Evidence for the Ready Insertion of Rhodium into a Carbon–Hydrogen Bond of Ethylene; Crystal and Molecular Structure of μ-But-2-ene-μ-ethylene-bis-(η^5-1-methylindenyl)dirhodium

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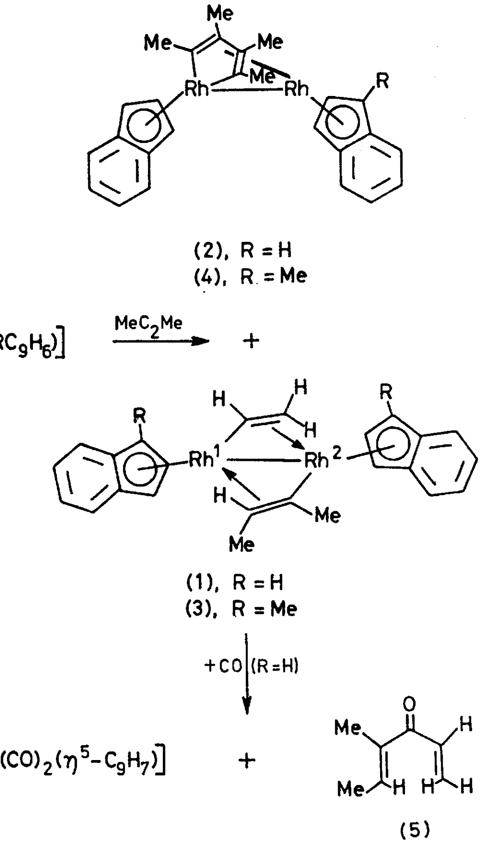
Summary But-2-yne reacts with [Rh(C_2H_4)$_2$(η^5-C_9H_7)] or [Rh(C_2H_4)$_2$(η^5-1-MeC_9H_6)] to give respectively [Rh$_2$-(CH=CH_2)(CMe=CHMe)(η^5-C_9H_7)$_2$], [Rh$_2$(C_4Me$_4$)(η^5-C_9H_7)$_2$], [Rh$_2$(CH=CH_2)(CMe=CHMe)(η^5-1-MeC_9H_6)], and [Rh$_2$-(C_4Me$_4$)(η^5-1-MeC_9H_6)$_2$] the structure of the 1-methyl analogue of the divinyl complex being established by *X*-ray crystallography; treatment of the dirhodium divinyl complex with carbon monoxide affords [Rh(CO)$_2$(η^5-C_9H_7)] and the ketone CH_2=CH·COC(Me)=C(H)Me.

THERE is only one previously reported example of the homogeneous oxidative insertion of a transition metal into a carbon–hydrogen bond of ethylene, and that is in the reaction of C_2H_4 with Os$_3$(CO)$_{12}$,[1] which only occurs at elevated (125 °C) temperatures. Clearly such a reaction is of considerable interest, particularly if this could be achieved under milder conditions. In continuing to explore the enhanced[2] reactivity of the indenyl complex [Rh(C_2H_4)$_2$(η^5-C_9H_7)] towards ligand substitution, we have observed an unusual reaction with but-2-yne leading to a ready attack on C_2H_4.

Reaction (room temperature; 2 days) of bis(ethylene)-(η^5-indenyl)rhodium with an excess of but-2-yne led to the catalytic formation of hexamethylbenzene, and two crystalline dinuclear (mass spectroscopy) complexes (**1**) and (**2**), which were separated by column chromatography (ethylene was the only volatile material evolved). Attempts to define the structure of (**1**) solely on the basis of the ^1H, ^{13}C, and ^{103}Rh n.m.r. data† were not successful; moreover, suitable crystals for *X*-ray diffraction studies could not be obtained. The related reactions of bis(ethylene)(η^5-1-methylindenyl) rhodium were therefore studied, resulting in the isolation of the 1-methyl substituted analogues (n.m.r.) (**3**) and (**4**).‡



SCHEME

A single crystal *X*-ray diffraction study of (**3**) established the structure shown in the Figure. *Crystal data*: $C_{26}H_{28}Rh_2$, $M = 546{\cdot}32$, triclinic, space group $P\bar{1}$, $a = 8{\cdot}302(2)$, $b = 15{\cdot}036(4)$, $c = 18{\cdot}351(5)$ Å, $\alpha = 86{\cdot}03(2)$, $\beta = 100{\cdot}66(2)$, $\gamma = 104{\cdot}67(2)°$, $U = 2177(1)$ Å^3, $D_c = 1{\cdot}67$ g, cm^{-3} $Z = 4$, $D_m = 1{\cdot}63$ (flotation) g cm^{-3}, μ(Mo-K_α) $= 14{\cdot}9$ cm^{-1}. Data (6928 with intensities $\geqslant 1{\cdot}96\sigma$) were recorded on a Syntex P2$_1$ four-circle diffractometer; the structure was solved by heavy atoms and refined by block-matrix least squares techniques to a current conventional *R* index of 0·057.§

There are two independent and identical dimers in the asymmetric unit; one of them is illustrated in the Figure. The Rh–Rh distance is 2·645 Å (average), which lies within the range expected for metal–metal bonding. The geometry about each rhodium atom is distorted octahedral, with three positions occupied by the η^5-indenyl ligand, one by the rhodium–rhodium bond, one by a carbon of a vinyl group, and one by the π-donating bond of the vinyl ligands. The bond length parameters [Rh(1)–C(04) 2·033, Rh(2)–C(01) 2·105, C(04)–C(05) 1·379, C(01)–C(02) 1·429 Å] for the rhodium–vinyl systems are consistent with the illustrated bonding arrangement involving little multiple bonding between the rhodium and α-carbon atoms.

Examination of the ^1H and ^{13}C n.m.r. spectra of (**2**) and (**4**) suggested that these complexes have the illustrated structure where a rhodacyclopentadiene system is co-ordinated to a second η^5-indenyl rhodium group. Complexes of this type have been previously observed[3] as products from the reaction of diphenylacetylene with dicarbonyl(η^5-cyclopentadienyl)rhodium. The formation of the bridged dinuclear vinyl complexes (**1**) and (**3**) is without precedent, and must involve cleavage of an ethylenic carbon–hydrogen bond under very mild conditions, resulting in the formation of Rh–H and RhCH=CH$_2$ bonds. This must then be followed by the *cis*-insertion of a co-ordinated but-2-yne into the generated Rh–H bond to form the second rhodium vinyl arrangement, i.e. *cis*-RhCMe=CHMe, present in (**3**). It is difficult to understand these reactions if they take place with mononuclear species. There is no obvious

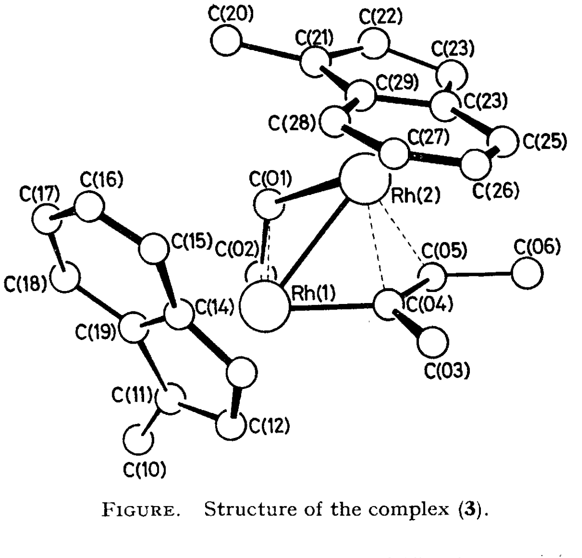


FIGURE. Structure of the complex (**3**).

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† A mixture of isomers *syn* and *anti* with respect to the indenyl methyl substitute is formed in the case of (**4**), whereas only one isomer of (**3**) is produced.

‡ The ^{103}Rh spectrum (C_6D_6; INDOR) of (**1**) showed resonance [reference used X (^{103}Rh) 3·16 MHz.] at −574 [Rh$_2$ *J*(Rh^{1}Rh^2) 17·0 Hz] and −560 [Rh^1, *J*(Rh^{1}Rh^2) 17·0 Hz] p.p.m.

§ 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.

reason why a molecule such as [Rh(C_2H_4)(MeC_2Me)(η^5-1-Me-C_9H_6)] should be so reactive, and even if reaction did occur it would then be necessary to transfer a vinyl group from [Rh(CH=CH_2)(CMe=CHMe)(η^5-1-Me-C_9H_6)] to another rhodium centre in order to generate complex (**3**), and by analogy (**1**). We believe that it is more likely that oxidative attack on co-ordinated ethylene takes place within a polynuclear species.

The dinuclear divinyl complexes (**1**) and (**3**) are effective catalysts¶ for the trimerisation of acetylenes, for example, the conversion of but-2-yne into hexamethylbenzene and 2,2-dimethylbut-1-yne into 1,2,4-tri-t-butylbenzene, and the mechanisms of these reactions are being studied. Of considerable interest is the reaction (room temperature; hexane) of (**1**) with carbon monoxide to form (rapidly) dicarbonyl(η^5-indenyl)rhodium and the $\alpha\beta$-unsaturated ketone (**5**) (Scheme), which was identified by g.l.c.–mass spectrometry and n.m.r. spectroscopy. There was no evidence for the formation of symmetrical divinyl ketones, suggesting that the organic product is formed *via* an initial carbonyl insertion followed by reductive elimination from adjacent bonded metal centres. This result is particularly interesting in the light of recent observations[4] with diosmium complexes.

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¶ The complexes (**2**) and (**4**) are not catalysts under comparable conditions for acetylene trimerisation. In the catalytic reactions of (**1**) and (**3**) the inert complexes (**2**) and (**4**) are slowly formed resulting in a decline in activity.

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