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NEW RHODIUM COMPLEXES OF DIPYRROMETHENES

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Dipyrromethenes are highly coloured compounds which have been used extensively as intermediates in porphyrin synthesis.[1] Although porphyrin complexes of Rh (I)[2,3,5] and (III)[5,6,7] have been previously synthesized and characterized, no Rh-dipyrromethene complexes have yet been prepared so far. We wish to report the addition of $[Rh(CO)_2Cl]_2$ to dipyrromethene.

Table 1 lists the various dipyrromethenes (1-5) used and the complexes (1a-5a) formed. Equimolar amounts of dipyrromethenes and $[Rh(CO)_2Cl]_2$ were refluxed in benzene for 1 hour in the presence of sodium acetate. The intense brown mixture gradually turned into marron. The solvent was removed under reduced pressure and the Rh complexes were crystallized from methanol to afford marron crystals of 1a-5a. These Rh-dipyrromethene complexes on treatment with $Br_2/CHCl_3$ or HCl (gas)/benzene gave back the parent compounds. The structures were assigned on the basis of elemental analysis,[8] NMR, IR and U.V. spectra. Thus, for example, the NMR spectrum of (1a) in $CDCl_3$ (TMS as internal standard) exhibits signals at 1.02 (triplets, 6H, 3 and '3-CH_2-CH_3), 2.15 and 2.5 (singlets, 6H each, 2,4,'2 and '4-CH_3), 2.38 (quartet, 4H, 3 and '3-CH_2-CH_3) and 6.8 ppm (singlet, 1H, ms-H) as compared with the original dipyrromethene (1) which exhibits signals at 1.05 (triplet, 6H, 3 and '3-CH_2-CH_3), 2.3 and 2.65 (singlet, 6H each, 2,4,'2 and '4-CH_3), 2.42 (quartet, 4H, 3 and '3-CH_2-CH_3) and 7.05 ppm (singlet, 1H, ms-H). The IR spectrum of (1a) did not exhibit any N-H absorption but showed two strong bands at 2010 and 2080 cm^{-1} assigned to the terminal carbonyl stretching vibration of the metal carbonyl group. The UV of (1a) showed a maximum at 546 nm (broad band) as compared to (1) which showed a maximum at 488 nm (sharp band). The elemental analysis is as follows. Found C, 54.96; H, 5.83; N, 6.72 $C_{19}H_{23}N_2O_2Rh$ requires C 55.05; H, 5.59; N, 6.761.

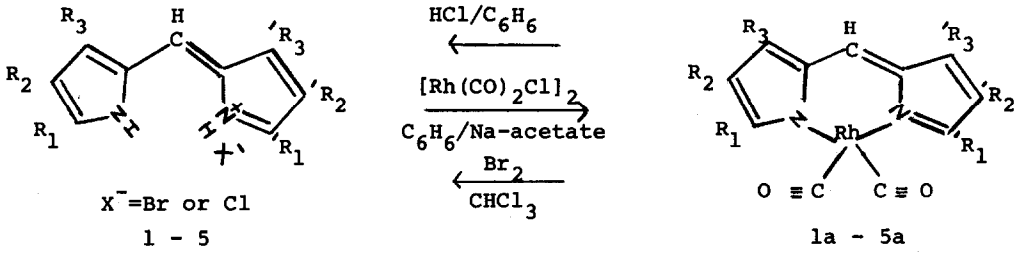

TABLE 1

Compound	R_1	R_2	R_3	$'R_1$	$'R_2$	$'R_3$	Product	Yield	m.p.
1	CH_3	C_2H_5	CH_3	CH_3	C_2H_5	CH_3	1a	77	128-130
2	CH_3	CH_3	CH_3	CH_3	H	CH_3	2a	72	118-120
3	CH_3	$CO_2C_2H_5$	CH_3	CH_3	$CO_2C_2H_5$	CH_3	3a	80	161-163
4	CH_3	CH_3	CH_3	CH_3	$CO_2C_2H_5$	CH_3	4a	68	160-162
5	CH_3	$CO_2C_2H_5$	H	CH_3	$CO_2C_2H_5$	CH_3	5a	75	148-150

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