$C_5H_5Cr(CO)_3H$ †	C_6H_{12}	5·22	15·46					
π-$C_5H_5Cr(CO)_3CH_3$ †	CCl_4	5·24			9·32			
π-$C_5H_5Mo(CO)_3H$ †	C_6H_{12}	4·70	15·52					
π-$C_5H_5Mo(CO)_3CH_3$ †	CCl_4	4·73			9·66			
π-$C_5H_5Mo(CO)_3C_2H_5$ † ‡	CCl_4	4·74		8·31	8·56	+14·20	7·61	+0·54
π-$C_5H_5W(CO)_3H$ †	C_6H_{12}	4·65	17·33					
π-$C_5H_5W(CO)_3CH_3$ †	CCl_4	4·62			9·60			
π-$C_5H_5W(CO)_3C_2H_5$ † ‡	CCl_4	4·65		8·39	8·54	+8·62	7·54	+0·88
π-$C_5H_5W(CO)_3C_2H_5$ † ‡	CH_2Cl_2	4·63		8·34	8·52	+9·55	7·54	+0·79

* Cotton, Down, and Wilkinson, *J.*, 1959, 833. † Earlier measurements at 40 Mc./sec.,[2] not made with $SiMe_4$ as internal reference. ‡ No analysis of C_2H_5 spectrum reported.

TABLE 2.

Observed and calculated chemical shifts of the transition-metal ethyl and methyl complexes.

(The data are referred in cycles/sec. to the line position of CH_4 at 60 Mc./sec.; positive values indicate protons less shielded than those in CH_4.)

Compound R–X (R = C_2H_5)	CH_3–X	α-CH_3 in ethyl	β-CH_3 in ethyl	ε *	CH_3–X −α-CH_2 in ethyl	Residual β-shift in ethyl	Calc. methyl shift †	Methyl shift difference, obs. − calc.
$Mn(CO)_5R$	−16·6	+52·4	+77·0	1·500	69·0	+8·0	−1·0	+15·6
$Re(CO)_5R$	−23·8	+50·0	+96·2	1·254	73·8	+23·6	−25·6	−1·8
π-$C_5H_5Fe(CO)_2R$	−3·4	+83·0	+65·0	1·985	86·4	−21·4	+47·6	+50·9
π-$C_5H_5Ru(CO)_2R$	+7·5	+69·4	+48·2	2·020	62·3	−14·1	+51·6	+44·0
π-$C_5H_5Mo(CO)_3R$	+10·4	+91·4	+76·4	1·951	81·0	−4·6	+44·1	+33·7
π-$C_5H_5W(CO)_3R$	+14·0	+86·6	+77·6	1·881	72·6	+5·0	+37·1	+23·1

* Calc. from δ values in Table 1 by using equation (1). † Calc. from ε values by using equation (2).

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[8] Potter and Wilkinson, unpublished work.

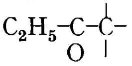
p.p.m. lower than the observed values. Hence the proton resonance spectra of CH_3X and C_2H_5X compounds of the transition elements show that, as with non-transition-metal alkyls, the screening of the alkyl protons cannot be described adequately on the basis of a sum of the contributions of the inductive and the paramagnetic effects. Some evidence that the lack of correlation depends on the close proximity of X to the alkyl group is shown by the introduction of a carbonyl group between the transition metal and the ethyl group since the spectra of the resulting propionyl derivatives are all very similar to those of a normal  $C_2H_5{-}\underset{O}{C}{-}\overset{|}{\underset{|}{C}}{-}$ group. Further, calculations of electronegativities utilising δ in C_2H_5X compounds or the position of methyl shifts in CH_3X compounds are not valid and at best may provide, in a very closely related series of compounds, only a qualitative indication of relative electronegativities (see Table 3). It should also be noted that X is not just a transition-metal atom but a transition metal carrying groups such as π-C_5H_5 and CO which can also produce long-range screening contributions at the alkyl-proton positions.

TABLE 3.

Electronegativity data calculated for the Group IV alkyls.

Element	ε *	For the ethyls (p.p.m.)	τ_{CH_3} *	ε †	Observed ‡ shift of CH_3X *vs.* CH_4	Calc. shift of CH_3X *vs.* CH_4 §	Diff.
C	2·6	+0·438 **	9·11	2·08	+43·44	+57	+14
Si	1·9	−0·420 ††	10·00	1·49	−9·96	−3	+7
Ge	2·0	−0·307 ††	9·88	1·57	−2·76	+6	+8
Sn	1·93	−0·390	9·96	1·51	−7·56	0	+8
Pb	2·45	0	9·27	1·78	+33·44	+27	−7

* Data from Allred and Rochow.[3] † Calc. by using equation (1). ‡ In cycles/sec. from CH_4 at 60 Mc./sec.; positive values indicate protons less shielded than CH_4 (τ 9·83). § Calc. by using equation (2). ** Data from Slomp.[6] †† Data from Narasimhan and Rogers.[5]

Recent studies of the proton magnetic resonance spectra of ethyl groups bonded to nuclei of spin ½ have shown, by analysis of the A_3B_2X spectra using the effective internal chemical shifts, δ′ and δ″, as two sets of A_3B_2 spectra[5] or by spin decoupling,[9] that the spin-coupling constants of the X nuclei with methyl (J_{AX}) and methylene groups (J_{BX}) are of opposite sign. The spectrum of π-$C_5H_5W(CO)_3CH_3$ showed that $J_{^{183}W-H}$ for the methyl group is 4·1 cycles/sec. Thus it is likely that in the corresponding ethyl, the values of coupling constants would be $J_{BX} < J_{AX} < 5$ cycles/sec. The main multiplet of the ethyl spectrum was analysed as an A_3B_2 system. The analysis of the relatively weak A_3B_2X spectrum ($X = {}^{183}W$, abundance 14·28%) would be difficult because the effective internal chemical shifts, δ′ and δ″, would not differ greatly from δ of the main multiplet. At high radio-frequency power, a satellite line was observed at 1·6 cycles/sec. on the high-field side of the principal A_6 line which did not correspond to any of the main multiplet lines. This line can be considered as part of the doublet produced by the ^{183}W splitting of the principal line of the methyl group, A_6 (the most intense line in observed and calculated

TABLE 4.

^{183}W–proton coupling constants.

Compound	*J* (cycles/sec.)	Compound	*J* (cycles/sec.)
(π-$C_5H_5)_2WH_2$ *	73·2	π-$C_5H_5W(CO)_3C_2H_5$	*ca.* 4·5 with CH_3 protons of $-C_2H_5$ group
(π-$C_5H_5)_2WH_3^+$ *	47·8 for A_2 protons of A_2B group	[{π-$C_5H_5W(CO)_3\}_2H]^+$ †	38·6
π-$C_5H_5W(CO)_3H$	37·7	[{(π-$C_5H_5)_2MoW(CO)_6\}H]^+$ †	38·0
π-$C_5H_5W(CO)_3CH_3$	4·1 with CH_3 protons		

* Data from Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854. † Data from Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.

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[9] Evans and Maher, *Proc. Chem. Soc.*, 1961, 208.

A_3B_2 spectra).[4,10] The corresponding line on the low-field side of A_6 was partially obscured by the stronger lines of the main multiplet. Thus the ^{183}W coupling to the protons in the β-CH_3 group is *ca.* 4·2 cycles/sec. The magnitudes of other ^{183}W–proton spin–spin coupling constants (Table 4) are considerably lower than proton spin coupling constants found in compounds of other heavy elements of spin ½ such as ^{117}Sn, ^{119}Sn, ^{207}Pb, etc. (*e.g.*, $^{117}/^{119}$Sn bonded directly to H, J_{Sn-H} = *ca.* 2000 cycles/sec.; [8] ^{183}W bonded directly to H, $J_{^{183}W-H}$ = *ca.* 30—80 cycles/sec.).

EXPERIMENTAL

Microanalyses were done by the Microanalytical Laboratory of this College.

Preparations.—All preparations were carried out under oxygen-free nitrogen or in a vacuum and all solvents were carefully degassed before use. Known methods were used with minor modifications noted below.

Carbonyl-π-cyclopentadienyl-metal Hydrides and Deuterides.—The chromium, molybdenum, and tungsten compounds, π-$C_5H_5M(CO)_3H(D)$, were prepared by the standard methods.[2] The *deuterides* were obtained by treating the sodium salt, π-$C_5H_5M(CO)_3Na$ (10 g.), in tetrahydrofuran (10 ml.) with deuteroacetic acid (3 ml.; 60% isotopic substitution).

The iron compound, π-$C_5H_5Fe(CO)_2H$,[11] was obtained by treating the carbonyl π-$C_5H_5Fe(CO)_2Cl$ (0·5 g.) with sodium borohydride (1 g.) in tetrahydrofuran (10 ml.). After 15 min. the red solution had become orange-yellow and was poured into water (50 ml.), and the hydride was extracted into light petroleum (b. p. 30—40°; 10 ml.). Removal of the solvent at 0°/0·1 mm. left a pale yellow liquid which was distilled in a vacuum. The corresponding deuteride was obtained by reduction of π-$C_5H_5Fe(CO)_2I$ in diethyl ether by lithium aluminium deuteride. After removal of the solvent at 0°/0·1 mm. the liquid was fractionally distilled but complete separation from ether is difficult.

The ruthenium complexes, π-$C_5H_5Ru(CO)_2H(D)$, were obtained similarly from π-$C_5H_5Ru(CO)_2I$ (see below). Dicarbonyl-π-cyclopentadienylhydridoruthenium is a colourless, volatile liquid with an obnoxious odour and, like its iron analogue, is very sensitive to air. It was characterised by its infrared and proton magnetic resonance spectra. When pure at 25° it rapidly dimerises to the binuclear carbonyl, but in solution the rate is much lower so that the spectra can be obtained readily.

Carbonyl-π-cyclopentadienyl and Carbonyl Alkyls and Propionyls.—The alkyls were prepared by a standard procedure, namely, treatment of the appropriate sodium salts of the carbonylate anion with methyl or ethyl iodide or propionyl chloride [12] in tetrahydrofuran. Because of their volatility, the compounds $Mn(CO)_5C_2H_5$, $Re(CO)_5C_2H_5$, and π-$C_5H_5Cr(CO)_3CH_3$ were recovered from the tetrahydrofuran solution by pouring the reaction mixture into water and extracting the product into light petroleum (b. p. 30—40°). The compounds were purified by fractional distillation *in vacuo*. The new derivatives of ruthenium were prepared from sodium dicarbonyl-π-cyclopentadienylruthenate {from $[\pi\text{-}C_5H_5Ru(CO)_2]_2$ and an excess of 1% sodium amalgam in tetrahydrofuran} in the same way as the corresponding iron derivatives.[2] *Dicarbonyl-π-cyclopentadienylmethylruthenium* is a white, volatile solid, m. p. 39—40°, which sublimes at 40°/0·1 mm. (Found: C, 40·6; H, 3·4; O, 13·7. $C_8H_8O_2Ru$ requires C, 40·4; H, 3·4; O, 13·5%), and *dicarbonyl-π-cyclopentadienylethylruthenium* is a colourless, volatile oil, m. p. *ca.* −5° (Found: C, 43·1; H, 4·4; O, 12·9. $C_9H_{10}O_2Ru$ requires C, 42·9; H, 4·0; O, 12·7%). They are more stable than their iron analogues. Solutions of π-$C_5H_5M(CO)_2C_2H_5$ (M = Fe and Ru) in carbon tetrachloride decompose rapidly, but, in the absence of air, their solutions in hydrocarbon solvents are stable.

Dicarbonyl-π-cyclopentadienyliodoruthenium. The preparation was analogous to that of π-$C_5H_5Fe(CO)_2I$.[13] The addition of iodine in carbon tetrachloride to tetracarbonyldi-π-cyclopentadienyldiruthenium [14] gave *dicarbonyl-π-cyclopentadienyliodoruthenium* as orange crystals, m. p. 103—105°, which sublimed at 100°/0·1 mm. (Found: C, 23·7; H, 1·4; I, 36·3. $C_7H_5IO_2Ru$ requires C, 24·0; H, 1·4; I, 36·3%).

Other Experiments.—The proton resonance spectrum of the pure carbonyl $Mn(CO)_5C_2H_5$ (sealed tube *in vacuo*) showed marked line broadening during 10 min. (the sample darkened

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[10] Corio, *Chem. Rev.*, 1960, **60**, 363.

[11] Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, **14*b***, 738.

[12] Closson, Kozikowski, and Coffield, *J. Org. Chem.*, 1957, **22**, 598.

[13] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 38.

[14] Jones and Wilkinson, unpublished work; see also Fischer and Vogler, *Z. Naturforsch.*, 1962, **17*b***, 421.

noticeably in this time) which indicates that decomposition gives a paramagnetic species as well as $Mn(CO)_5(CO{\cdot}C_2H_5)$.[15] Solutions of the complex in hydrocarbon solvents are more stable. Pentacarbonylpropionylmanganese can be obtained by treatment of the compound $Mn(CO)_5C_2H_5$ with carbon monoxide under pressure [16] or from sodium pentacarbonylmanganate with propionyl chloride in tetrahydrofuran.[12] We have found that although the compound $Mn(CO)_5C_2H_5$ was completely carbonylated at 60—80°/100 atm. in 10 min., the corresponding reaction with pentacarbonylethylrhenium was not complete after 1 hr. at 100°/100 atm. The proton resonance spectrum of the product after two sublimations showed the presence of some $Re(CO)_5C_2H_5$.

Decacarbonyldirhenium.—Previous procedures [17] for making this carbonyl $Re_2(CO)_{10}$ have not involved halides of rhenium as these give only the halogen derivatives, $Re(CO)_5X$ (X = halogen). We have adapted the reductive carbonylation procedure [18] to prepare $Re_2(CO)_{10}$ from rhenium trichloride or pentachloride. The halides were treated with a slight excess over the stoicheiometric amount of sodium in dry tetrahydrofuran and with carbon monoxide at 130°/250—280 atm. in an autoclave (*e.g.*, $ReCl_5$, 9·0 g.; Na, 5·0 g.; tetrahydrofuran, 150 ml.). After 8 hr. the pressure was released and the tetrahydrofuran solution was filtered, acidified with *ca.* 2N-sulphuric acid, and extracted with diethyl ether. The ether extract was washed repeatedly with dilute sulphuric acid and finally with water and then dried ($CaSO_4$). The solvent was removed at 25°/0·1 mm. and the residue acidified with dilute sulphuric acid and steam-distilled. The rhenium carbonyl was separated from the distillate by filtration and purified by sublimation (yield, 4·0 g., 70% based on $ReCl_5$).

Di-π-cyclopentadienyl Hydride Salts of Rhenium, Molybdenum, and Tungsten.—These hydrides were prepared in aqueous solution as previously described [19] and were precipitated as hexafluorophosphates. The deuterides were prepared by dissolving the neutral hydrides in ~0·1N-trideuterophosphoric acid and were precipitated with a solution of ammonium hexafluorophosphate in *ca.* 0·01N-trideuterophosphoric acid; in these conditions complete isotopic exchange takes place and high-field lines are absent from the proton magnetic resonance spectra of these solutions in D_2O).

High-resolution Proton Magnetic Resonance Spectra.—Measurements were made with a Varian Associates model 4311 spectrometer at 56·46 Mc./sec. and 22° ± 2°. Whenever possible, the alkyl spectra were measured in carbon tetrachloride solutions but, as it was found that some of the ethyls reacted rapidly with halogenated solvents, it was convenient to use benzene since the internal chemical shifts, δ, are relatively insensitive to solvent changes. The ethyl spectra were analysed as A_3B_2 systems by using Corio's tables.[10] In all cases, the positions of the spectral lines, in cycles/sec., were converted into units of δ, and from these J/δ was calculated. The observed lines were then compared with those calculated from the J/δ value by interpolation from Corio's tables. The neutral hydrides were measured in cyclohexane. Tetramethylsilane was used as an internal reference and the line positions were determined by conventional side-band techniques.

Infrared Spectra.—Measurements were made with a Perkin-Elmer model 21 spectrophotometer with sodium chloride and calcium fluoride optics. Solutions of the carbonyl-π-cyclopentadienyl-metal hydrides, with the exception of the liquids, were made up in carbon disulphide in a nitrogen-filled glove-box. Solutions of the liquid hydrides were prepared by condensing carbon disulphide on to the purified complex in a vacuum-line. These solutions were then transferred to the infrared cells in the glove-box. The cationic hydrides were studied in hexachlorobutadiene, Nujol, and Fluorolube mulls. The alkyls of the Group VI metals and π-$C_5H_5Fe(Ru)(CO)_2R$ (R = CH_3 and C_2H_5) were measured as carbon disulphide solutions, as was π-$C_5H_5Ru(CO)_2I$. Only those parts of the spectra relevant to the discussion are given.

Transition metal-hydrogen stretching frequencies have been found [20] in the region 2300—1700 cm.$^{-1}$, but few assignments have been made for carbonyl hydrides. The infrared spectra of pentacarbonylhydridomanganese [21] showed that ν_{Mn-H} occurs at 1783 cm.$^{-1}$. The spectra

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[15] Coffield, personal communication.

[16] Closson, Coffield, and Kozikowski, abstract of a paper presented at the International Conference on Coordination Chemistry, London, 1959, *Chem. Soc. Spec. Publ.*, 1959, No. 13, 126.

[17] Hieber and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 256.

[18] Podall, *J. Chem. Educ.*, 1961, **38**, 187, and references therein.

[19] Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854.

[20] Green, *Angew. Chem.*, 1960, **72**, 719, and references therein.

[21] Cotton, Down, and Wilkinson, *J.*, 1959, 833.

of the Group VI tricarbonyl-π-cyclopentadienyl-metal complexes have been published [22] but no assignment of the metal–hydrogen stretching modes was attempted. A number of weak absorptions were observed close to the very intense carbonyl bands; these were also noted in the spectra of the corresponding alkyls and π-$C_5H_5Mn(CO)_3$. One of these bands was considerably more intense for the hydrides than for the deuterides and was assigned to the metal–hydrogen stretching frequency. A band in the deuteride in the region 1385—1000 cm.$^{-1}$, absent from the spectrum of the hydride, was assigned to the metal–deuterium stretching frequency. The ratio ν_{M-H}/ν_{M-D} was 1·395 for the molybdenum and tungsten complexes; the weak bands at 1790 and 1845 cm.$^{-1}$, previously reported without assignment,[2] are the Mo–H and W–H stretching modes, respectively.

The M–H stretching frequencies in the cationic hydrides, $[(\pi\text{-}C_5H_5)_2MH_x]^+$, were found by comparing the mull spectra in range 2200—1700 cm.$^{-1}$. Weak bands at 2055, 1915, and 1943 cm.$^{-1}$, in the spectra of the rhenium, molybdenum, and tungsten hydrides, respectively (absent for the deuterides), are assigned to the metal–hydrogen stretching mode. The expected M–D stretches were not found. These should occur (calculated from ν_{M-H}/ν_{M-D}, *ca.* 1·4) very close to or under the more intense C–H deformation frequencies in the region 1500—1200 cm.$^{-1}$.

π-$C_5H_5Fe(CO)_2H$: 3113w, 2014vs, 1960vs, 1930sh, 1900w, 1835w (Fe–H str.), 1772w, 1762w, 1670w, 1430m, 1363m, 1330vw, 1289w, 1258w, 1246vw, 1220w, 1168w, 1113m, 1058m, 1013s, 1000s, 936vw, 917w, 830m, 806vw, 782w, 747s, 689s. The band at 1772 cm.$^{-1}$ is due to the bridging CO of the binuclear species which is slowly formed.

π-$C_5H_5Fe(CO)_2D$: 3110w, 2014vs, 1960vs, 1932sh, 1900w, 1835vw, 1770w, 1762w, 1670w, 1428m, 1363m, 1330m (Fe–D str?), 1290w, 1258w, 1240vw, 1219w, 1168w, 1113m, 1060m, 1010s, 1002s, 917w, 830m, 782w, 747s, 689s.

π-$C_5H_5Ru(CO)_2H$: 3100w, 2025vs, 1966vs, 1938sh, 1853w (Ru–H str.), 1812w, 1730w, 1435m, 1353m, 1257m, 1199w, 1090m, 1061sh, 1010m, 1001sh, 904vw, 816sh, 805s, 729m, 688m.

π-$C_5H_5Ru(CO)_2D$: 3098w, 2025vs, 1966vs, 1935sh, 1852vw, 1810w, 1730w, 1435m, 1353m, 1325vw (Ru–D str?), 1257m, 1199w, 1090m, 1061sh, 1008m, 1000sh, 819sh, 806s, 729m, 685m.

π-$C_5H_5Mo(CO)_3H$: · · · 2027vs, 2020sh, 1940vs, 1904m, 1790 (Mo–H str.), 1730w, 1640w · · · 1350w, 1275w · · ·

π-$C_5H_5Mo(CO)_3D$: · · · 2027vs, 2020sh, 1939vs, 1906m, 1847vw, 1790vw, 1731w, 1635w · · · 1353w, 1285m (Mo–D str.), 1262w · · ·

π-$C_5H_5W(CO)_3H$: · · · 2026vs, 2016sh, 1935vs, 1900sh, 1845m (W–H str.), 1735w, 1635w · · · 1352w, 1320w, 1253vw · · ·

π-$C_5H_5W(CO)_3D$: · · · 2026vs, 2016sh, 1935vs, 1900sh, 1843vw, 1735w, 1655w · · · 1352w, 1322m (W–D str.), 1253vw · · ·

π-$C_5H_5Fe(CO)_2CH_3$: · · · 2016vs, 2005sh, 1925vs, 1845w, 1734w, 1655w · · ·

π-$C_5H_5Ru(CO)_2CH_3$: 3095w, 2960w, 2905m, 2028vs, 1960vs, 1933sh, 1845vw, 1805vw, 1740vw, 1425m, 1354m, 1196m, 1105sh, 1062m, 1002s, 977s, 810s, 756m, 680w.

π-$C_5H_5Ru(CO)_2C_2H_5$: 3092w, 3053m, 2910s, 2029vs, 1960vs, 1930sh, 1807vw, 1756vw, 1428m, 1371w, 1342m, 1304w, 1294w, 1276w, 1256s, 1242sh, 1222m, 1187sh, 1169m, 1160sh, 1128m, 1100s, 1065s, 1022m, 1001s, 938w, 906s, 895sh, 805m, 745s, 725s, 702m.

π-$C_5H_5Mo(CO)_3CH_3$: · · · 2023vs, 1934vs, 1904sh, 1828w, 1730w, 1642w · · ·

π-$C_5H_5Mo(CO)_3C_2H_5$: · · · 2022vs, 2005sh, 1932vs, 1900sh, 1817w, 1727w, 1643w · · ·

π-$C_5H_5W(CO)_3CH_3$: · · · 2019vs, 1924vs, 1843w, 1737w, 1653w · · ·

π-$C_5H_5W(CO)_3C_2H_5$: · · · 2016vs, 1928vs, 1841w, 1762w, 1667w · · ·

π-$C_5H_5Ru(CO)_2I$: 3083w, 2055vs, 2007vs, 1976sh, 1840vw, 1420m, 1374vw, 1345w, 1262m, 1090m, 1058m, 1001m, 920w, 823s, 756w, 666w.

We thank the Department of Scientific and Industrial Research (A. D.) and the Carnegie Trust for the Universities of Scotland (J. A. McC.) for studentships, Johnson, Matthey and Co. Ltd. for a loan of platinum metals, the International Nickel Co. (Mond) Ltd., Climax Molybdenum Co., and Ethyl Corporation for gifts of metal carbonyls. We also thank Drs. L. Pratt and D. F. Evans for helpful discussions.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.

[*Received, August 8th,* 1962.]

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