876. π-cyclo*Pentadienylrhenium Carbonyl Compounds.*

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The infrared and high-resolution nuclear magnetic resonance spectra of the compound $C_{10}H_{11}Re(CO)_2$, together with its chemical properties and hydrogenation to $C_{10}H_{13}Re(CO)_2$, have shown that it must be formulated as π-*cyclo*pentadienyl*cyclo*pentadienerhenium dicarbonyl.

π-*cyclo*Pentadienylrhenium tricarbonyl has also been prepared.

DI-π-*cyclo*PENTADIENYLRHENIUM HYDRIDE [1] with carbon monoxide at 100°/250 atm. gives pale yellow crystals of $C_{10}H_{11}Re(CO)_2$ (*A*), first reported by Fischer and Wirzmüller [2] who suggested a structure (I) in which both a π-*cyclo*pentadienyl and a σ-*cyclo*pentadienyl ring were bound to the metal atom and that the additional proton was located between the metal atom and the π-*cyclo*pentadienyl ring as in the structure suggested by Liehr [3] for the di-π-*cyclo*pentadienylrhenium hydride. No physical measurement other than the dipole moment (3·85 D) was reported to support this formulation, but it was noted that the compound showed no acid or base character of the type shown by other transition-metal complex hydrides (cf. ref. 1). Our examination has shown that a different formulation (II) is necessary.

(a) *Nuclear Magnetic Resonance.*—For all compounds containing a hydrogen atom bound to a transition metal this proton is heavily diamagnetically shielded,[1] having a resonance peak in the region 400—800 cycles/sec. (at 40 Mc./sec.) on the high-field side relative to water. Careful measurement of *A* in concentrated solutions in several organic solvents did not give evidence of the presence of such a shielded proton. Structure (I) can thus be eliminated since a band in this region of intensity 0·2 of that of the band due to the protons of the π-*cyclo*pentadienyl ring would have been expected. All proton resonances observed can be accounted for as discussed below. In addition, examination of the sharp peak due to the π-*cyclo*pentadienyl ring protons under very high resolution showed no

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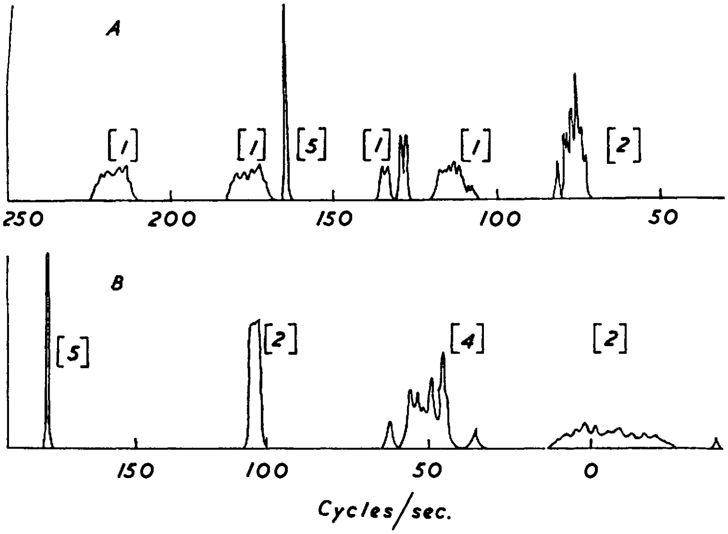
[1] Green, Pratt, and Wilkinson, *J.*, 1958, 3916.
[2] Fischer and Wirzmüller, *Z. Naturforsch.*, 1957, **12**b, 737.
[3] Liehr, *Naturwiss.*, 1957, **44**, 61.

evidence of fine structure. In the compound $(\pi\text{-}C_5H_5)_2ReH$ [1] the π-*cyclo*pentadienyl proton line was split into a doublet with peak separation $1{\cdot}0_5$ cycles/sec. due to indirect spin–spin coupling interaction between the proton bound to the metal and those of the ring. The failure to observe such splitting in $C_{10}H_{11}Re(CO)_2$ again indicates the absence of a rhenium–hydrogen bond.

It would also have been expected from (I) that the compound would have a spectrum similar to that of $\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}C_5H_5$.[4] A new measurement in carbon disulphide confirms the previous observation; two peaks are found, one at 134 cycles/sec. (line-width $\leqslant 0{\cdot}7$ cycle/sec.) and one at 188 cycles/sec. (line-width $\approx 1{\cdot}5$ cycles/sec.), both on the low-field side relative to *cyclo*hexane as zero. The spectrum of the rhenium compound, however, bears no resemblance to that of the iron compound, other than having a sharp π-*cyclo*pentadienyl proton resonance (Figure); there are five other main bands each showing fine structure.

High-resolution nuclear magnetic resonance spectra of $\pi\text{-}C_5H_5(C_5H_6)Re(CO)_2$ (*A*) *and* $\pi\text{-}C_5H_5(C_5H_8)Re(CO)_2$ (*B*) *at* 40 *Mc./sec. with reference to* cyclo*hexane in cycles/sec. The direction of increasing field is from left to right and the figures in brackets indicate the relative peak areas.*



(b) *Infrared Spectra.*—The infrared spectra of compounds containing $\sigma\text{-}C_5H_5$ groups [4] show two peaks at about 3000 cm.$^{-1}$ due to this ring. The spectrum of *A* (Table) shows six peaks in the C–H stretching region in addition to the one at 3112 cm.$^{-1}$ which is assignable to the C–H stretches of the π-*cyclo*pentadienyl ring. The assignment of the other peaks is discussed below.

(c) *Chemical Studies.*—The compound *A* is stable in air and only slowly decomposes in light petroleum; it is stable in carbon tetrachloride even on boiling. It has neither acidic nor basic properties.[2] These properties are quite different from other known metal-complex hydrides (cf. ref. 1).

The unsaturated nature of *A* is shown by rapid decolorisation of bromine in carbon tetrachloride and the formation of an unstable orange precipitate which we have been unable to characterise. On catalytic hydrogenation, however, 1 mol. of hydrogen is absorbed; a white crystalline product, $C_{10}H_{13}Re(CO)_2$, (*B*), was isolated essentially quantitatively. This observation is consistent with structure (II) whereas structure (I) would have required the absorption of 2 mol. of hydrogen. Compound (*B*) must be formulated as π-*cyclo*pentadienyl*cyclo*pentenerhenium carbonyl (III).

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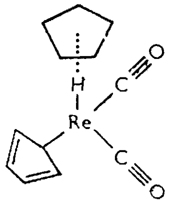
[4] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

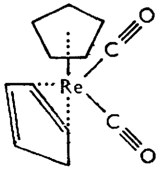
Infrared spectra in carbon disulphide and carbon tetrachloride.

π-$C_5H_5Re(CO)_2C_5H_6$ (cm.$^{-1}$)	π-$C_5H_5Re(CO)_2C_5H_8$ (cm.$^{-1}$)	π-$C_5H_5Re(CO)_3$ (cm.$^{-1}$)	Assignment *
3112 w	3115 w	3117 w	1
3063 m	—	—	2
3025 m	3020 m	—	3
2954 m	2960 s	—	4
2931 m	2895 m	—	4
2871 s	2855 vs	—	4
2824 m	—	—	
1973 vs	1971 vs	2041 vs	5
1893 vs	1890 vs	1939 vs	5
2480 w	2485 w	2520 w	
2420 w	2425 w	2438 w	
1470 m	—	1820 m	
1450 m	—	—	
1424 m	—	1422 s	
1356 w	1345 m	1349 w	
1292 w	1278 w	—	
1280 m	1257 m	1262 w	
1262 w	—	—	
1220 m	1215 w	—	
1171 vw	1134 s	1190 w	
1127 w	—	—	
1105 s	1103 s	1101 m	
1057 w	1078 s	—	
1040 m	1055 w	1053 w	
1003 m	1003 s	1001 s	
940 m	966 m	—	
914 w	910 w	907 w	
862 m	879 m	—	
—	828 s	—	
810 s	807 s	815 vs	

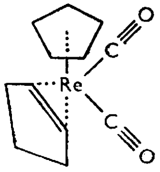
* *Assignments*: 1, C–H stretch of π-C_5H_5; 2, –HC=CH– stretch; 3, –HC=CH– stretch; 4, $>CH_2$ stretch; 5, C≡O stretch.



(I)



(II)



(III)

DISCUSSION

Since the compound $C_{10}H_{11}Re(CO)_2$ has, on the above evidence, neither a σ-*cyclo*pentadienyl ring nor a hydridic proton and contains an olefinic group, it is necessary to assume that one of the double bonds in *cyclo*pentadiene is acting as a donor in a manner similar to that of other olefins in complexes with metals at the end of the transition series.[5] The rhenium atom in this case would then have a closed configuration and the compound would be diamagnetic, as found. The same consideration applies in the case of the hydrogenated compound.

A comparison of the infrared spectra of *A* and *B* in the C–H stretching region indicates that the band at 3063 cm.$^{-1}$ in the former disappears on hydrogenation, whilst the band at 3025 cm.$^{-1}$ is essentially unchanged. The 3063 cm.$^{-1}$ band is hence assigned as the C–H stretch of the unco-ordinated olefinic group in the *cyclo*pentadiene compound. The band at 3025 cm.$^{-1}$ in the *cyclo*pentadiene compound and that at 3020 cm.$^{-1}$ in the *cyclo*pentene compound may be assigned to C–H stretches of the co-ordinated olefin; these are in the same region as the C–H stretches reported in other olefin–metal complexes.[5]

[5] For references see Chatt and Venanzi, *J.*, 1957, 4735.

At present we have too few data on the nuclear magnetic resonance spectra of olefin–metal complexes to allow a detailed analysis of the spectra of compounds *A* and *B*. However, the spectra (Figure) are consistent with the structures (II) and (III). The sharp single peaks at 164—165 cycles/sec. come from the protons in the π-*cyclo*pentadienyl rings. The two bands which occur at *ca.* 175 and ~217 cycles/sec. in the spectrum of *A* are absent from the spectrum of *B*, and can probably be assigned to the protons of the unco-ordinated olefinic group in *A*. The following tentative assignment of the peaks is based on comparisons with the spectra of available measurements on hydrocarbon–metal complexes. In the spectrum of *A*, the lines between 100 and 150 cycles/sec. are assigned to the protons of the co-ordinated olefin group, and the band at 75 cycles/sec. to the methylene group. *cyclo*Pentadiene itself shows two bands, each with much fine structure, at about 185 and 40 cycles/sec. respectively, the latter due to the methylene group. The three bands at 103, 50, and ~0 cycles/sec. in the spectrum of *B* are assigned respectively to the protons of the co-ordinated olefin group, the adjacent ($C_{(3)}$ and $C_{(5)}$) methylene groups, and the $C_{(4)}$ methylene group.

An attempt to prepare *A* directly by refluxing di*cyclo*pentadiene with rhenium carbonyl led to the isolation only of the white crystalline π-*cyclo*pentadienylrhenium tricarbonyl. This compound is very similar in its physical and chemical properties to its manganese analogue.[6] Attempts to substitute one of the carbon monoxide groups in either the manganese or the rhenium compound by *cyclo*pentadiene and *cyclo*hexene in the sealed-tube reactions at 150—200° were unsuccessful.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratories, Imperial College. Light petroleum had b. p. 60—80°.

Infrared spectra were measured on a Perkin-Elmer Model 21 spectrometer with both sodium chloride and calcium fluoride optics. High-resolution nuclear magnetic resonance spectra were measured at 40 mc./sec. on a Varian Associates Model 4300B spectrometer with "super-stabiliser." The samples were measured at 22° ± 2° c in concentrated solutions in carbon disulphide, contained in spinning 5 mm. o.d. tubes. A loose sealed capillary containing *cyclo*hexane was used as an external reference, and the line positions were measured by the conventional side-band technique.

π-cyclo*Pentadienyl*cyclo*pentadienerhenium Carbonyl.*—Di-π-*cyclo*pentadienylrhenium hydride[1] (1·91 g.) was treated with carbon monoxide at 250 atm. and 100° for three days.[2] The crude brown product was sublimed *in vacuo* at 100°. The pale yellow sublimate was washed with dilute hydrochloric acid to remove unchanged hydride, which was recovered. The remaining solid was crystallised from light petroleum and the product sublimed twice *in vacuo* (1·02 g., 45%), m. p. 111—112° (Found: C, 38·68; H, 3·28; O, 8·25. Calc. for $C_{12}H_{11}O_2Re$: C, 38·58; H, 2·77; O, 8·57%).

π-cyclo*Pentadienyl*cyclo*pentenerhenium Carbonyl.*—An ethyl acetate solution of *A* (19·57 mg. in 25 ml.) with Adams's catalyst absorbed 0·804 ml. of hydrogen, but no more after 12 hr. The solvent was removed and the product crystallised from light petroleum and sublimed, m. p. 95—96° (Found: C, 38·68; H, 3·88. $C_{12}H_{13}O_2Re$ requires C, 38·4; H, 3·90%).

π-cyclo*Pentadienylrhenium Carbonyl.*—Rhenium carbonyl (0·5 g.) was refluxed in 3 ml. of di*cyclo*pentadiene for 4 hr. To the dark brown solution was added 0·5 ml. of light petroleum; on cooling to −70° a pale brown solid was obtained. This was crystallised twice from light petroleum to give white crystals (0·3 g.), m. p. 104—105° (Found: C, 29·0; H, 1·7. $C_8H_5O_3Re$ requires C, 28·7; H, 1·5%). The compound is stable in air and is soluble in common organic solvents; it has a strong camphoraceous odour.

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[6] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.