Notes

Dinuclear Mono-μ-chloro-pyridyldiaza Rhodium(I) Complexes derived from Pyridyldi-imines *via* Hydrogen Transfer from Ethanol

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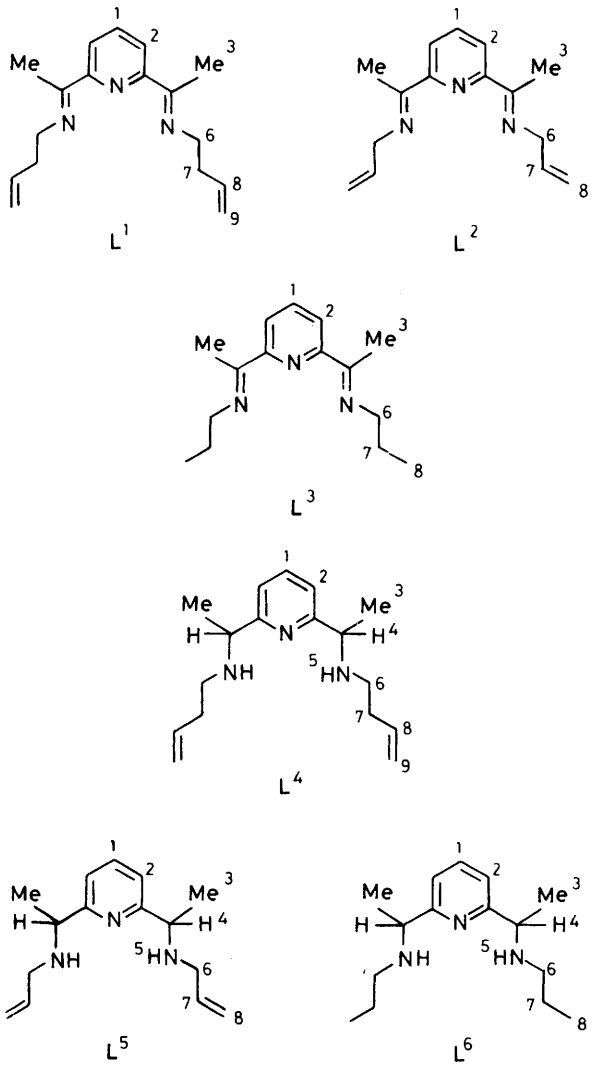
Reaction of $[\{Rh(C_2H_4)_2Cl\}_2]$ in ethanol with some pyridyldi-imine ligands with and without olefin-containing side-chains affords dinuclear monochloro-bridged rhodium(I) complexes of the corresponding reduced pyridyldiaza ligands. The product complexes, in which the pendant olefinic groups are not co-ordinated, have been characterised by analytical and spectroscopic methods and by their separate preparation from the pre-formed pyridyldiaza ligands. A mechanism for the solvent-to-imine hydrogen transfer involving oxidative addition of EtOH at the rhodium(I) centres is proposed.

In the course of studies[1,2] on binucleating macrocyclic polyimine ligands derived from the condensation of 2,6-diacetylpyridine with di-primary amines it was found advantageous to examine the co-ordination chemistry of some related acyclic Schiff-base ligands formed by reaction of the diketone with mono-primary amines. These include the ligands L^1—L^3, two of which contain terminal olefinic groups in the side arms. Since the planar conjugated trimethine 'N_3' donor set is well suited to co-ordinate at three corners of an approximate square plane it was of interest to see whether L^1 and L^2 might complex with d^8 ions such as Pd^{II} and Rh^I such that one olefinic group would occupy the fourth co-ordination site. If this proved to be the case there was then the possibility of activation of the olefinic group, for example, to attack by nucleophiles as in Wacker-type reactions. For the case of the (mononuclear) products of the reaction of $[Pd(MeCN)_2Cl_2]$ with L^1 and L^2 it has been shown[3] that the (pendant) olefinic groups are not co-ordinated but that they do interact intermolecularly with other Pd^{II} ions present in solution with accompanying activation to nucleophilic attack by water leading to complexes of the corresponding ketones. For the case of reactions with Rh^I quite different behaviour is observed. Here, as described below, the olefinic functions are unaffected while the co-ordinated imine groups are hydrogenated *via* hydrogen transfer from solvent ethanol leading to dinuclear complexes of the corresponding reduced pyridyldiaza ligands L^4—L^6. The results are of interest because of the very small number of examples of imine hydrogenation *via* hydrogen transfer without C–N bond cleavage[4,5] as well as the unexpected binuclear nature of the product complexes containing a single chloride bridge.



Experimental

2,6-Diacetylpyridine, allylamine, and 1-aminopropane were used as supplied commercially. 4-Aminobut-1-ene was prepared by a modification of the method of Roberts and Mazur[6] as described previously.[3] $[\{Rh(C_2H_4)_2Cl\}_2]$ was prepared by the method of Cramer.[7]

Preparation of the Ligands L^1—L^3.—These were prepared in *ca.* 90% yield by reaction of 2,6-diacetylpyridine (0.01 mol) with the appropriate amine (0.023 mol) in dry benzene (80 cm^3) over 3 A molecular sieves at room temperature for periods of up to 10 d. The molecular sieves were changed from time to time. The products were isolated as yellow oils by rotary evaporation of the benzene and excess amine at reduced pressure. The products were characterised by chemical analysis, mass spectra, and ^1H n.m.r. spectra (Tables 1 and 2).

Table 1. Analytical, electrical conductance, mass spectral, and i.r. data for the ligands and complexes

Compound	Analysis: Found C	H	N	Cl	Calc. C	H	N	Cl	Λ_M[a]/S cm^2 mol^{-1}	P^+[b]	I.r. (cm^{-1}): ν(NH)	ν(C=N)	ν(C=C)
L^1	75.4	8.6	15.2		75.8	8.6	15.6			269		1 636[c]	1 636[c]
$L^2 \cdot H_2O$	69.9	7.9	15.6		69.5	8.2	16.2			241		1 638[c]	1 638[c]
L^3	73.0	9.1	16.3		73.4	9.4	17.1			245		1 640	
L^4	72.1	9.7	13.9		74.7	9.9	15.4			273	3 280		1 638
L^5	70.8	9.4	16.4		73.4	9.4	17.1			245	3 300		1 600
L^6	70.0	10.5	15.9		72.2	10.9	16.8			249	3 340		
$[Rh_2(L^4)_2Cl]BPh_4$	63.1	6.4	7.6	2.9	63.1	6.4	7.6	3.2	80		3 320		1 640
$[Rh_2(L^5)_2Cl]BPh_4$	61.2	6.1	8.0		61.2	6.3	7.9		112		3 340		1 640
$[Rh_2(L^6)_2Cl]BPh_4$	61.8	6.1	8.0		61.3	6.3	7.9		110		3 340		

[a] Solutions (10^{-3} mol dm^{-3}) in MeCN at 20 °C. [b] Parent ion peak in mass spectrum. [c] Overlapping ν(C=N) and ν(C=C) vibrations.

Table 2. Hydrogen-1 n.m.r. data (δ/p.p.m.) for the ligands and complexes in CD_3CN

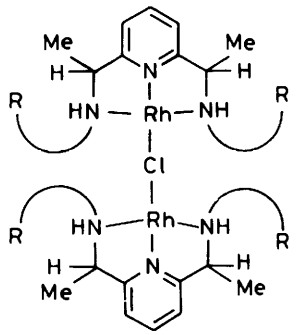
Compound	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9
L^1	7.60 (t)	8.02 (d)	2.32 (s)			3.50 (t)	2.46 (q)	5.96 (m)	5.09 (m)
L^2	7.55 (m)	8.10 (d)	2.30 (s)			4.11 (t)	5.99 (m)	5.18 (m)	
L^3	7.12 (m)	7.63(d)	1.83 (s)			2.92 (t)	1.30 (m)	0.52 (t)	
L^4	7.11 (t)	7.60 (d)	1.36 (d)	3.82 (q)	2.47 (s)	2.49 (m)	2.27 (m)	5.76 (m)	5.00 (m)
L^5	7.17 (t)	7.60 (t)	1.21 (d)	3.72 (q)	2.78 (s)	2.95 (d)	5.75 (m)	4.97 (m)	
L^6	7.00 (t)	7.40 (m)	1.32 (d)	3.80 (q)	2.40 (s)	2.47 (m)	1.51 (m)	0.85 (t)	
$[Rh_2(L^4)_2Cl]BPh_4$	7.29 (m)		1.11 (d)	3.53 (q)	2.31 (s)	2.44 (t)	2.30 (m)	5.77 (m)	5.07 (m)
$[Rh_2(L^5)_2Cl]BPh_4$	7.28 (m)		1.33 (d)	3.64 (q)	2.25 (s)	3.20 (d)	5.90 (m)	5.19 (m)	
$[Rh_2(L^6)_2Cl]BPh_4$	7.30 (m)		1.42 (d)	3.60 (q)	2.39 (s)	2.60 (m)	1.31 (m)	0.71 (t)	

Preparation of the Ligands L^4—L^6.—To a refluxing solution of the appropriate ligand L^1, L^2, or L^3 (0.004 mol) in MeOH (200 cm^3), an excess (0.6 g) of solid sodium tetrahydroborate was added carefully. The mixture was refluxed for 2 h, then filtered and the filtrate evaporated to dryness by rotary evaporation at reduced pressure. The white residue was dissolved in water (10 cm^3). Addition of NaOH pellets released the free amine as an oily top layer. This was extracted into $CHCl_3$ (3 × 30 cm^3). Rotary evaporation of the $CHCl_3$ extracts gave the products as yellow oils in *ca.* 70% yield. Analytical data (Table 1) indicated the presence of some impurity. However, i.r., mass, and ^{1}H n.m.r. spectra (Tables 1 and 2) of the crude products were fully consistent with expected structures. Since the crude ligands also gave pure crystalline rhodium complexes (method B below) they were used without further purification.

Preparation of the Complexes of Ligands L^4—L^6.—*Method A.* The appropriate ligand L^1, L^2, or L^3 (0.001 mol) was dissolved in EtOH—MeCN (3:2, 50 cm^3) solvent mixture along with $Na[BPh_4]$ (0.001 mol). In a separate solution $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.001 mol) was dissolved in MeCN (30 cm^3) by heating to reflux. This was added to the solution of ligand giving an immediate colour change from yellow to brown. The mixture was gently refluxed for 1 h before concentrating to 20 cm^3. A yellow-brown solid separated on standing which could be recrystallised from MeCN. Yields were 60—80%.

Method B. This method involved the use of the ligands L^4—L^6 instead of L^1—L^3. Otherwise the procedure was the same. The 1-h reflux was not necessary in these cases, however. The identity of the products obtained from methods A and B was established by chemical analysis and by i.r. and ^{1}H n.m.r. spectra (Tables 1 and 2).

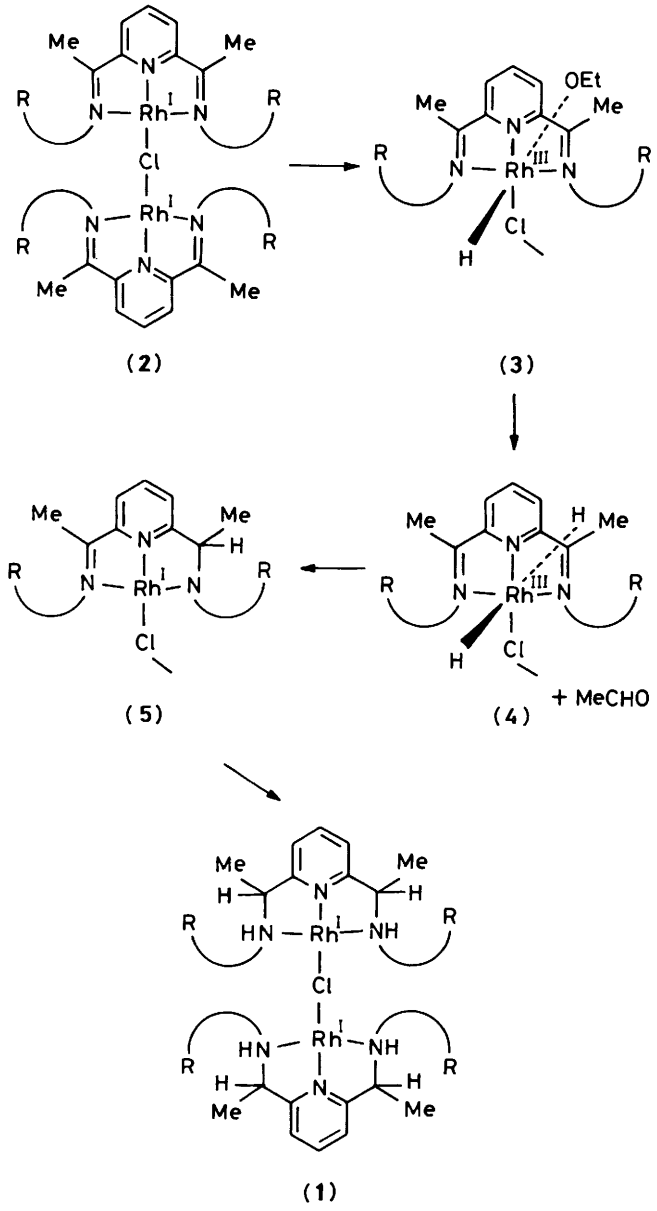
Physical Measurements.—Infrared spectra were recorded between 4 000 and 200 cm^{-1} as thin films (oils) between KBr plates or as KBr pellets or paraffin mulls (solids) using Perkin-Elmer 577 and 598 grating spectrophotometers. ^{1}H N.m.r. spectra in CD_3CN solution were measured using Bruker WH90 or WM250 Fourier-transform spectrometers at 25 °C. A conductivity cell of cell constant 0.0368, constructed from bright platinum electrodes, in conjunction with a conventional resistance/capacitance bridge was used for measurements of electrical conductance. Mass spectra were obtained using an A.E.I. MS902 instrument at an ionising voltage of 70 eV (*ca.* 1.1 × 10^{-17} J).



(1)

Results and Discussion

Analytical, electrical conductance, and selected i.r. data for the ligands and complexes are summarised in Table 1 while ^{1}H n.m.r. data for CD_3CN solutions are given in Table 2. The results clearly demonstrate that the products of reaction of L^1, L^2, and L^3 with $[\{Rh(C_2H_4)_2Cl\}_2]$ in EtOH-containing solvent mixtures are complexes of the reduced ligands L^4, L^5, and L^6 in which the imine groups have been hydrogenated to secondary amine groups. The reduction of the ligands is apparent in the



Scheme. Proposed mechanism for the hydrogen-transfer reduction of ligands L^1—L^3 to L^4—L^6. For structures (**3**)—(**5**) only one metal co-ordination environment is shown

appearance of a ν(NH) vibration at *ca.* 3 340 cm^{-1} in the i.r. spectra of the complexes not present in the spectra of the reactant ligands L^1—L^3, and in the absence in the spectrum of the L^6 complex of any absorption at *ca.* 1 640 cm^{-1} attributable to ν(C=N). The band at this frequency in the spectra of the complexes of L^4 and L^5 is assigned to ν(C=C) of unco-ordinated terminal alkene functions; significantly, it is of reduced intensity compared to that of the precursor ligands L^1 and L^2 where the absorption comprises overlapping ν(C=N) and ν(C=C) modes.

The conclusions drawn from the i.r. spectra are fully confirmed by the ^1H n.m.r. spectra of the complexes which, aside from the expected co-ordination shifts, are closely similar to those of the free ligands L^4—L^6 in coupling patterns as well as in the number and relative intensities of the resonances, but quite distinct from those of the precursor imine ligands L^1—L^3 (see Table 2). Finally, proof of the metal-promoted reduction of L^1—L^3 to L^4—L^6 is provided by the separate preparation of the identical complexes starting from the free ligands L^4—L^6.

The assignment of the binuclear mono-chloro-bridged structure (**1**) (R = $CH_2CH_2CH{=}CH_2$, $CH_2CH{=}CH_2$, or Pr^n), to the product complexes is based on their stoicheiometry, and the observed uni-univalent electrolyte behaviour in acetonitrile (Table 1). The occurrence of ν(C=C) at the same frequency (*ca.* 1 640 cm^{-1}) in the i.r. spectra of both the free ligands L^4 and L^5 and of their complexes indicates that the pendant olefinic groups are not co-ordinated. No band in the 1 500—1 600 cm^{-1} region attributable to co-ordinated olefin was apparent in the spectra of either complex. This contrasts with the situation in a Cu^I complex of L^1, shown by an *X*-ray structure determination[8] to contain both co-ordinated and unco-ordinated olefinic groups where two ν(C=C) vibrations, at 1 567 and 1 636 cm^{-1}, can be identified. Moreover, in the n.m.r. spectra, olefinic protons H^8 and H^9 (of L^4) and H^7 and H^8 (of L^5) are scarcely affected by co-ordination of the ligands whereas substantial upfield shifts would be expected[9] if these groups were bound to the Rh^I centres.

Since no reduction of L^1—L^3 to L^4—L^6 was observed when the reactions were carried out (in pure acetonitrile) in the absence of ethanol it is reasonable to conclude that ethanol is the source of hydrogen. Indeed, no clean products of any kind could be isolated from reactions carried out in the absence of ethanol. The reduction of some aldimines to secondary alcohols in the presence of Wilkinson's Catalyst and sodium carbonate has been attributed[4] to hydrogen transfer from solvent propan-2-ol. A probable mechanism for the hydrogen transfer is summarised in the Scheme (for the case of L^1). The first step is seen as substitution of two ethylene and one Cl^- ligand of $[\{Rh(C_2H_4)_2Cl\}_2]$ by the trimethine group of L^1. The co-ordinatively unsaturated 16-electron Rh^I ion in (**2**) then undergoes an oxidative addition with EtOH to give the six-co-ordinate hydrido-Rh^{III} species (**3**). Elimination of acetaldehyde would give the dihydrido-species (**4**). This is followed by a reductive elimination with hydrogen transfer to the co-ordinated imine group and regeneration of the four-co-ordinate 16-electron Rh^I centre. Repetition of steps (*ii*)—(*iv*) leads to reduction of the second imine bond.

Acknowledgements

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