A Novel Type of Diazadiene Co-ordination Behaviour. X-Ray Structure of a Rhodium Complex with Bridging Azomethine Groups

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The single crystal X-ray diffraction study of the complex with seemingly simple stoicheiometry (dad)RhCl (dad = Bu^tN_CH-CH_NBu^t), obtained from the room temperature reaction of $[(C_2H_4)_2RhCl]_2$ with dad, indicates a cleavage of the central C-C bond in one out of two dad ligands to result in two bridging azomethine groups in $[(dad)CIRh(\mu-HC=N-Bu^t)_2Rh(\mu'-Cl)]_2$ (4).

It is well established that diazadienes (dad = RN=CR'-CR'= NR) can co-ordinate to metals in formally low oxidation states in many other geometries than the simple N,N'-chelates (4e-donor);¹ e.g., as a 5e-donor with a coupling of two dads in '(dad)₂Mo₂(CO)₆'² [similar to the coupling of L = RN=CH-CO₂R in L₂Fe₂(CO)₆]³, as a 6e-donor in (dad)Fe₂(CO)₆⁴ and similar molecules, or as an 8e-donor in some ruthenium complexes.⁵ So far no fragmentation of dad ligands has been observed under any reaction conditions with low valent metals.

While treatments with dad of $[(cod)RhCl]_2$ (cod = cyclooctadiene) and $[(OC)_2RhCl]_2$ afford substitution products with chelating or bridging dad ligands,⁶ the ethylene complex $[(C_2H_4)_2RhCl]_2$ (1) behaves differently. Treatment of (1) with 2 (dad $[(2) R = Bu^t, R' = H; or (3) R = Pr^i, R' = H]$ at room temp. in acetone leads to complexes of stoicheiometry (dad)RhCl, which are not just simple chloro-bridged dimers with dad in place of the two olefin ligands. The i.r. spectra show bands for terminal and bridging chloro-ligands (295, 270, 245, and 222 cm⁻¹) and several absorptions in the v(C=N) region (1535, 1555, and 1572 cm⁻¹).

$$[(C_{2}H_{4})_{2} Rh Cl]_{2} RN=CR'-CR'=NR$$
(1)
(2); R = Bu^t, R' = H
(3); R = Pr¹, R' = H
[(dad)Cl Rh (μ -R'C=NR)_{2} Rh(μ '-Cl)]_{2}
(4); R = Bu^t, R' = H
(5); R = Pr¹, R' = H

In the ¹H n.m.r. spectrum complex (4) ($R = Bu^t, R' = H$) exhibits two absorptions for the azomethine protons R' [δ 10.1 (J_{Rh-H} 5 Hz) and 8.5 (J_{Rh-H} 1.5 Hz)] and two

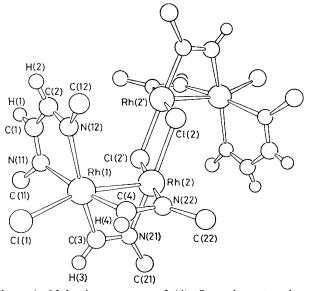


Figure 1. Molecular structure of (4). Some important bond lengths and angles are Rh(1)–Rh(2) 2.596(1), Rh(1)–Cl(1) 2.461(2), Rh(1)–N(11) 2.232(5), N(11)–C(1) 1.256(9), C(1)–C(2) 1.454(10), Rh(1)–C(3) 1.955(5), C(3)–N(21) 1.269(7), Rh(2)– N(21) 2.013(4), Rh(2)–Cl(2) 2.383(2), Rh(2)–Rh(2') 3.554(1), and C(3)–C(4) 2.563Å; Cl(1)–Rh(1)–Rh(2) 160.8(0), Cl(1)– Rh(1)–C(3) 96.6(2), Cl(1)–Rh(1)–C(4) 95.5(2), Rh(1)–C(3)–N(21) 113.6(4), C(3)–N(21)–Rh(2) 105.6(3), N(21)–Rh(2)–Rh(1) 71.1(1), N(21)–Rh(2)–N(22) 85.4(2), N(22)–Rh(2)–Cl(2) 95.7(1), N(11)– Rh(1)–N(12) 75.9(2), C(3)–Rh(1)–Rh(2) 69.7(2), Rh(1)–N(11)– C(1) 110.9(4), N(11)–C(1)–C(2) 121.1(6), and N(21)–C(3)–H(3) 122.6(5)°. The Bu^t groups on N(11), N(12), N(21), and N(22) have been omitted for clarity.

signals for Bu^t protons (δ 1.3 and 1.45). A double set of signals is also observed for complex (5) (R = Pr¹, R' = H). We have therefore investigated complex (4) by single crystal X-ray structure analysis.

Crystal data: C40H80Cl4N8Rh4, monoclinic, space group $P2_1/n, a = 15.069(3), b = 11.587(3), c = 15.114(3) \text{ Å}, \beta =$ 96.91(2)°, Z = 2, M = 1226.7, $D_c = 1.56$ g cm⁻³. Least squares refinement, based on 3848 observed reflections (4631 symmetry independent) measured on a Syntex P2₁ diffractometer and unit weights converged to R = 0.0368 ($R_w =$ 0.038).⁷[†] The molecular structure is shown in Figure 1. The tetranuclear complex consists of two enantiomorphic halves connected via chloro-bridges. Each half carries one normal chelating dad ligand, whereas the other dad has undergone oxidative addition with concomitant rupture of the central C-C bond. While in many low valent metal dad complexes the central C-C bond is shortened because of back bonding (down to 1.36 Å)¹ rhodium shows another way to get rid of high electron density. To our knowledge this is the first example of C-C bond cleavage in a simple, non-strained diene system; the bond cleavage of strained ring systems by rhodium is of course well established.8

Perhaps the most interesting feature of the reaction is the easy formation of bridging azomethine groups; this is in contrast to the low stability usually observed for known formyl complexes.⁹ The reaction invokes the possibility of another type of hydroformylation reaction.

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[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.