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Carbon Monoxide-promoted Migratory Insertion Reactions at a Diene(hydrido)ruthenium(II) Centre

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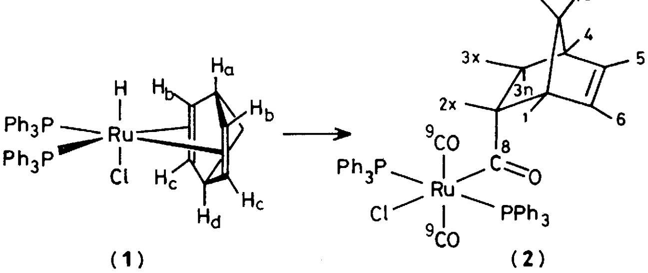
The hydrido-norbornadiene (nbd) complex $RuHCl(nbd)(PPh_3)_2$ exists in solution as a single isomer with a coplanar arrangement of metal, hydride, and an alkene π-bond, the requisite geometry for olefin insertion; the insertion to give an alkenyl is promoted by reaction with carbon monoxide that itself subsequently inserts to give an acyl derivative.

Hydrido-olefin species are key intermediates in many important catalytic processes but, because of their intrinsic high reactivity, examples of such complexes are relatively rare and there has been little opportunity to study their chemistry.[1,2] We report here on a well known hydrido-norbornadiene (nbd) complex[3] $RuHCl(nbd)(PPh_3)_2$ (**1**), that on treatment with carbon monoxide undergoes consecutive olefin and CO insertion reactions to give an acyl isolated as the dicarbonyl derivative (**2**) [equation (1)].

$$\underset{(\mathbf{1})}{RuHCl(C_7H_8)(PPh_3)_2} \xrightarrow{3CO} \underset{(\mathbf{2})}{RuCl(COC_7H_9)(CO)_2(PPh_3)_2} \qquad (1)$$

^1H and ^{31}P n.m.r. studies of the diene complex in solution show that it exists as the single isomer (**1**) with equivalent phosphines.† The coplanar arrangement of metal, hydride, and alkene π-bond is a required geometry for the stereospecific migration–insertion of the olefin to form an alkyl,[1,4] but the observed sharp hydride resonances suggest there is no measurable dynamic insertion–elimination equilibrium. However, toluene or *N,N*-dimethylacetamide solutions of (**1**) react with 1 atm of CO at 20 °C within 30 min according to the stoicheiometry of equation (1); the product, which arises from consecutive olefin and CO insertion reactions, is characterized by elemental analysis and spectroscopic data [ν_{CO} 1935 (terminal, *trans*) and 1604 cm^{-1} (acyl)]. There is no metal hydride and in C_6D_6 solution the $^{31}P\{phenyl\}$ signal now appears as a singlet at 30.6 p.p.m. The $^{13}C\{^1H\}$ n.m.r. spectrum (Table 1) shows five resonances for the saturated carbons and two attributable to free olefin, the multiplicities that arise from associated hydrogens being determined by a single-frequency-off-resonance-decoupling (S.F.O.R.D.) experiment; the co-ordinated CO ligands and acyl carbon



(1) (2)

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† ^1H N.m.r. data in the early report (ref. 3) were interpreted in terms of a mixture of isomers; however, more extensive data, including $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ measurements, are consistent with the presence of (**1**) only, in which H_a and H_b are in different environments to H_d and H_c, respectively: ^1H n.m.r. (Me_4Si; C_6D_6): δ 3.63 and 3.45 (H_b, H_c), 3.93 and 3.20 (H_a, H_d), 0.90 ($-CH_2$), and −8.9 (t, J_{PH} 24 Hz); ^{31}P n.m.r. (85% H_3PO_4; $CD_3C_6D_5$; +30 to −60 °C): δ 40.6 p.p.m. downfield ({^1H}, s; {selective, phenyl}, d, J_{PH} 24 Hz).

Table 1. N.m.r. data[a] for $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ (**2**).

$\delta(^{13}C)$/p.p.m., assignment[b]		$\delta(^1H)$, assignment[c]	
32.3 (t)	C-3	0.86 (d,m)	7a
43.3 (d)	C-4	1.04 (d,d,d)	3n
46.8 (d)	C-1	1.13 (d,d,m)	7s
49.1 (t)	C-7	1.25 (d,d)	3x
60.5 (d)	C-2	2.52 (m)	4
132.9 (d)	C-6	2.62 (m)	1
136.5 (d)	C-5	4.53 (d,d,d)	2x
203.3 (t)[d]	C-9	5.85 (d,d)	6
243.0 (t)[d]	C-8	6.13 (d,d)	5

[a] In C_6D_6 at 25 °C; ^1H n.m.r. (Me_4Si) at 400 MHz; ^{13}C n.m.r. (Me_4Si) at 100 MHz. [b] Multiplicity abbreviation in parentheses for C-1 to C-7 gives splitting observed from S.F.O.R.D. experiment; assignment based on this and data from refs. 5, 6. [c] n = *endo*, x = *exo*, s and a = *syn* and *anti* to the double bond. J(H–H) values Hz: (1–2x) 3.6, (1–6) 2.8, (2x–3n) 5.0, (2x–3x) 9.0, (3n–3x) 11.0, (3n–7s) 2.0, (3x–4) 3.9, (4–5) 3.0, (4–7a) 2.0, (5–6) 5.5, (7a–7s) 8.0; others not resolved. [d] $^2J(C^9\text{–}P)$ 15.1 Hz; $^2J(C^8\text{–}P)$ 7.6 Hz.

appear as triplets owing to coupling to the two phosphines. The ^1H n.m.r. spectrum (Table 1) shows nine resolved resonances of equal intensity for the organic moiety; a series of selective homonuclear decoupling experiments were done to determine the coupling constants and assign the resonances.[7,8] The parity of the J(H–H) values of (**2**) with those of 2-substituted norbornenes[7] suggests very little distortion of the norbornenoyl moiety on co-ordination; the ^3J(1–2x) value is in the 3—4 Hz range found for coupling between a bridgehead proton and an *exo* position[7] and implies that the acyl substituent occupies the thermodynamically less favoured *endo* position.

Reaction (1) proceeds cleanly and irreversibly with no intermediate or free PPh_3 being detected, and the *in situ* product had n.m.r. parameters identical to those of the isolated complex. The required alkenyl intermediate must be generated, however, by stereospecific incorporation of the original hydride into the diene, while the kinetic lability of Ru–C σ-bonds[9] would account for its non-detectability. Reaction of CO with hydrido(ethylene) derivatives of molybdenum and rhodium cyclopentadiene complexes[10,11] leads simply to the hydrido(carbonyl) *via* displacement of the alkene, although the insertion reactions to give isolable ethyl products are promoted by addition of other ligands (PPh_3,[10] C_2H_4[11]); complex (**1**), however, is inert toward PPh_3 possibly for steric reasons. The important migratory insertion involving hydride and olefin is in general poorly understood; the discovery of reaction (**1**) with extension to analogous hydrido(diene) species should allow for a study of the factors (electronic and steric) governing such a process.

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