Unprecedented Reactivity of Vinylidene Complexes with Diazomethane: Insertion of the Methylene Group into a C–H Bond

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[(η-C$_5$H$_5$)Ru{Ph$_2$PCH(Me)CH(Me)PPh$_2$}(C=CHR)]PF$_6$ (R = Ph or Bu^t) react with diazomethane to give the corresponding methylvinylidene complexes [(η-C$_5$H$_5$)Ru{Ph$_2$PCH(Me)CH(Me)PPh$_2$}{C=C(Me)R}]PF$_6$; this novel type of reactivity suggests an alternative mechanism for the formation of branched hydrocarbons in the Fischer–Tropsch synthesis.

The reactivity of the alkylidenecarbene (vinylidene) ligand in transition metal complexes has recently attracted much attention both from a practical[1] and theoretical[2] point of view. The reaction of transition metal vinylidene complexes with diazomethane is of particular interest with regard to the mechanism of the carbon–carbon bond formation in the Fischer–Tropsch synthesis.[3,4] Previous studies have revealed two pathways for the reaction of vinylidene complexes with diazomethane (Scheme 1): electrophilic attack at the alkylidene carbon atom (route i) to give a cyclopropylidene complex;[4] or nucleophilic attack at the carbene atom of the vinylidene ligand (route ii) to give an allene complex.[5] The
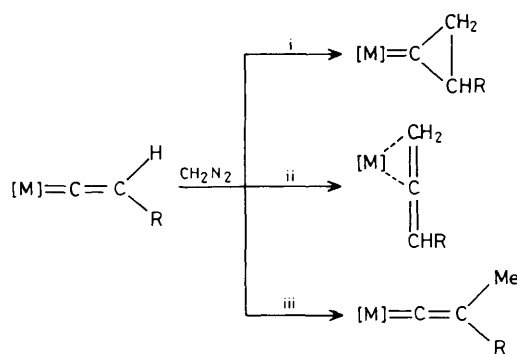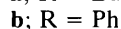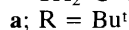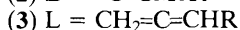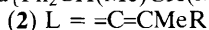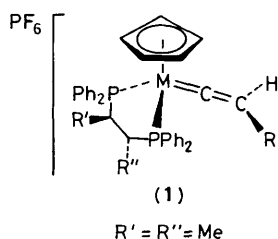
first kind of reaction was found for bridging alkylidenecarbene ligands,[4] but it was the second type of reactivity which was of particular interest to us as we have recently synthesized optically active complexes of the type (1) and found in some cases large differences in the population of the two possible diastereoisomeric conformers of (1).[6] Thus, treatment of the complexes (1) with suitably substituted diazocompounds was viewed as a possible synthetic route to optically enriched allenes. However, unexpectedly, treatment of ruthenium vinylidene complexes (1) with diazomethane yielded methyl substituted vinylidene complexes (Scheme 1, route iii), as described below.

A tetrahydrofuran (THF) solution of the complex [(η-C$_5$H$_5$)Ru{Ph$_2$PCH(Me)CH(Me)PPh$_2$}{C=CH(Bu^t)}]PF$_6$[†] (1a) was treated with excess of ethereal CH$_2$N$_2$ for 16 h at room temperature. The crude reaction mixture was dried *in vacuo*, dissolved in CH$_2$Cl$_2$, filtered over Celite, and dried again. ^{31}P N.m.r. studies of the crude reaction mixture revealed the presence of three major components: unchanged

Scheme 1

(1)

R' = R'' = Me

[(η-C₅H₅)Ru{Ph₂CH(Me)CH(Me)PPh₂}(L)]PF₆

$$[(\eta\text{-}C_5H_5)Ru\{Ph_2CH(Me)CH(Me)PPh_2\}(L)]PF_6$$

(2) L = =C=CMeR
(3) L = CH₂=C=CHR
a; R = Buᵗ
b; R = Ph

(1a) [~25%, δ(P_A) 77.3, δ(P_B) 71.5 p.p.m., J_{PP} 37.8 Hz]; (2a) [~70%, δ(P_A) 74.1, δ(P_B) 70.2 p.p.m., J_{PP} 39.6 Hz]; and complex (A) [~5%, δ(P_A) 73.2, δ(P_B) 69.8 p.p.m. J_{PP} 40 Hz]. Trace amounts of two other unidentified products were also observed. Attempts to obtain the major product (2a) in a pure form by fractional crystallization were unsuccessful. Structure (2a) for the major product was inferred from spectroscopic evidence† and was established by spectroscopic comparison with an authentic sample prepared by literature methods.[7,8] The absence of the allene complex (3a) in the reaction mixture was established by ³¹P n.m.r. spectroscopy by addition of an authentic sample of (3a)‡ to the crude reaction mixture; the nature of the product (A) has not yet been established.

A similar reaction was observed for the analogous complex (1b). In this case about 75% conversion had been reached in THF after 16 h at room temperature. The methylbenzylidene carbene complex (2b) was formed in about 50% yield, as indicated by ³¹P n.m.r. studies of the crude reaction mixture. Again (2b) was identified by comparison with authentic material.§ In this reaction about 25% of a second compound is formed, which has not yet been identified. Similarly, in this case none of the allene complex (3b) was observed.¶

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‡ (3a) was prepared starting with t-butylallene and [(η-C₅H₅)Ru{Ph₂PCH(Me)CH(Me)PPh₂}]Cl (ref. 9) in the presence of NH₄PF₆ in methanol solution (ref. 10): ³¹P n.m.r. δ(CD₂Cl₂): 78.2 and 70.7 p.p.m. (d, J_{PP} 43.3 Hz); ¹H n.m.r. δ(CD₂Cl₂): 0.64 (s, 9H), 0.64 (dd, 3H, overlapped with the previous signal), 0.86 (dd, J_{HH} 6.6, J_{PH} 13.1 Hz, 3H), 1.18 (m, 1H), 2.12 (m, 1H), 2.46 (m, 1H), 2.67 (m, 1H), 4.56 (s, 5H), 6.57—7.84 (m, 20H); ¹³C n.m.r., δ(CD₂Cl₂): 14.6 (d, J_{PC} 3.6 Hz, CH₂) overlapped with 14.6 (dd, J_{PC} 4.6 and 17.9 Hz, Me), 15.3 (dd, J_{PC} 4.5 and 17.7 Hz, Me); 34.7 (dd, J_{PC} 16.3 and 31.6 Hz, CH) 40.5 (dd, J_{PC} 17.6 and 32.8 Hz, CH), 91.1 (s, C₅H₅); 123—134 (m, Ph), 147.8 (d, J_{PC} 7.2 Hz, =C=).

§ Complex (2b) was prepared starting with [(η-C₅H₅)Ru{Ph₂PCH(Me)CH(Me)PPh₂}(C≡CPh)] (ref. 11) using the same procedure used for (2a). ³¹P n.m.r. δ(CD₂Cl₂): 71.1 and 77.1 (d, J_{PP} 35.7 Hz); ¹H n.m.r. δ(CD₂Cl₂): 0.83 (dd, J_{HH} 6.6, J_{PH} 14.0 Hz, 3H), 1.04 (dd, J_{HH} 6.4, J_{PH} 13.6 Hz, 3H), 1.30 (s, 3H), 2.62 (m, 1H), 2.73 (m, 1H), 5.17 (s, 5H), 6.70–7.76 (m, 25H); ¹³C n.m.r. δ(CD₂Cl₂): 8.2 (s, Me), 15.1 (m, Me, two overlapped signals), 38.2 (J_{PC} 14.8 and 34.2 Hz, CH), 38.7 (dd, J_{PC} 15.4 and 32.8 Hz, CH), 93.5 (s, C₅H₅), 125—134 (m, Ph and =CMePh), 356.4 (t, J_{PC} 13.5 Hz, =C=).

¶ The preparation of (3b) is analogous to that of (3a). ³¹P n.m.r. δ(CD₂Cl₂): 68.4 and 80.3 (d, J_{PP} 42.1 Hz); ¹H n.m.r. δ(CD₂Cl₂): 0.66 (dd, J_{HH} 6.6, J_{PH} 12.9 Hz, 3H), 0.91 (dd, J_{HH} 6.5, J_{PH} 13.3 Hz, 3H), 1.55 and 2.51 (m, =CH₂), 2.26 (m, 1H), 2.50 (m, 1H), 4.78 (s, 5H) 6.56—7.88 (m, 25H); ¹³C n.m.r. δ(CD₂Cl₂): 14.9 (d, J_{PC} 3.8 Hz, =CH₂), 14.7 (dd, Me, overlapped with the previous signal), 15.2 (dd, J_{PC} 4.4 and 17.5 Hz, Me); 36.2 (dd, J_{PC} 16.0 and 32.1 Hz, CH), 38.6 (dd, J_{PC} 7.4 and 33.0 Hz, CH), 91.7 (s, C₅H₅), 125—137 (m, Ph).

To the best of our knowledge the reactivity of the ruthenium complexes (1a) and (1b) with diazomethane (Scheme 1, route iii) has no precedents in the literature. In fact, even unsaturated organic systems strongly prefer addition to the double bond rather than insertion into any C–H bond.[12] The observed reactivity could be a consequence of the electrophilic[13] nature of the carbenoid methylene group derived from the decomposition of diazomethane. Attack on the alkylidene carbon atom and proton migration would eventually lead to the formation of the methyl group. It is noteworthy that the reaction takes place also on a carbon atom directly bound to a quaternary carbon centre and is therefore sterically hindered. Another reaction pathway, however, appears possible as a consequence of the acidic† nature of the hydrogen atom of the alkylidenecarbene moiety. Formation of the electrophilic methylating agent[14] MeN₂⁺ followed by attack on the intermediate nucleophilic ruthenium acetylide complex[7] would also lead to the observed reaction product.

This novel type of reactivity shown by the ruthenium vinylidene complexes (1a) and (1b) may be relevant to the mechanism of carbon–carbon bond formation in the Fischer–Tropsch synthesis[3] or in related reactions, e.g., the conversion of methanol into hydrocarbons.[15] In particular, the insertion of a carbene into a C–H bond of a vinylidene intermediate would lead to the direct formation of branched hydrocarbon products, as a possible alternative to the formation of intermediate cyclopropylidene species.[3] Experiments to test the generality of this kind of reaction, particularly for analogous iron complexes, are in progress.

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