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ACYL C–O BOND CLEAVAGE IN $Cp_2^{\star}TiCOR$ COMPOUNDS: FORMATION OF BENZENE DERIVATIVES BY $Cp^{\star}$-RING EXPANSION INVOLVING INCORPORATION OF THE ACYL CARBON ATOM ($Cp^{\star} = \eta^5$-C_5Me_5)

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Summary

Reaction of $Cp_2^{\star}TiR$ ($R = CH_3$, neo-C_5H_{11}) with CO gives labile acyl compounds $Cp_2^{\star}TiCOR$. The latter react with $(CpMo(CO)_3)_2$ to yield complexes $Cp_2^{\star}Ti(\eta^2$-$COR)(\mu$-$OC)MoCp(CO)_2$, which undergo acyl C–O band scission with concomitant formation of benzene derivatives at room temperature. The benzene derivatives are formed through ring expansion of the $Cp^{\star}$ ligand by incorporation of the R–C≡ fragment of the acyl group. The acyl oxygen is incorporated into a dimeric titanium oxo complex.

Introduction

Acyl complexes of early-transition and actinide elements often show η^2-coordination of the acyl function. An interesting aspect of these compounds is the reactivity of the η^2-acyl group, which includes a tendency to undergo carbon–carbon coupling [1,2]. Calculations have shown that the electrophilic nature of the acyl carbon atom is at the basis of this reactivity [3].

We have prepared labile tervalent titanium acyl compounds $Cp_2^{\star}Ti$-η^2-COR, ($Cp^{\star} = \eta^5$-$C_5(CH_3)_5$), and explored the behaviour of the acyl function in reactions with $(CpMo(CO)_3)_2$.

Results and discussion

Synthesis of $Cp_2^{\star}Ti$-η^2-COR

Paramagnetic compounds $Cp_2^{\star}TiR$ ($R = CH_3$, neo-C_5H_{11}) [4] readily reacted with one equivalent of CO at 0°C to yield paramagnetic acyl compounds I and II (eq. 1).

$$Cp_2^{\star}TiR + CO \rightarrow Cp_2^{\star}Ti\text{-}\eta^2\text{-}COR \qquad (1)$$
$$(\text{I}: R = CH_3;$$
$$\text{II}: R = \text{neo-}C_5H_{11})$$

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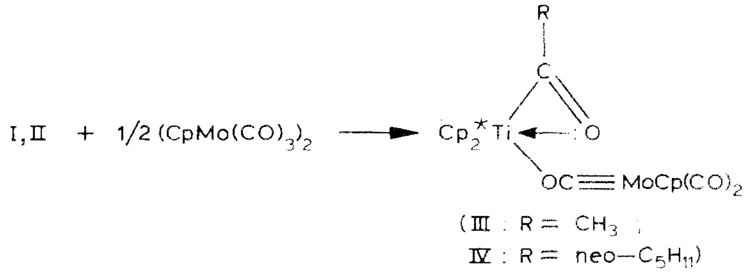
An excess of CO caused further reactions and deterioration of the product solutions. Attempts to isolate the acyl species in the solid state were unsuccessful owing to extensive decomposition of the compounds upon evaporation of the solvent. However, solutions freshly, prepared in situ appeared to be sufficiently pure for direct use.

Reactions of I, II with $(CpMo(CO)_3)_2$

Solutions of I and II reacted immediately with $(CpMo(CO)_3)_2$ (0.5 equivalent based on $Cp_2^{\star}TiCH_3$) to yield yellow precipitates of the diamagnetic species III and IV (eq. 2).

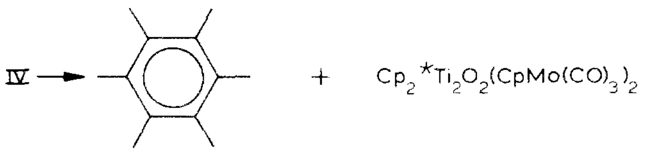


(2)

The ^1H NMR spectra indicated that III and IV were the only titanium-containing products formed in reaction 2.

Compounds III and IV showed a limited stability, which prevented their full characterization. However, the spectral data for III and IV taken together were consistent with the (η^2-acyl)(μ-CO) strucure shown in eq. 2. The IR spectrum of III showed a strong band at 1700 cm^{-1} (μ-CO) [5], a medium band at 1548 cm^{-1} (η^2-acyl) [3], and two bands at 1909 and 1809 cm^{-1} (terminal CO groups) [5]. Attempts to confirm the presence of η^2-acyl function in III by ^{13}C NMR spectroscopy were unsuccessful owing to the instability of III at room temperature and insolubility at lower temperatures. However, the ^{13}C NMR spectra of IV showed a resonance at δ 299 ppm, consistent with the presence of a η^2-acyl moiety [6].

Benzene or tetrahydrofuran solutions of III decomposed cleanly overnight to yield hexamethylbenzene as the major organic product (80% based on $Cp_2^{\star}TiCH_3$) and a titanium oxo compound, V, as the major organometallic compound (90% based on $(CpMo(CO)_3)_2$) as shown in eq. 3.



(3)

^{13}C-labelling of the acyl carbon in I yielded mono-^{13}C-enriched hexamethylbenzene with the label in the ring, demonstrating that hexamethylbenzene was formed by ring expansion of a Cp* ligand by incorporation of the "$CH_3C\equiv$" fragment of the acetyl group. The oxygen of the acetyl group remained attached at titanium and ended up in compound V. No other products which might have contained the acyl oxygen could be identified.

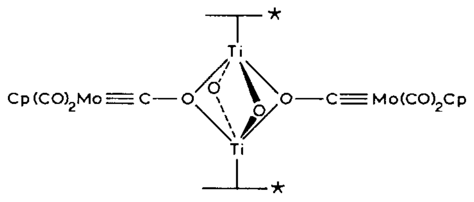


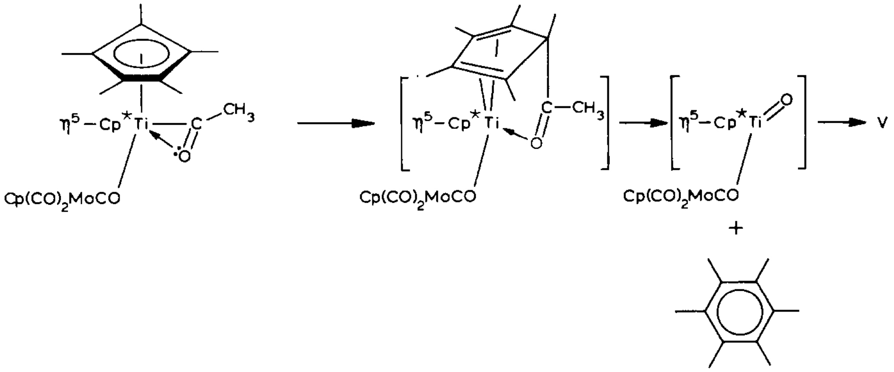
Fig. 1. Proposed structure of V.

Compound V is formulated as "Cp*Ti(O)CpMo(CO)$_3$", although elemental analyses cast some doubt on its purity. However, we did not observe bands of other compounds in its the spectra. The IR spectrum showed the presence of CpMo(CO)$_3$ fragments (bands at 1948, 1869, 1543 cm^{-1}) and titanium–oxygen bridges (strong band at 779 cm^{-1}) [7]. The presence of Cp*Ti and CpMo moieties, in a ratio of 1/1, was confirmed by ^{13}C and ^{1}H NMR spectroscopy. The data suggest a dimeric structure for V (see Fig. 1) in which two oxo ligands and two CpMo(CO)$_3$ fragments bridge between two Cp*Ti entities. The bridging mode for the CpMo(CO)$_3$ fragment is inferred from the CO stretching frequency of the isocarbonyl ligand which is at 1543 cm^{-1}, a frequency considerably lower than that for other compounds containing CpMo(CO)$_2$(μ-CO) fragments [5].

Compound IV decomposed in solution in a similar way to III to yield pentamethylneopentylbenzene. However, the reaction was slower and less clean. In this case the only organometallic product observed was (CpMo(CO)$_3$)$_2$.

Mechanism

A two-step mechanism can be suggested to account for the formation of hexamethylbenzene and V from the decomposition of III. In the first step the electrophilic acyl carbon atom [3] reacts with the electron-rich Cp* ring; the formation of pentamethylcyclopentadienyl methyl ketone in the ^{13}C-labelling study is in agreement with this. In the second step, the most interesting part of the reaction, scission of the acyl C–O band [8] occurs, with concomitant formation of the benzene ring [9].



The main cause of the C–O scission (and also of the principal difference from the well-known acylation of cyclopentadienyl ligands in, for example, ferrocene) is the oxophilicy of the titanium; the main driving force for the reaction will be the formation of titanium–oxygen bands in V.

We have not been able to detect organometallic intermediates that would support the suggested stepwise mechanism. The ^1H NMR spectra recorded at the beginning and the end of the reaction are well-resolved, but in between all the resonances are broadened. Whether this is caused by radicals or exchange processes or a combination of both is not clear.

In conclusion, we can say that the rearrangement described here extends the range of interesting reactions of η^2-acyl groups.

Experimental

All the experiments were carried out with rigorous exclusion of oxygen and water. Solvents were dried over sodium and distilled before use. Compounds $Cp^\star_2TiR$ were prepared by published procedures [4]. Commercially available $(CpMo(CO)_3)_2$ was recrystallized before use. Instrumentation: ^{13}C NMR: Bruker WM-250; ^1H NMR; Bruker WM-250 and HR 90; IR: Digilab Qualimatic; GC: HP 5840 and 5800 with capillary columns CpSil 50; MS: Finigan TSQ. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen.

Syntheses

Preparation of $Cp^\star_2Ti$-η^2-COR *(I, II)*

The complexes $Cp^\star_2TiR$ ($R = CH_3$, neo-C_5H_{11}) were dissolved in toluene and one equivalent of CO gas was slowly added to the solution from a syringe with continuous stirring at a temperature below 0 °C. Solutions of I were brownish green and those of II blue. Quantitative conversion of $Cp^\star_2TiR$ was observed.

Preparation of $Cp_2Ti(\text{-}\eta^2\text{-}COR)(\mu\text{-}OC)MoCp(CO)_2$ *(III, IV)*

A freshly prepared toluene solution of I or II was treated with toluene solution of $(CpMo(CO)_3)_2$ (0.5 equivalent based on $Cp^\star_2TiR$) at ~0 °C. A burgundy-red solution formed and the yellow precipitate of either III or IV separated. The precipitate was filtered off immediately, thoroughly washed with hexane, and dried in vacuo.

III: IR (Nujol, cm^{-1}): 1909, 1809, 1700, 1584. ^1H NMR (C_6D_6, δ, ppm): 5.44 (s,5), 1.95 (s,3), 1.51 (s,15).

IV: ^1H NMR (C_6D_6, δ, ppm): 5.45 (s,5), 3.07 (s,2), 1.55 (s,15), 1.06 (s,9). ^{13}C NMR (C_6D_6, δ, ppm): 299.8 (C=O), 121.5 ($(C\text{-}CH_3)_5$), 88.8 (C_5H_5), 55.8 ($\text{-}CH_2\text{-}$), 32.2 ($C\text{-}(CH_3)_3$) 30.7 ($C\text{-}(CH_3)_3$) 12.4 ($C\text{-}CH_3)_5$); the M=C=O resonances were not observed.

Formation of hexamethylbenzene and $Cp_2Ti_2O_2(CpMo(CO_3)_2$ *(V)*

A concentrated benzene solution of III was left overnight at room temperature without stirring. Greenish-red crystals separated out, and these were separated by decantation of the mother liquor and carefully washed with pentane to give V in 90% yield.

V: IR (Nujol mull, cm^{-1}); 1948, 1869, 1543, 779. ^1H NMR (C_6D_6, δ, ppm): 5.30 (s,5), 2.13 (s,15). ^{13}C NMR (C_6D_6, δ, ppm): 243.4 ($Mo\equiv C\text{-}O$), 230.9 ($Mo=C=O$) 130.2 ($(C\text{-}CH_3)_5$), 89.9 (C_5H_5), 11.9 ($(C\text{-}CH_3)_5$). Elemental analyses. Found: C, 50.17; H, 4.67; Ti 8.78; Mo, 13.85. $C_{18}H_{20}O_4TiMo$ calc: C, 48.69; H, 4.50; Ti, 10.79; Mo, 21.61%.

Chromatography of the mother liquor over Al_2O_3 with hexane as the eluent yielded hexamethylbenzene as the first band. (The identity was confirmed by spectral and chromatographic comparison with an authentic sample).

^{13}C- labelling: $Cp_2^{\star}Ti$-η^2-$^{13}COCH_3$, I-^{13}C was prepared by reaction of $Cp_2^{\star}TiCH_3$ with ^{13}CO. Reaction of I-^{13}C with $(CpMo(CO)_3)_2$ yielded V-^{13}C. V-^{13}C: ^1H NMR (C_6D_6, δ, ppm): 5.45 (s,5), 1.96 (d, J 6 Hz, 3), 1.50 (s,15).

^{13}C NMR of the crude reaction product from rearrangement of V-^{13}C in C_6D_6 showed that the main part of the ^{13}C-label is recovered in hexamethylbenzene. Of the other ^{13}C-labelled compounds, pentamethylcyclopentadienyl methyl ketone (confirmed by GC/MS) was most abundant. Other products were present in trace amounts and were not identified.

References

1 P.T. Wolczanski and J.E. Bercaw, Acc. Chem. Res., 13 (1980) 121.

2 T.J. Marks and V.W. Day in T.J. Marks and I.L. Fragalia (Eds.), Fundamental and Technological Aspects of Organo-*f*-element Chemistry, Reidel Publ. Comp., Dordrecht (1985), pp. 115–159.

3 R. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert and R. Hoffmann, J. Am. Chem. Soc., 107 (1985) 4440.

4 J.W. Pattiasina, C.E. Hissink, J.L. de Boer, A. Meetsma and J.H. Teuben, J. Am. Chem. Soc., 107 (1985) 7758.

5 (a) D.M. Hamilton Jr., W.S. Willis and G.D. Stucky, J. Am. Chem. Soc., 103 (1981) 4255; (b) J.S. Merola, K.S. Campo, R.A. Gentile, M.A. Modrick and S. Zentz, Organometallics, 3 (1984) 334; (c) J.S. Merola, R.A. Gentile, G.B. Ansell, M.A. Modrick and S. Zentz, Organometallics, 1 (1982) 1731; (d) R.T. Edidin, B. Longato, B.D. Martin, S.A. Matchett, and J.R. Norton in B.L. Shapiro (Ed.), 'Organometallic Compounds' Texas A&M University Press, 1983.

6 ^{13}C NMR spectra of established examples of η^2-acyl compounds show low-field shifts for the acyl carbon atom.

7 F. Bottomley, I.J.B. Lin and P.S. White, J. Am. Chem. Soc., 103 (1981) 703.

8 (a) J.R. Shapley, J.T. Park, M.R. Churchill, J.W. Ziller and L.R. Beanan, J. Am. Chem. Soc., 106 (1984) 1144; (b) P.A. Belmonte, F.G.N. Cloke and R.R. Schrock, J. Am. Chem. Soc., 105 (1983) 2643; (c) W.-K. Wong, K.W. Chiu, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1983) 1557.

9 For ring expansions on cobalt see: (a) U. Kölle and F. Khouzami, Chem. Ber., 114 (1981) 2929; (b) G.E. Herberich and J. Schwarzer, Chem. Ber., 103 (1970) 2016.