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Preliminary communication

Vinyl-plus-vinyl coupling in rhodium complexes: formation of $[(C_5Me_5)RhBr(\eta^3\text{-}syn\text{-}1\text{-methylallyl})]$ by reaction of $[(C_5Me_5)RhBr_2(Me_2SO)]$ with vinylmagnesium bromide in homogeneous solution [☆]

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Abstract

The *syn*-1-methylallyl complex $[(C_5Me_5)RhBr(\eta^3\text{-}CH_2CHCHMe)]$ was obtained by reaction of $[(C_5Me_5)RhBr_2(Me_2SO)]$ with vinylmagnesium bromide, via a vinyl-plus-vinyl coupling. This reaction is related to the vinyl-plus-vinyl coupling reactions of vinyl bromide on rhodium particles under Fischer–Tropsch conditions.

Keywords: Rhodium; Cyclopentadienyl; Coupling; Vinyl; Fischer–Tropsch reaction

We are currently engaged in evaluating how closely certain reactions that are heterogeneously catalyzed by rhodium can be mimicked by model complexes under homogeneous conditions. In this connection we recently proposed that Fischer–Tropsch reactions over heterogeneous rhodium catalysts give alkenes by a mechanism involving the interaction (polymerization) of surface alkenyl species with surface methylenes [1]. This hypothesis was based on detailed studies of the reactions of model dirhodium complexes, such as $[\{(C_5Me_5)Rh\text{-}\mu\text{-}CH_2\}_2R(L)]^+$ and $[\{(C_5Me_5)Rh\text{-}\mu\text{-}CH_2\}_2(CH{=}CH_2)_2]$ in solution [2].

The Fischer–Tropsch reactions over heterogeneous rhodium–ceria–silica catalysts using doubly labelled vinyl bromide ($^{13}CH_2{=}^{13}CHBr$) as probe showed that considerable $^{13}C_2$ was incorporated into the alkenes. This was in strong preference to $^{13}C_1$ or $^{13}C_3$, which were only present at natural abundance levels. However, substantial amounts of $^{13}C_4$ were observed, both in the C_4 fraction (e.g. but-1-ene was 35% $^{13}C_4$-labelled), as well as in the higher olefins [1].

The $^{13}C_4$ and related species must arise via a dimerisation on the rhodium surface of a $^{13}C_2$ species, presumably a surface vinyl–rhodium. Because such species are expected to have only transient existence, they must undergo coupling with remarkable ease. We have now tested this hypothesis using a homogeneous model system, and we find that vinyl-plus-vinyl coupling does indeed occur very readily within mononuclear rhodium complexes.

Vinylmagnesium bromide (1.5 cm^3; Aldrich, 1 M in THF) was slowly added at −80°C to an orange-red solution of $[(C_5Me_5)Rh(Me_2SO)Br_2]$, **1**, made from $[\{(C_5Me_5)RhBr_2\}_2]$ (0.20 g, 0.25 mmol) and Me_2SO (0.15 cm^3) in dry THF (20 cm^3). The mixture was allowed to warm to room temperature, then was hydrolyzed (H_2O, 2 cm^3), the volatiles were removed and the residue extracted with diethyl ether. The ethereal extract was chromatographed (neutral alumina column) to give the analytically pure *syn*-1-methylallyl complex $[(C_5Me_5)Rh(\eta^3\text{-}CH_2CHCHMe)Br]$, **2**, in 82% yield. The related complex $[(C_5Me_5)Rh(\eta^3\text{-}CH_2CHCHMe)Cl]$ was formed similarly from $[\{(C_5Me_5)RhCl_2\}_2]$ in 52% yield. Complex **2** was identified spectroscopically [3], and by comparison with $[(C_5Me_5)Rh(\eta^3\text{-}CH_2CHCHMe)Cl]$ which one of us had made earlier by reaction of $[\{(C_5Me_5)RhCl_2\}_2]$ with butadiene in the pres-

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[☆] Dedicated to Professor Fausto Calderazzo on his 65th birthday, with best wishes.

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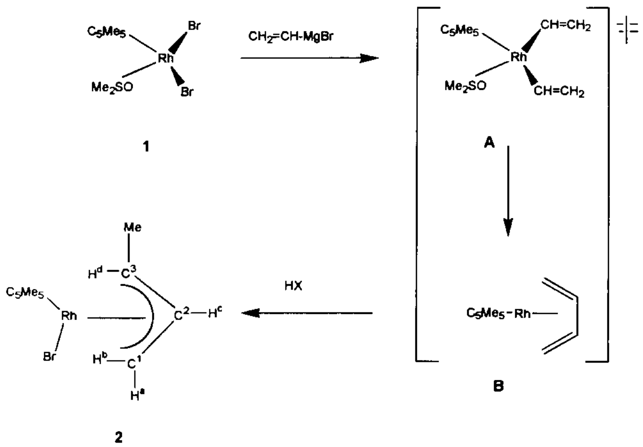

Scheme 1.

ence of ethanol and base [4]. That also gave the *syn*-1-methylallyl, which is presumably the thermodynamically favoured isomer. Thus it is not unreasonable to assume that intermediates in the reactions of $[\{(C_5Me_5)RhX_2\}_2]$ with the vinyl Grignard reagent are the di-σ-vinyl and the η^4-butadiene complexes, and that the reaction proceeds as shown in Scheme 1.

Thus one may conclude that vinyl-plus-vinyl coupling occurs readily, and via vinyl–rhodium species, in situations as different as those involving homogeneous mononuclear rhodium complexes in solution, or rhodium particles under heterogeneous gas-solid phase reactions. In some very interesting experiments under ultra-high vacuum conditions, White and coworkers have recently demonstrated that the coupling of two vinyls to butadiene also takes place on clean metal single-crystal surfaces (e.g. Pt(111) [5].

The coupling of two vinyl groups on a diruthenium centre has also been demonstrated; in that case a dehydrogenation occurs to give a diruthenacyclopentadiene [6]. A μ-η^4-coordinated butadiene has also been obtained by combining a μ-, σ-vinyl and an ethylene on a diruthenium centre; here again hydrogen is lost [7].

Acknowledgements

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References and notes

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[3] Complex **2**: ^{1}H NMR ($CDCl_3$): H^a: 3.09 (1H; d, J(ac) = 6.5 Hz); H^b: 3.05 (1H; d, J(bc) = 10 Hz); H^c, H^d: 3.70 (2H; m); H^e: 1.51 (3H; d, J(de) = 6 Hz); C_5Me_5; 1.70 (15H; s). ^{13}C NMR ($CDCl_3$): C^1: 56.1 (d, J(Rh–C) = 11 Hz); C^2: 94.85 (d, J(Rh–C) = 6.5 Hz); C^3: 70.2 (d, J(Rh–C) = 8.0 Hz); 17.95 (Me, s); 9.7 ($C_5\mathit{Me}_5$, s); 97.7 (C_5Me_5 d, J(Rh–C) = 6 Hz). Mass Spec. FAB$^+$: m/e 373 $(M)^+$ 10%; m/e 372 $(M{-}H)^+$ 12%; m/e 293 $(M{-}Br)^+$, 100%; m/e 318 $(M\text{-}\eta^3\text{-}CH_2CHCHMe)^+$, 33%; m/e 237 $(M{-}Br\text{-}\eta^3\text{-}CH_2CHCHMe)^+$, 62%. Anal. Calc. for $C_{14}H_{22}BrRh$: C, 45.1; H, 5.9; Br, 21.4. Found: C, 45.0; H, 5.9; Br, 21.2%.

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