The Formation of Acetone Complexes from the Reaction of CO with $[Ti(C_5Me_5)MeY]_2(\mu\text{-}O)$ (Y = Me, Cl) and their Decomposition Reactions

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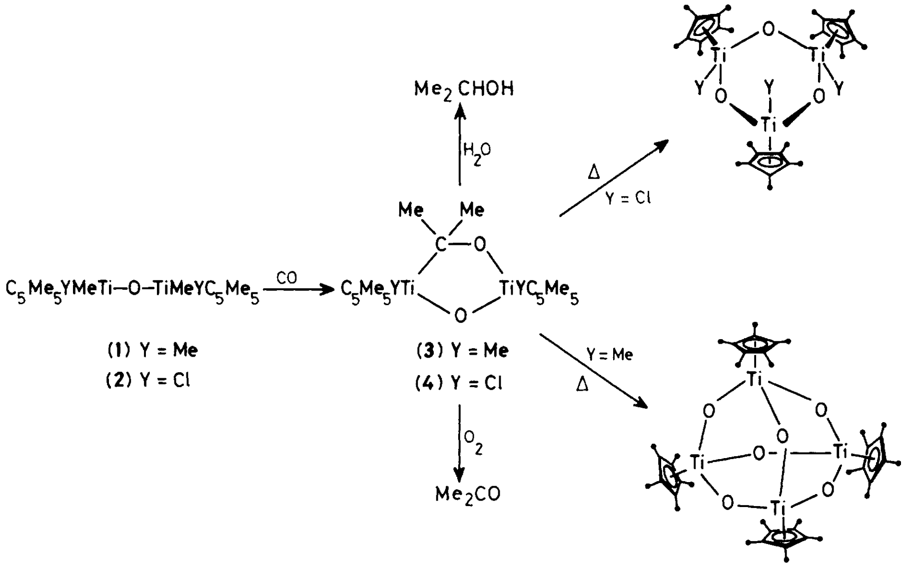
The reaction of $[Ti(C_5Me_5)MeY]_2(\mu\text{-}O)$ (Y = Me, Cl) and CO gives η^2-acetone complexes, which liberate Me_2CO upon treatment with oxygen and Me_2CHOH upon hydrolysis, and their thermal decomposition proceeds with deoxygenation of the acetone ligand and propene formation; spectroscopic data and labelling experiments are discussed.

We have recently described several oxo-organotitanium compounds containing particularly reactive electron deficient metal centres connected through oxygen bridges[1] and we now report the results of the reactions between the dimers $[Ti(C_5Me_5)MeY]_2$ (μ-O) [(**1**), Y = Me; (**2**), Y = Cl)] and carbon monoxide leading to the functionalization of the CO molecule (Scheme 1).

When CO is bubbled through a yellow solution of (**1**) in hexane, benzene or diethyl ether a red colour develops in some minutes and the subsequent work-up of the solution



Scheme 1

affords a red crystalline compound (**3**) [(**3**)-^{13}C from (**1**) and ^{13}CO] in 65—70% yield. The spectroscopic† and analytical data along with its reactivity suggest the formulation shown in Scheme 1 in which a μ-η^2-Me_2CO group has been formed and is co-ordinated to both metal atoms. ν(CO), which appears in (**3**) at 1190 cm^{-1} and is shifted to 1170 cm^{-1} in 3-^{13}C, shows similar values to those observed for other rather scarce acetone complexes: 1200 cm^{-1} for $Ta(C_5Me_5)Me_2(\mu^2$-$Me_2CO)$,[2] 1230 cm^{-1} for $W(\mu^2$-$Me_2CO)Cl_2(PMePh_2)_2$[3] and 1163 cm^{-1} for $Zr(C_5H_5)_2(\mu$-$CO)Mo(C_5H_5)(CO)_2(\mu$-η^2-$Me_2CO)Zr(C_5H_5)_2Me$[4]. The ^{1}H-n.m.r. spectrum of (**3**) shows two well-separated C_5Me_5 peaks indicative of different electronic environments around the Ti atoms, and four methyl resonances of which the two at higher field correspond to Me groups bonded to different Ti atoms, as suggested by the 0.42 p.p.m. difference between them,‡ while the remaining two at lower field are due to Me groups bonded to the carbon monoxide C atom as indicated by the splitting of the signals in (**3**)-^{13}C ($^2J_{CH}$ = 5.04 Hz) (Figure 1). The $^{13}C\{^1H\}$ n.m.r. spectrum is in line with the above assignments, the carbonyl C signal appearing in (**3**)-^{13}C at δ 121.2 whereas the methyl C bonded to it show doublets with a typical C(sp^3)-C(sp^3) coupling constant,[5] ($^1J_{CC}$ = 35.6 Hz).

The reaction of (**2**) with CO is notably slower but proceeds in a similar way giving red (**4**) [(**4**)-^{13}C using ^{13}CO] which exhibits i.r. and n.m.r. features§ analogous to those of (**3**). If hexane solutions of (**3**) are stirred in an O_2 atmosphere, acetone and traces of methanol, isopropyl alcohol and methane are detected (g.c.; the two last components are probably formed because of adventitious moisture), and starting from (**3**)-^{13}C, $Me_2{}^{13}CO$ (label at δ 203.8) and traces of $Me_2{}^{13}$ CHOH (label at δ 63.4) are identified.||

A similar reaction with (**4**)-^{13}C gives only $Me_2{}^{13}CO$ and traces of $Me_2{}^{13}CHOH$. With excess water, (**3**)-^{13}C gives $Me_2{}^{13}CHOH$ and methane (unlabelled) while (**4**)-^{13}C gives only $Me_2{}^{13}CHOH$.

Both (**3**) and (**4**) are thermally unstable substances that must be stored at −40 °C because they decompose at room temperature in a few days. The thermolysis of (**3**)-^{13}C (solid state, N_2 atmosphere, 140 °C) gives a yellow residue from which $[Ti(C_5Me_5)]_4O_6$ can be extracted and characterized,¶ representing *ca.* 60—65% of the total residue. The analysis of the volatiles (g.c. and ^{13}C n.m.r.) gives predominantly CH_4 and Me-$^{13}CH{=}CH_2$ (label at 135.0) along with minor amounts (0.5—2%) of $Me_2{}^{13}CO$, Me-$^{13}CH_2$-Me (label at δ 16.5), $Me_2{}^{13}CHOH$, C_2H_4 and C_2H_6. In the case of (**4**)-^{13}C the thermal decomposition takes place much faster and cleaner to give $[Ti(C_5Me_5)Cl(\mu$-$O)]_3$¶ as the solid residue in *ca.* 95% yield and Me-$^{13}CH{=}CH_2$ as the very predominant gaseous product. The main decomposition mode seems to involve then the deoxygenation of the formed acetone and the rearrangement of the resultant fragments to propene and the trimeric titanium compound.

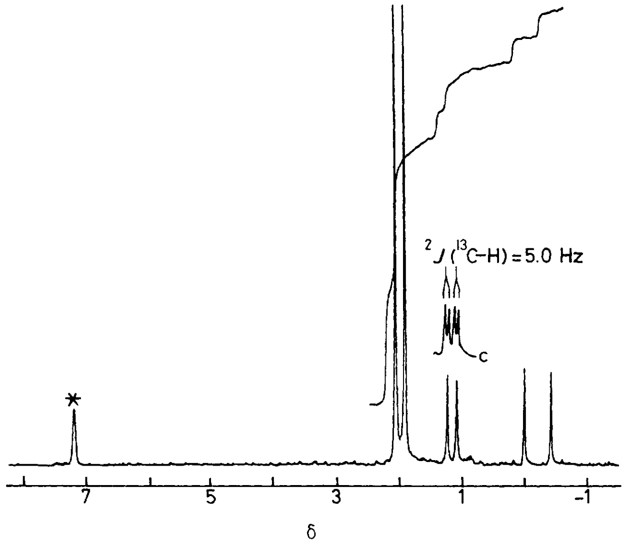


Figure 1. ^{1}H n.m.r. spectrum of **3** in C_6D_6.* solvent protio impurities. ^{c} (**3**)-^{13}C.

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† *Selected spectroscopic data* for (**3**): i.r. ν(CO) 1190 (vs) cm^{-1}, ν(TiOTi) 750 (vs) cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 2.07 (s, 15H, C_5Me_5), 1.92 (s, 15H, C_5Me_5), 1.24 (s, 3H, Me_2CO), 1.09 (s, 3H, Me_2CO), 0.00 (s, 3H, Me–Ti) and −0.42 (s, 3H, Me–Ti); $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ 121.33 (C_5Me_5), 121.17 (C_5Me_5), 51.25 (s, $Me_2\mathit{C}O$), 35.60 (Me_2CO), 29.74 (Me–Ti), 27.52 (Me–Ti), 11.72 ($C_5\mathit{Me}_5$) and 11.53 ($C_5\mathit{Me}_5$). (**3**)-^{13}C: i.r. ν(CO) 1170 (vs) cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ as in (**3**) excepting 1.24 (d, $^2J_{CH}$ = 5.04 Hz, 3H, $Me_2{}^{13}CO$) and 1.09 (d, $^2J_{CH}$ = 5.04 Hz, 3H, $Me_2{}^{13}CO$); $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ as in (**3**) excepting 121.25 (s, $Me_2{}^{13}\mathit{C}O$), 51.25 (d, $^1J_{CC}$ = 35.6 Hz, Me_2CO) and 35.60 (d, $^1J_{CC}$ = 35.6 Hz, Me_2CO). Satisfactory analytical data were obtained.

‡ *Note added in proof*: when one molecule of Ph_2CN_2 inserts into one Ti–Me bond of (**1**) to give $[Ti(C_5Me_5)Me(\eta^2$-$MeN_2CPh_2)(\mu$-$O)Ti$-$(C_5Me_5)Me_2]$ the signals of the two methyls bonded to the same Ti atom differ by 0.03 p.p.m. while those of methyls belonging to different Ti atoms are separated *ca.* 0.2 p.p.m.[7]

§ *Selected spectroscopic data* for (**4**): i.r. ν(CO) 1188 (vs) cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ 2.16 (s, 15H, C_5Me_5), 1.96 (s, 15H, C_5Me_5), 1.65 (s, 3H, Me_2CO) and 1.29 (s, 3H, Me_2CO); $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ 127.32 (C_5Me_5), 126.87 (C_5Me_5), 32.80 (Me_2CO), 27.15 (Me_2CO), 12.28 ($C_5\mathit{Me}_5$) and 12.17 ($C_5\mathit{Me}_5$). (**4**)-^{13}C: i.r. ν(CO) 1166 (vs) cm^{-1}; ^{1}H n.m.r. (C_6D_6) δ as in (**4**) excepting 1.65 (d, $^2J_{CH}$ = 5.6 Hz, 3H, Me_2CO) and 1.29 (d, $^2J_{CH}$ = 5.6 Hz, Me_2CO); $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ as in (**4**) excepting 127.63 ($Me_2{}^{13}\mathit{C}O$), 32.80 (d, $^1J_{CC}$ = 36.3 Hz, Me_2CO) and 27.15 (d, $^1J_{CC}$ = 36.3 Hz, $Me_2{}^{13}CO$).

|| $^{13}C\{^1H\}$ n.m.r. spectrum in C_6D_6.

¶ Identified by elemental analysis and comparison of its i.r. and ^{1}H n.m.r. spectrum with that of an authentic sample (see refs. 6 and 8).