Titanoxycarbene complexes of Ti(IV) with O- and N-donor ligands†

Stefan D. Nogai, Oliver Schuster, Jocelyn Bruce and Helgard G. Raubenheimer*

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Heterobimetallic complexes of the general formula $[\{(OC)_5M{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ with M = Cr (**1**), W (**2**) were synthesized by reacting $(OC)_5M{=}C(Me)OLi$ (M = Cr, W) with $ClTi(OiPr)_3$. X-Ray crystallography revealed dimeric molecular structures based on four-membered Ti_2O_2-rings for both compounds. Most intriguingly crystals of **1** virtually "shattered" upon cooling below −60 °C. Treatment of **1** and **2** with an excess of pyridine did not effect symmetric cleavage of the dimers, but afforded the unique rearrangement products $[(OC)_5M{=}C(Me)O]_2Ti(OiPr)_2(C_5H_5N)_2$ with M = Cr (**3**) and W (**4**). The isomorphous structures, determined by means of X-ray diffraction, are only the second examples of an unrestrained titanium center coordinated by four OR and two N-donor ligands. Complexes **3** and **4** were also accessible from $Cl_2Ti(OiPr)_2(C_5H_5N)_2$ (**5**) and $(OC)_5M{=}C(Me)OLi$. Owing to the inherent dynamic behaviour of all complexes, low-temperature NMR studies were undertaken. The formation of nanoparticles upon thermolysis of complex **2** lends support to the notion that the presented (or related) compounds could be useful as single source precursors for nano-sized mixed metal oxides or oxo nitrides.

Introduction

Titanium dioxide has successfully been used as a support for heterogeneous catalysts for decades. Attempts to increase the surface area by scaling down the TiO_2 primary particle size has not only led to improved activity, but also to new materials acting surprisingly different from the bulk material, once the nanometre scale is approached. This has proven to be true for metals, metal oxides, metal sulfides, *etc*. Since the new and sometimes unique properties are a function of size in this domain, it is vital to develop routes to uniform particles.

While the preparation of nano-sized TiO_2 powder from titanium alkoxides $Ti(OR)_4$ has been studied carefully and a certain control over particle sizes established,[1] difficulties in the synthesis of monodisperse chromium and chromium oxide nanoparticles have been overcome only recently by the application of Fischer-type carbene complexes.[2]

In an attempt to combine both types of precursors, we synthesized complexes of the fashion $[\{(OC)_5M{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ with M = Cr (**1**), W (**2**), extending the pioneering work of Sabat *et al*. on related compounds (M = Cr).[3] Controlled thermal decomposition of such compounds will presumably yield nano-structured mixed metal oxides $MTiO_x$ different from known metal doped titania species.[4–6] Similar ligands coordinated to the metal fragment Cp_2ZrCl (in the presence of MAO) have recently shown a propensity to catalyze the copolymerization of ethylene–1-pentene mixtures and to oligomerise 1-pentene or 1-hexene.[7] Related cyclopentadienyl compounds of titanium have been prepared by Fischer and co-workers in the early 1970s[8,9] and many other examples in subsequent years.[10] We have recently reported the utilisation of anionic Fischer-type carbene complexes as bidentate N^O ligands towards a number of metal centra.[11] Since the chemical reactivity of complexes such as **1** and **2** was not known, we investigated conversions with pyridine and discovered an unusual rearrangement that involves *inter alia* carbene oxide ligand transfer to give unprecedented bis-carbene complexes $[(OC)_5M{=}C(Me)O]_2Ti(OiPr)_2(C_5H_5N)_2$ with M = Cr (**3**) and W (**4**). These or related compounds do possibly offer access to rarely studied mixed metal oxo nitrides by thermal activation.[12–14]

While preliminary investigations on the thermolysis of the title compounds confirmed the formation of nano-sized particles (see ESI†), we herein focus on the synthesis and characterisation of the precursors using X-ray crystallography and low-temperature NMR.

Results and discussion

Initial reactions

Treatment of $ClTi(OiPr)_3$ with equimolar amounts of $(OC)_5M{=}C(Me)OLi$ (M = Cr, W) in diethyl ether gave the heterobimetallic complexes $[\{(OC)_5M{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ in good yields (eqn (1)).

Complexes **1** and **2** were isolated as moisture-sensitive, red crystals by cooling the concentrated reaction mixtures to −20 °C. The compounds dissolve readily in chlorinated solvents and ether. ^1H NMR studies revealed that the products are loosely bound in solution, giving rise to rapid monomer–dimer equilibration at room temperature, but form rather rigid dimers (on the NMR timescale) at low temperatures. Since the NMR-characteristics of both compounds are almost

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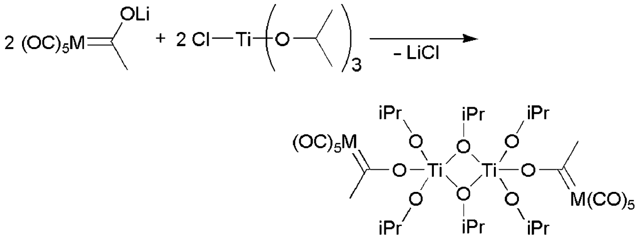
Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Stellenbosch, South Africa. E-mail: hgr@sun.ac.za; Fax: +27 21 808 3849; Tel: +27 21 808 3850

† Electronic supplementary information (ESI) available: Crystallographic details for compounds **1–5** in CIF format and preliminary studies of the thermolysis of **2**. See DOI: 10.1039/b715075j



1 M = Cr
2 M = W

identical, the temperature dependence will only be discussed explicitly for the chromium complex **1**. At room temperature the ^{1}H NMR spectrum of **1** shows two broad resonances for the isopropoxide groups at 4.89 ppm [OCH(CH$_3$)$_2$] and 1.37 ppm [OCH(CH_3)$_2$] as well as a singlet for the carbene-methyl protons at 2.79 ppm. At −80 °C these signals split into two main sets of resonances with an intensity ratio of 2 : 1. The stronger signals at 4.93 and 1.30 ppm can be assigned to lateral and the weaker ones at 4.59 and 1.21 ppm to bridging isopropoxide groups. ^{13}C NMR spectra recorded at −80 °C reveal the expected resonances of the target compounds. In Table 1, a comparison of carbene and carbonyl carbon shifts with those of related methoxycarbene complexes (OC)$_5$M=C(Me)OMe (M = Cr, W)[13] is given. The data show that substitution of the methyl group by the electron-deficient titanium affects the carbene signals only slightly. No change is observed with regard to the carbonyl ligands. It can be concluded that a significant amount of carbene character of the complexes is maintained in the product.

Molecular structure determinations

The formation of dimers was unambiguously confirmed by X-ray crystal structure determinations. From diethyl ether, compounds **1** and **2** both crystallize in the triclinic space group $P\bar{1}$ with $Z = 1$ formula unit (dimer) in the unit cell. The asymmetric unit contains one half of the dimers related to the other half *via* a center of inversion (Fig. 1 and Fig. 2).

As reported by Sabat *et al.* for similar complexes, [{(OC)$_5$Cr=C(R)OTi(OiPr)$_2$}(μ-OiPr)]$_2$ (R = *n*-Bu, 2-furyl, CMeCH$_2$),[3] the central four-membered Ti$_2$O$_2$ rings are skewed with the longer bridging bond Ti–O21 being diagnostic for the *trans* influence of the isopropoxide ligand (O41A). The co-ordination geometry around the titanium centers is best described as a distorted trigonal bipyramid with the carbene-oxygen atom, one oxygen atom of a terminal isopropoxide group and one bridging oxygen atom occupying the equatorial positions (O11, O31 and O21′ for **1** and **2**). The apical positions are therefore occupied by the oxygen atoms of one bridging and one terminal isopropoxide group (O21 and O41A for **1**; O41 and O21 for **2**). Careful examination of the bond lengths along Cr–C–O–Ti led Sabat *et al.* to the conclusion that these complexes exhibit distinct "acyl" character, while remaining significantly carbenoid (see ^{13}C NMR studies above). This is noteworthy because the two mesomeric forms are usually regarded as competitive in Fischer-type carbene complexes (Scheme 1). As a modification to this simple picture it was rationalised that the O-bound electron-deficient metal increases π-electron delocalization across the carbenoxide unit.[3] Since compounds **1** and **2** feature very similar structural characteristics (Table 2), this result transfers easily to our work

Table 1 ^{13}C NMR chemical shift data (ppm) of the carbene and carbonyl resonances in [{(OC)$_5$M=C(Me)OTi(OiPr)$_2$}(μ-OiPr)]$_2$ and (OC)$_5$M=C(Me)OMe[15]

Complex	C_{carbene}	*trans* CO	*cis* CO
1[a]	350.7	224.0	216.8
(OC)$_5$Cr=C(Me)OMe[b]	360.4	223.3	216.3
2[a]	326.9	204.9	198.0
(OC)$_5$W=C(Me)OMe[b]	333.0	203.4	197.2

Chemical shifts were measured in CD$_2$Cl$_2$ ([a]) and CDCl$_3$ ([b]) relative to the solvent.

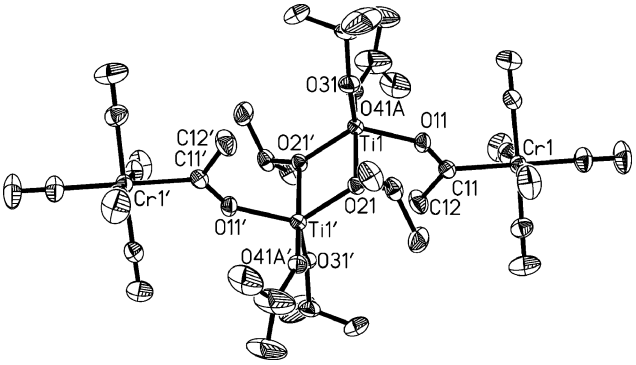


Fig. 1 Molecular structure of **1** (ORTEP, 30% ellipsoids, H atoms omitted). The isopropoxide groups at O31 and O41A are each disordered over two sites. This has been omitted in the drawing for clarity. Selected bond lengths [Å] and angles [°], $' = (-x, -y, 2 - z)$: Cr1–C11 2.043(2), C11–C12 1.508(3), C11–O11 1.272(2), O11–Ti1 1.962(2), Ti1–O21 2.099(2), Ti1–O21′ 1.923(2), Ti1–O31 1.767(2), Ti1–O41A 1.757(5); Cr1–C11–O11 123.1(2), C11–O11–Ti1 139.6(2), O11–Ti1–O21 83.82(5), O11–Ti1–O21′ 131.86(6), O11–Ti1–O31 109.26(7), O11–Ti1–O41A 93.5(7), O21–Ti1–O31 91.72(6), O21–Ti1–O41A 166.7(7), O21′–Ti1–O31 113.20(6), O21′–Ti1–O41A 99.3(6), O31–Ti1–O41A 101.5(8), O21–Ti1–O21′ 73.43(5), Ti1–O21–Ti1′ 106.57(5).

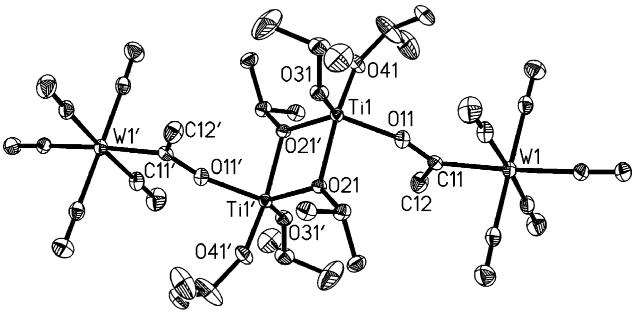
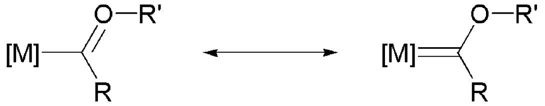


Fig. 2 Molecular structure of **2** (ORTEP, 50% ellipsoids, H atoms omitted). Selected bond lengths [Å] and angles [°], $' = (-x, -y, -z)$: W1–C11 2.190(2), C11–C12 1.518(5), C11–O11 1.273(5), Ti1–O11 1.941(3), Ti1–O21 2.095(2), Ti1–O21′ 1.917(2), Ti1–O31 1.770(3), Ti1–O41 1.760(3); W1–C11–O11 122.0(3), C11–O11–Ti1 150.2(3), O11–Ti1–O21 83.3(2), O11–Ti1–O21′ 132.7(2), O11–Ti1–O31 109.7(2), O11–Ti1–O41 90.4(2), O21–Ti1–O31 91.2(2), O21–Ti1–O41 165.8(2), O21′–Ti1–O31 111.9(2), O21′–Ti1–O41 101.2(2), O31–Ti1–O41 102.9(2), O21–Ti1–O21′ 74.4(2), Ti1–O21–Ti1′ 105.6(2).



Scheme 1 Acyl and carbene resonance forms of Fischer-type carbene complexes (formal charges omitted in the first structure).

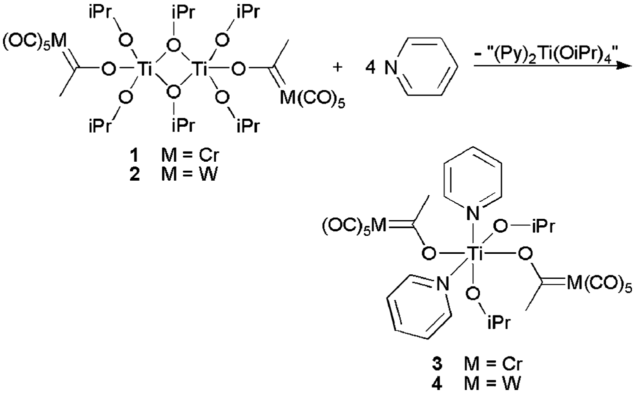
now extending the idea to Fischer carbene complexes derived from tungsten.

Despite their obvious similarities, complexes **1** and **2** are not isomorphous, most likely due to the difference in M–C$_{carbene}$ bond lengths for Cr and W. The biggest difference is found in the torsion of the $(OC)_5M$ moiety around that bond. This is illustrated by a superposition of the two structures (Fig. 3). The chromium compound's torsion angle C5–Cr1–C11–C12 is −32.7(2)° whereas the analogous atoms are almost co-planar in the tungsten compound [1.2(3)°].

This little twist gives rise to significantly different behavior of the crystals upon cooling. While the data collection of **2** was carried out under standard conditions at −173 °C, crystals of **1** had to be measured at −60 °C, because they virtually "exploded" once cooled below this temperature (Fig. 4). This rare behavior is most probably due to a phase transition by the crystals. Unfortunately all attempts to determine the unit cell after the transition or to crystallize **1** in the low temperature modification were unsuccessful.

Subsequent ring cleavage

Dimers of **1** and **2** were readily cleaved by addition of an excess of pyridine to ethereal solutions of these compounds. However, rearrangement to **3** and **4** (both approx. 50% yield) occurs while the expected product of a symmetric cleavage, $(OC)_5M{=}C(Me)OTi(OiPr)_3(C_5H_5N)_2$, was not observed (eqn (2)). The by-products in the mother liquor were not identified but it can be assumed that homoleptic $Ti(OiPr)_4$ and/or its pyridine adducts would be formed. In accordance with the oxophilic character of titanium, even the use of an excess of pyridine did not displace the carbenoxide moieties from the isolated products.



The same complexes **3** and **4** were also deliberately synthesized in satisfactory yields by combining $Cl_2Ti(OiPr)_2(C_5H_5N)_2$ (**5**) and $(OC)_5M{=}C(Me)OLi$ (M = Cr, W) (eqn (3)).

Table 2 Bond distances (Å) within the M–C–O–Ti fragment of heterobimetallic Fischer carbene complexes

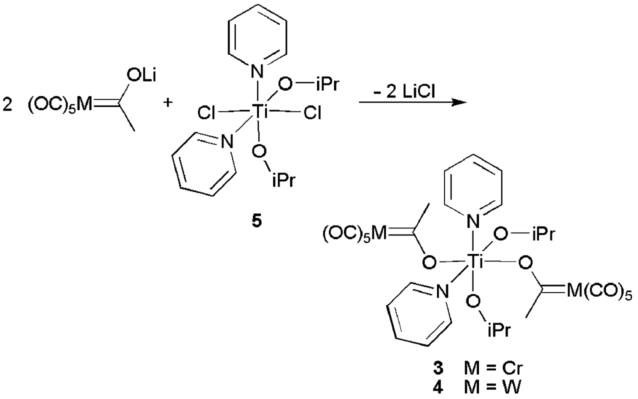
$[\{(OC)_5M{=}C(R)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$

M	R	M–C	C–O	O–Ti
Cr	Me	2.042(2)	1.271(2)	1.961(1)
Cr	*n*-Bu	2.040(4)[a]	1.272(4)[a]	1.938(2)[a]
Cr	2-Furyl	2.046(8)[a]	1.290(9)[a]	2.016(5)[a]
Cr	$CMeCH_2$	2.072(2)[a]	1.284(3)[a]	1.942(2)[a]
W	Me	2.190(2)	1.273(5)	1.941(3)

$[\{(OC)_5M{=}C(R)O]_2Ti(OiPr)_2(C_5H_5N)_2$

M	R	M–C	C–O	O–Ti
Cr	Me	2.071(2)	1.293(3)	2.010(2)
W	Me	2.190(6)	1.275(7)	1.977(4)

[a] Ref. 3.



The pyridine complexes are very sensitive towards moisture. In solution even traces of water result in fast decomposition. Amongst the decomposition products acetaldehyde, $(OC)_5Cr(C_5H_5N)$ and $(OC)_4W(C_5H_5N)_2$ were verified spectroscopically or by unit-cell determinations. Based on these observations we speculate that H_2O readily substitutes pyridine which in turn coordinates to $M(CO)_5$ by replacing the anionic carbene ligand affording carbonyl(pyridine)metal(0) complexes. Protonation of the extruded ligand yields acetaldehyde and OH^- which is able to replace another pyridine and so forth.

The ^{1}H NMR-spectra of **3** and **4** in CD_2Cl_2 recorded at room temperature show only one set of resonances for the two pyridines (8.75, 7.95 and 7.49 ppm for **3**; 8.78, 7.94 and

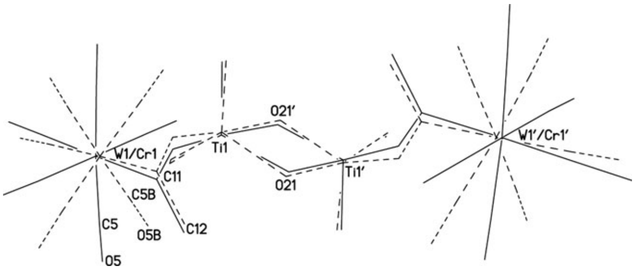


Fig. 3 Superposition of the structures of **1** (broken lines) and **2** (solid lines). The superimposed atoms of both structures are the four-membered Ti–O-ring and W/Cr. The carbon atoms of the isopropoxide groups have been omitted for clarity.

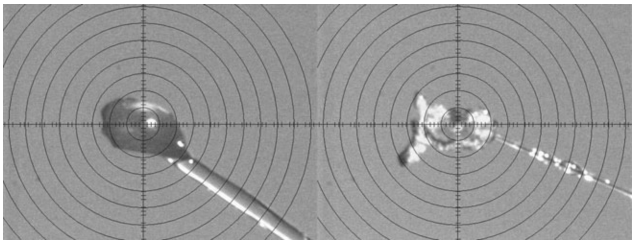


Fig. 4 Crystals of **1** at room temperature (left) and after cooling below −60 °C (right).

7.50 ppm for **4**), isopropoxide (4.91 and 1.20 ppm for **3**; 4.81 and 1.22 ppm for **4**) and carbenoxide ligands (2.80 ppm **3** and **4**). All signals are broad, indicating rapid ligand exchange. Variable temperature NMR spectroscopy shows that at −60 °C the resonances split into multiple sets of resonances, most likely representing different possible isomers. Owing to their high complexity no attempts were made to investigate the spectra in more detail.

Molecular structure determinations

Crystallizing **3** and **4** from diethyl ether–pentane or dichloromethane–hexane yielded isomorphous crystals with the monoclinic space group symmetry $P2/c$ with $Z = 6$ molecules in the unit cell. The asymmetric unit consists of 1.5 formula units, the incomplete fragment being completed by a twofold rotation axis (C_2 symmetry) passing through Ti1 and intersecting the Ti1–O121 and Ti1–O121′ vectors (Fig. 5 and Fig. 6). The central titanium atom is coordinated in a distorted octahedral fashion by two carbenoxide, two isopropoxide and two pyridine ligands, with the two Fischer-type carbene units oriented mutually *trans* towards each other, while the isopropoxy ligands occur in a *cis* arrangement. The bond lengths along M–C–O–Ti (M = Cr, W) show no notable differences compared to the parent complexes **1** (or its analogues)[3] and **2** (Table 2), therefore, the same measure of delocalisation can be assumed. The related complex $\mathrm{[(OC)_5Cr{=}C(Me)O]_2Ti(Cp^*)_2}$ exhibits similar features.[16] Note that only one unrestrained structure (*i.e.* without bidentate ligands) with four alkoxide and two nitrogen donor ligands, $\mathrm{(MeCN)_2Ti[OCH(CF_3)_2]_4}$, was hitherto reported.[17] This octahedral compound crystallises readily from an acetonitrile solution of $\mathrm{Ti[OCH(CF_3)_2]_4}$, whereas $\mathrm{(iPrO)_2Ti[OCH(CF_3)_2]_2}$ yields solely solvent-free crystals. Apparently the oxophilic titanium center becomes susceptible to N-donors only when the donation of the alkoxide ligands is reduced. This enhanced Lewis acidity of the "$\mathrm{TiO_4}$"-moiety in **3** and **4** is also illustrated by the moisture sensitivity discussed before (*vide supra*).

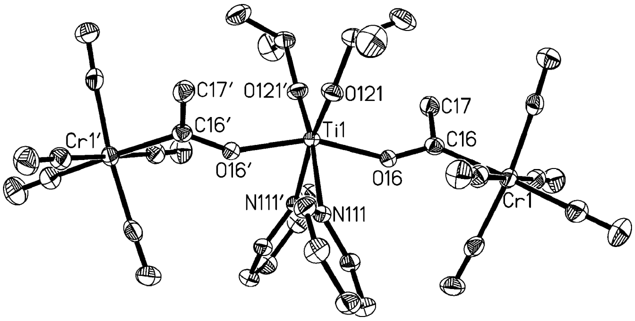


Fig. 5 Molecular structure of **3** (ORTEP, 50% ellipsoids, H atoms omitted). Only the structure of the symmetric molecule is shown. Selected bond lengths [Å] and angles [°], ′ = (1 − *x*, *y*, 3/2 − *z*): Cr1–C16 2.053(2), C16–C17 1.511(3), C16–O16 1.273(3), O16–Ti1 1.979(2), Ti1–O121 1.769(2), Ti1–N111 2.301(2); Cr1–C16–O16 121.6(2), C16–O16–Ti1 151.1(2), O16–Ti1–O16′ 157.73(9), O16–Ti1–N111 83.42(6), O16–Ti1–N111′ 80.31(6), O16–Ti1–O121 94.50(7), O16–Ti1–O121′ 99.90(7), N111–Ti1–N111′ 85.78(9), N111–Ti1–O121 87.68(7), N111–Ti1–O121′ 172.07(7), O121–Ti1–O121′ 99.2(2).

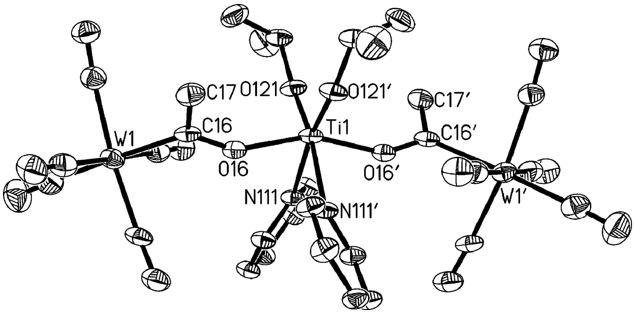


Fig. 6 Molecular structure of **4** (ORTEP, 50% ellipsoids, H atoms omitted). Only the structure of the symmetric molecule is shown. Selected bond lengths [Å] and angles [°], ′ = (1 − *x*, *y*, 3/2 − *z*): W1–C16 2.171(6), C16–C17 1.503(8), C16–O16 1.255(7), O16–Ti1 1.946(4), Ti1–O121 1.753(4), Ti1–N111 2.288(4); W1–C16–O16 121.1(4), C16–O16–Ti1 150.8(4), O16–Ti1–O16′ 157.2(2), O16–Ti1–N111 83.1(2), O16–Ti1–N111′ 80.3(2), O16–Ti1–O121 94.1(2), O16–Ti1–O121′ 100.6(2), N111–Ti1–N111′ 85.3(2), N111–Ti1–O121 87.9(2), N111–Ti1–O121′ 171.6(2), O121–Ti1–O121′ 99.3(3).

The structure of the starting material $\mathrm{Cl_2Ti(OiPr)_2(C_5H_5N)_2}$ (**5**), first reported by Brusilovets *et al.*,[18] was now also determined. This compound crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The

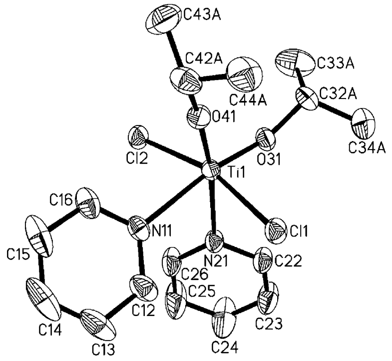


Fig. 7 Molecular structure of **5** (ORTEP, 50% ellipsoids, H atoms omitted). Both isopropoxide ligands are disordered over two sites by a rotation around the O31–C32A and O41–C42A bond, respectively. In the drawing this has been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl1–Ti1 2.3927(6), Cl2–Ti1 2.3736(6), Ti1–O31 1.775(2), Ti1–O41 1.761(2), Ti1–N11 2.310(2), Ti1–N21 2.293(2); Cl1–Ti1–Cl2 164.42(2), Cl1–Ti1–N11 82.90(4), Cl1–Ti1–N21 84.41(4), Cl1–Ti1–O31 94.27(5), Cl1–Ti1–O41 94.20(5), Cl2–Ti1–N11 84.07(4), Cl2–Ti1–N21 85.31(4), Cl2–Ti1–O31 96.93(5), Cl2–Ti1–O41 94.02(5), N11–Ti1–N21 81.79(6), N21–Ti1–O31 87.40(6), O31–Ti1–O41 102.04(7), O41–Ti1–N11 88.77(6), N11–Ti1–O31 169.03(6), N21–Ti1–O41 170.55(6).

asymmetric unit consists of one molecule without any crystallographically imposed symmetry (Fig. 7) despite its C_2-symmetric framework. The central titanium atom is coordinated in a distorted octahedral environment by two chloride, two alkoxide and two pyridine ligands. The chloride ligands are *trans* disposed towards each other, whereas the two pyridine ligands are occupying positions *trans* to the isopropoxide donors. The structure of **5**, therefore, reflects a similar situation to that found in the structures of compounds **3** and **4** but with chlorides replaced by the anionic carbene-complex ligands.

Conclusion

This study has established a convenient synthesis of heterobimetallic Fischer-type carbene complexes of the type $[\{(OC)_5M{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ with M = Cr (**1**), W (**2**) with central four-membered Ti_2O_2 rings. X-Ray crystal structure determinations and NMR studies demonstrated that these complexes exhibit distinct "acyl" character, while remaining significantly carbenoid in accordance with the findings of Sabat *et al.*[3] VT-NMR studies revealed that, in solution at room temperature, these molecules are highly dynamic systems undergoing rapid monomer–dimer equilibration, whereas at low temperatures the dimers are rather rigid on the NMR timescale. In the presence of suitable donor ligands (in this study pyridine) these dimers are readily cleaved. Surprisingly the expected products of a symmetric cleavage, $(OC)_5M{=}C(Me)OTi(OiPr)_3(C_5H_5N)_2$ were not observed, but instead unique rearrangement products $[(OC)_5M{=}C(Me)O]_2Ti(OiPr)_2(C_5H_5N)_2$ with M = Cr (**3**) and W (**4**) were obtained. In the latter complexes each Ti-center is now coordinated by two oxycarbene units.

Preliminary thermal decomposition experiments with complex **2** led to the formation of nanoparticles (ESI†). This supports the notions that complexes such as **1** and **2** could be useful single source precursors for mixed metal oxides of the type $MTiO_x$. Furthermore, complexes like **3** and **4** with appropriate N-donor ligands could in a similar fashion provide useful precursors for elusive mixed metal oxo nitrides $M_xTiN_yO_z$. Systematic investigations of these possibilities are under way in our laboratories.

Experimental

General methods

All manipulations were performed in a dry argon atmosphere using standard Schlenk techniques. $Cl_2Ti(OiPr)_2$ was prepared from $TiCl_4$ and $Ti(OiPr)_4$ *via* a literature procedure.[18] All other chemicals were commercially available. Diethyl ether, hexane and pentane were distilled under N_2 from sodium wire, CH_2Cl_2 from CaH_2 and pyridine from KOH. Melting points (uncorrected) were determined on a Stuart SMP3 apparatus. The infrared spectra were recorded on a Nicolet 380 FTIR instrument and the NMR spectra on a Varian ^{Unity}Inova 400 spectrometer (chemical shifts reported relative to the solvent resonance).

Preparations

$[\{(OC)_5Cr{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ (1). $(OC)_5Cr{=}C(Me)OLi$ was prepared from 2.1 ml of MeLi (3.3 mmol; 1.6 M in diethyl ether) and 0.73 g $Cr(CO)_6$ (3.3 mmol).[19] The resulting solution was added drop-wise to 0.87 g $ClTi(OiPr)_3$ (3.3 mmol) in diethyl ether with stirring at 0 °C. After the addition was completed, the deep red solution was warmed to room temperature and stirred for another 30 minutes. LiCl was removed by filtration. The filtrate was slowly evaporated under reduced pressure (about 2/3 of the solvent) until a precipitate formed which redissolved upon warming to room temperature. Orange-red crystals of the product were obtained by slow cooling of the remaining solution to −20 °C. The crystals were filtered off, washed with cold hexane (2 × 10 ml, −20 °C) and dried *in vacuo* (yield: 0.87 g, 63%). Mp 41 °C (dec.). IR (ATR, neat, cm^{-1}): 2050 m, 1973 s, 1892 vs (all ν_{CO}). ^1H-NMR (CD_2Cl_2, 25 °C): 4.89 [3H, s(br), $OCH(CH_3)_2$], 2.79 [3H, s, $Cr{=}C(CH_3)O$], 1.37 [18H, m, $OCH(CH_3)_2$]. ^1H-NMR (CD_2Cl_2, −80 °C): 4.93 [2H, m, $OCH(CH_3)_2$], 4.59 [1H, m, μ-$OCH(CH_3)_2$], 2.67 [3H, s, $Cr{=}C(CH_3)O$], 1.30 [12H, m, $OCH(CH_3)_2$], 1.21 [6H, m, μ-$OCH(CH_3)_2$]. ^{13}C-NMR (CD_2Cl_2, −80 °C): 350.7 [s, $Cr{=}C(CH_3)O$], 224.0 [s, CO_{trans}], 216.8 [s, CO_{cis}], 83.0 [s, $OCH(CH_3)_2$], 76.3 [s, μ-$OCH(CH_3)_2$], 24.1 [s, $OCH(CH_3)_2$], 22.3 [s, μ-$OCH(CH_3)_2$]; $Cr{=}C(CH_3)O$ obscured by solvent. Anal. calc. for $C_{32}H_{48}Cr_2O_{18}Ti_2$: C 41.76; H 5.26. Found: C 41.47; H 5.15%.

$[\{(OC)_5W{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ (2). The compound was prepared following the route for **1**. Amounts used: $W(CO)_6$ (0.94 g; 2.7 mmol), MeLi 1.6 M (1.7 ml; 2.7 mmol), $ClTi(OiPr)_3$ (0.70 g; 2.7 mmol); (yield: 1.01 g; 64%). Mp 81 °C (dec.). IR (ATR, neat, cm^{-1}): 2060 m, 1957 s, 1882 vs (all ν_{CO}). ^1H-NMR (CD_2Cl_2, 25 °C): 4.88 [3H, s(br), $OCH(CH_3)_2$], 2.69 [3H, s, $Cr{=}C(CH_3)O$], 1.36 [18H, m, $OCH(CH_3)_2$]. ^1H-NMR (CD_2Cl_2, −80 °C): 4.91 [2H, m, $OCH(CH_3)_2$], 4.56 [1H, m, μ-$OCH(CH_3)_2$], 2.63 [3H, s, $Cr{=}C(CH_3)O$], 1.29 [12H, m, $OCH(CH_3)_2$], 1.21 [6H, m, μ-$OCH(CH_3)_2$]. ^{13}C-NMR (CD_2Cl_2, −80 °C): 326.9 [s, $Cr{=}C(CH_3)O$], 204.9 [s, CO_{trans}], 198.0 [s, CO_{cis}], 82.9 [s, $OCH(CH_3)_2$], 76.4 [s, μ-$OCH(CH_3)_2$], 56.2 [s, $Cr{=}C(CH_3)O$], 24.3 [s, $OCH(CH_3)_2$], 22.3 [s, μ-$OCH(CH_3)_2$]. Anal. calc. for $C_{32}H_{48}O_{18}Ti_2W_2$: C 32.46; H 4.09. Found: C 32.28; H 3.97%.

$[(OC)_5Cr{=}C(Me)O]_2Ti(OiPr)_2(C_5H_5N)_2$ (3). **(A)** To a solution of $[\{(OC)_5Cr{=}C(Me)OTi(OiPr)_2\}(\mu\text{-}OiPr)]_2$ (**1**) (0.28 g; 0.30 mmol) in diethyl ether (15 ml), an excess of pyridine (0.14 g; 1.8 mmol) was added at room temperature and the mixture was stirred for 20 min. After evaporation of about half the solvent, 20 ml of pentane was slowly added. The red precipitate was filtered off, washed with pentane (2 × 10 ml) and dried *in vacuo* (yield: 0.13 g; 54%). **(B)** $(OC)_5Cr{=}C(Me)OLi$ was prepared from 1.5 ml of MeLi (2.4 mmol; 1.6 M in diethyl ether) and 0.52 g $Cr(CO)_6$ (2.4 mmol).[19] The resulting solution was added drop-wise to a stirred solution of 0.47 g $Cl_2Ti(OiPr)_2(C_5H_5N)_2$ (**5**) (1.2 mmol) in diethyl ether (15 ml) at 0 °C. A deep red solution was formed and allowed to warm to room temperature. After another 30 minutes of stirring, the solution was filtered to remove precipitated LiCl. Removal of about 2/3 of the solvent *in vacuo* and addition of pentane

Table 3 Crystal data, data collection and structure refinement for compounds **1**, **2**, **3**, **4** and **5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{32}H_{48}Cr_2O_{18}Ti_2$	$C_{32}H_{48}O_{18}Ti_2W_2$	$C_{30}H_{30}Cr_2N_2O_{14}Ti$	$C_{30}H_{30}N_2O_{14}TiW_2$	$C_{16}H_{24}Cl_2N_2O_2Ti$
M	920.50	1184.20	794.46	1058.16	395.17
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2/c$	$P2/c$	$P2_1/c$
a/Å	10.4677(6)	9.6870(5)	23.528(2)	23.520(2)	8.7977(5)
b/Å	10.9006(6)	10.6893(6)	15.423(1)	15.415(1)	13.4237(7)
c/Å	11.5402(7)	11.7611(6)	14.9208(8)	14.9223(9)	16.4837(9)
α/°	87.771(1)	108.787(1)	90	90	90
β/°	67.023(1)	107.558(1)	100.695(2)	100.704(1)	97.906(1)
γ/°	70.163(1)	91.644(1)	90	90	90
V/Å^3	1133.7(2)	1088.5(2)	5320.3(5)	5316.2(6)	1928.2(2)
ρ_{calc}/g cm^{-3}	1.348	1.807	1.488	1.983	1.361
Z	1	1	6	6	4
FM(000)	476	576	2436	3036	824
T/K	213(2)	100(2)	100(2)	100(2)	100(2)
Refls. measured	8280	6461	29 084	31 409	10 977
Refls. unique [R_{int}]	4401 [0.0147]	4503 [0.0147]	10 099 [0.0285]	11 164 [0.0318]	3908 [0.0200]
Parameters/restraints	320/11	251/0	702/9	702/16	270/8
$R1$ [$I \geq 2\sigma(I)$]	0.0333	0.0250	0.0402	0.0380	0.0373
$wR2^a$	0.0961	0.0635	0.1051	0.0955	0.0991
Weighting scheme	$a = 0.0583$	$a = 0.0326$	$a = 0.0560$	$a = 0.0436$	$a = 0.0558$
	$b = 0.1961$	$b = 2.5027$	$b = 1.9762$	$b = 16.2353$	$b = 1.0083$
σ_{fin}(max/min)/e Å^{-3}	0.352/−0.186	2.352/−0.801	1.360/−0.491	3.152/−4.027	0.596/−0.245

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

(50 ml) yielded a crude product. The solution was filtered off and the residue washed with pentane (2 × 30 ml) and dried *in vacuo*. A pure second batch of crystalline product can be recovered from the mother liquor by cooling the diethyl ether–pentane solution to −20 °C (combined yield: 0.54 g; 58%). The product can be recrystallized from ether–pentane or dichloromethane–hexane. Mp 73 °C (dec.). IR (ATR, neat, cm^{-1}): 2047 m, 1959 w (shoulder), 1870 vs (all ν_{CO}). ^{1}H-NMR (CD_2Cl_2, 25 °C): 8.75 [2H, s(br), o-C_5H_5N], 7.95 [1H, s(br), p-C_5H_5N], 7.49 [2H, s(br), m-C_5H_5N], 4.91 [1H, s(br), OCH(CH_3)$_2$], 2.80 [3H, s, Cr=C(CH_3)O], 1.20 [6H, m, OCH(CH_3)$_2$]. Anal. calc. for $C_{30}H_{30}Cr_2N_2O_{14}Ti$: C 45.36; H 3.81; N 3.53. Found: C 45.24; H 3.76; N 3.59%.

[(OC)$_5$W=C(Me)O]$_2$Ti(OiPr)$_2$(C$_5$H$_5$N)$_2$ (4). The compound can be prepared following the routes described for **3**. Amounts used: (**A**) [{(OC)$_5$W=C(Me)OTi(OiPr)$_2$}(μ-OiPr)]$_2$ (**2**) (0.35 g; 0.30 mmol), pyridine (0.14 g; 1.8 mmol); (yield: 0.16 g; 51%). (**B**) W(CO)$_6$ (0.88 g; 2.5 mmol), MeLi 1.6 M (1.6 ml; 2.5 mmol), Cl$_2$Ti(OiPr)$_2$(C$_5$H$_5$N)$_2$ (**5**) (0.49 g; 1.2 mmol); (yield: 0.75 g; 57%). Mp 76 °C (dec.). IR (ATR, neat): 2057 m, 1962 w, 1866 vs (all ν_{CO}). ^{1}H-NMR (CD_2Cl_2, 25 °C): 8.78 [2H, s(br), o-C_5H_5N], 7.94 [1H, m br, p-C_5H_5N], 7.50 [2H, m br, m-C_5H_5N], 4.81 [1H, s(br), OCH(CH_3)$_2$], 2.80 [3H, s, W=C(CH_3)O], 1.22 [6H, m, OCH(CH_3)$_2$]. Anal. calc. for $C_{30}H_{30}N_2O_{14}TiW_2$: C 34.05; H 2.86; N 2.65. Found: C 33.91; H 2.80; N 2.70%.

Preparation of Cl$_2$Ti(OiPr)$_2$(C$_5$H$_5$N)$_2$ (5). To a solution of Cl$_2$Ti(OiPr)$_2$ (0.62 g; 2.6 mmol) in diethyl ether (15 ml), an excess of pyridine (0.29 g; 3.7 mmol) was added at room temperature and the mixture was stirred for about 20 minutes. A small amount of precipitate was filtered off. Cooling the filtrate to −20 °C yielded colorless crystals that were filtered off, washed with pentane (2 × 20 ml) and dried *in vacuo* (yield: 0.71 g; 69%). Analytical data have been reported before.[18] Anal. calc. for $C_{16}H_{24}Cl_2N_2O_2Ti$: C 48.63; H 6.12; N 7.09. Found: C 48.52; H 6.15; N 7.13%.

Crystal structure determinations

Specimens of suitable quality and size of **1**, **2**, **3**, **4** and **5** were mounted on the ends of glass fibers in inert oil and used for intensity data collection on a Bruker SMART Apex CCD diffractometer,[20] employing graphite-monochromated Mo Kα radiation. Data reduction was carried out using the SAINT[21] suite of programs and multi-scan absorption corrections were performed with SADABS.[22] The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97)[23] within the X-Seed environment.[24] The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated in ideal positions and refined using a riding model. Some of the isopropoxide groups in the structures of **1**, **3**, **4** and **5** are disordered. Similarity restraints were applied to model the disorder as best as possible. Details of the data collections and structure determinations are listed in Table 3. CCDC reference numbers 670773–670777. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b715075j

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