Tetrahedron Letters,Vol.24,No.36,pp 3935-3936,1983
Printed in Great Britain
0040-4039/83 $3.00 + .00

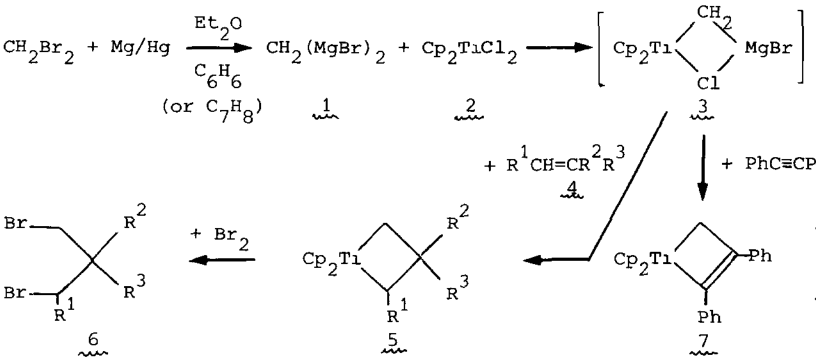
METHYLENEDIMAGNESIUM DIBROMIDE AS PRECURSOR OF METAL CARBENE COMPLEXES, PREPARATION OF TITANACYCLOBUTANES.

J.W Bruin, G. Schat, O S Akkerman and F Bickelhaupt*
Vakgroep Organische Chemie, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract. The reaction of $CH_2(MgBr)_2$ with Cp_2TiCl_2 gives a titanium methylene complex which, similar to Tebbe's reagent, forms four-membered titana-heterocycles with alkenes and alkines.

Methylene di-Grignard reagents were first prepared in 1926 by Emschwiller.[1] Their synthesis was considerably improved by Cainelli et al., who also investigated their application in carbonyl-methylenation reactions [2] It occurred to us that these reagents might open a direct access to transition metal carbene complexes, a class of compounds which for a variety of reasons currently draws much attention [3] A communication by Eisch and Piotrowski[4] on the application of a methylenedizinc reagent for the preparation of the analogue $Cp_2TiCH_2\ ZnX_2\ (THF)_x$ of Tebbe's reagent, $Cp_2TiCH_2AlClMe_2$,[3a] prompts us to report our preliminary results on the reaction of $CH_2(MgBr)_2$ (1) with Cp_2TiCl_2 (2), in the presence of alkenes or alkines, titanacyclobutanes or titanacyclobutenes, respectively, are formed

According to Cainelli at al.,[2] 1 can be obtained in 50-60% yield by the reaction of dibromomethane with magnesium amalgam in ether/benzene (ca 1 1) When 1 molar equivalent of 2 was added to a solution of 1 in ether/toluene at -20 °C, a dark red colour developed which is indicative of a Tebbe-type complex such as 3 With crude 1, which contains ethylene (4a) and propylene (4b) as byproducts from the formation reaction, the titanacyclobutanes 5a and 5b were formed directly.[5] This complication could be largely suppressed by evaporating the reaction mixture containing 1 to dryness before addition of 2 and of an alkene 4, under these conditions, no 5b and only traces of 5a (presumably derived from ethylene which is formed by decomposition of 3)[9] were observed. After evaporation of the reaction mixture, the titanacyclobutanes 5c-5g were identified by their NMR-spectra in toluene-d_8, and, in the case of 5d and 5e, by reaction with Br_2 to give 6d and 6e, respectively. Reaction of 3 with PhC≡CPh gave 7.[10]



a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = H$, $R^3 = Me$
c $R^1 = R^2 = H$, $R^3 = n\text{-}Bu$
d $R^1 = R^2 = H$, $R^3 = t\text{-}Bu$
e $R^1 = H$, $R^2 = R^3 = Me$
f $R^1 = R^3 = Me(cis)$, $R^2 = H$
g $R^1 + R^3 = (CH_2)_5$, $R^2 = H$

The reaction of 1 with Cp_2ZrCl_2 at -20 °C gave so far less clear-cut results. A rapid reaction analogous to that of 2 was indicated by the disappearance of the ^{1}H NMR signal of 1 (δ = -2.75 ppm, bs, $w_{1/2}$ ca 20 Hz, THF-d_8) and formation of a precipitate which reacted with Me_3SnCl to give $CH_2(SnMe_3)_2$ and with $Ph_2C{=}O$ to give $Ph_2C{=}CH_2$, however, it did not react with alkenes and did not give soluble products with PPh_3.[11]

Acknowledgement This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid (J.W.B.) from the Netherlands Organization for the Advancement of Pure Research (ZWO)

References and Notes

1. G. Emschwiller, Compt. rend., 183, 665 (1926).
2. F Bertini, P. Grasselli, G Zubiani and G. Cainelli, Tetrahedron, 26 1281 (1970), and references cited.
3. a) F.N. Tebbe, G.W. Parshall and G.S. Reddy, J Am. Chem Soc , 100, 3611 (1978); b) J.B. Lee, K.C. Ott and R.H. Grubbs, J. Am. Chem Soc , 104, 7491 (1982), c) W A. Hermann, Angew. Chem., 94, 118 (1982), d) R R. Schrock, Science 219, 13 (1983), e) C.P Casey, Reactive Intermediates, R.A. Moss and M Jones, Jr., Eds., Wiley, New York, 1982, vol 2, chapter 2.
4. J.J. Eisch and A. Piotrowski, Tetrahedron Letters, 24, 2043 (1983).
5. 5a[6] ^{1}H NMR (C_7D_8, 250 MHz) δ = 5.15 (s, 10H, Cp), 2.95 (AA'XX', 4H, α-CH_2), -0.19 (bm, 2H, β-CH_2). 5b ^{1}H NMR (C_7D_8, 250 MHz) δ = 5 39 (s, 5H, Cp), 5.25 (s, 5H, Cp), 3 05 (dd, ^2J ≈ 8.5 Hz, ^3J = 11 Hz, 2H, CHH), ca. 2 4-2.3 (partly obscured by C_7D_7H, CHH), 1 09 (d, ^3J = 6.5 Hz, 3H, CHMe), -0 17 (m, 1H, CHMe) 5c ^{1}H NMR (C_6D_6, 90 MHz) δ = 5.47 (s, 5H, Cp), 5 35 (s, 5H, Cp), 3.03 (dd, ^2J = 8.5 Hz, ^3J = 10 5 Hz, 2H, CHH), 2 16 (dd, ^2J = 8.5 Hz, ^3J ca. 8 Hz, 2H, CHH), 1 5-0 9 (m, 9H, n-Bu), -0.14 (m, 1H, CH-n-Bu) 5d ^{1}H NMR and ^{13}C NMR as reported.[7] 5e[6,8] ^{1}H NMR and ^{13}C NMR as reported[8] 5f· ^{1}H NMR (C_7D_8, 250 MHz) δ = 5.29 (s, 5H, Cp), 5.20 (s, 5H, Cp), 3.45 (m, 2H, α-CHMe, CHH), 2.29 (dd, ^2J = ^3J = 8 Hz, 1H, CHH), 1 55 (d, ^3J = 8 Hz, 3H, α-CH_3), 1.01 (d, ^3J = 6.5 Hz, 3H, β-Me), 0.00 (m, 1H, β-CHMe). 5g (C_7D_8, 250 MHz) δ = 5.34 (s, 5H, Cp), 5.25 (s, 5H, Cp), 3.64 (ddd, ^3J = 2 Hz, ^3J = ^3J = 12 Hz, 1H, α-$CHCH_2$), 3.46 (dd, ^2J = 8.5 Hz, ^3J = 12 Hz, 1H, CHH), 2 27 (dd, ^2J = ^3J = 8 5 Hz, CHH), -0.19 (m, 1H, β-$CHCH_2$). The assignments are based on decoupling experiments.
6 J.B. Lee, G.J. Gajda, W.P Schaefer, T R Howard, T Ikariya, D.A Straus and R H. Grubbs, J. Am. Chem. Soc., 103, 7358 (1981).
7. T.R. Howard, J.B. Lee and R.H Grubbs, J Am. Chem Soc., 102, 6876 (1980)
8. J.W.F.L. Seetz, G Schat, O.S. Akkerman and F. Bickelhaupt, Angew Chem , 95, 242 (1983).
9 On standing at -20 °C, 3 slowly decomposes. Apparently, MgX_2 is less effective in stabilizing the titanium carbene complex than $AlClMe_2$[3a] or ZnX_2[4]
10 F.N. Tebbe and R.L Harlow, J. Am. Chem. Soc., 102, 6149 (1980)
11. F.W Hartner, Jr , J. Schwartz and S M. Clift, J. Am. Chem Soc , 105, 640 (1983).

(Received in UK 12 July 1983)