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Synthesis of New Fischer-type Carbene Complexes: Characterization and Reactions of Titanoxycarbene–Metal Complexes derived from (η^5-C_5Me_5)$_2$Ti(C_2H_4) and Metal Carbonyls

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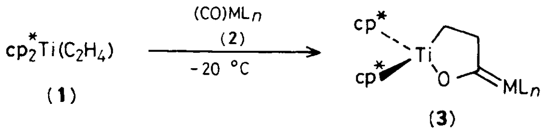
Titanoxycarbene–metal carbonyl complexes have been synthesized by the reaction of (η^5-C_5Me_5)$_2$Ti(C_2H_4) and various metal carbonyls of group 6 and 7, and characterised by spectroscopic and *X*-ray crystallographic techniques; at elevated temperatures, a novel cleavage of C(carbenic)–C bonds occurred to liberate ethylene and the metal carbonyl starting material.

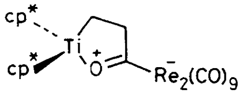
Recently, a new entry into Fischer-type carbene complexes has been provided by the reaction of (1,3-diene) zirconocene,[1a] (η^2-aryne)zirconocene,[1b] or (dinitrogen)zirconocene[2] complexes and metal carbonyls. We have investigated the synthesis of new titanoxycarbene–metal complexes by the reaction of titanocene–ethylene complex (**1**) (cp* = η^5-C_5Me_5) with various metal carbonyls of group 6 and 7.

Treatment of (**1**) with an equimolar amount of rhenium carbonyl (**2b**) in toluene below −20 °C for 48 h gave a deep red solution. ^{1}H N.m.r. spectroscopic measurement showed that 84% of (**1**) had reacted with (**2b**). The reaction mixture was diluted with hexane and kept at −80 °C overnight to afford pure titanoxycarbene complex (**3b**) as orange-red prisms in 57% yield.† The complex (**3b**) is thermally unstable in solution even at −20 °C, while the isolated (**3b**) is relatively stable and decomposes at 95—99 °C. Similar reaction of (**1**) with manganese carbonyl (**2a**) gave (**3a**) in 30% isolated yield. The present synthetic route to new Fischer-type carbene complexes is also applicable to group 6 transition metals. Thus, the complexes (**3c**) and (**3e**) were obtained in 26% and 34% yield, respectively, after recrystallization from a mixture of toluene and hexane. The complex (**3d**) was too unstable to be isolated in pure form (48% yield by ^{1}H n.m.r. spectroscopy). The structures of (**3a**—**e**) are based on spectroscopic data.‡



(**1**) (**3**)

a; ML$_n$ = $Mn_2(CO)_9$
b; ML$_n$ = $Re_2(CO)_9$
c; ML$_n$ = $Cr(CO)_5$
d; ML$_n$ = $Mo(CO)_5$
e; ML$_n$ = $W(CO)_5$



(**4**)

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† Satisfactory elemental analyses were obtained for all isolated new compounds. The complex (**3b**) crystallizes with 0.5 equiv. of toluene.

‡ All n.m.r. spectra were recorded on a JEOL GX400 spectrometer in [$^2H_8$]toluene at −30 °C using solvent absorptions at δ 2.31 and δ_c 137.70 as internal standards. ^{13}C N.m.r. absorptions due to sp^2 carbon atoms of the cyclopentadienyl ligands were not recorded because of overlap with those due to the aromatic carbon atoms of the solvent.

(**3a**): m.p. 115—118 °C (decomp.); ^{1}H n.m.r., δ 1.53 [t, *J* 6.8 Hz, C(5)H_2], 1.74 (s, CMe), 4.20 [t, C(4)H_2]; ^{13}C n.m.r., δ 11.93 (J_{C-H} 127 Hz, C*Me*), 65.99 [J_{C-H} 130 Hz, C(5)], 80.34 [J_{C-H} 124 Hz, C(4)], 218.58, 225.60, 226.45 (CO), 333.97 [C(3)].

(**3b**): m.p. 95—99 °C (decomp.); ^{1}H n.m.r., δ 1.60 [t, *J* 7.1 Hz, C(5)H_2], 1.78 (s, CMe), 4.02 [t, C(4)H_2]; ^{13}C n.m.r., δ 11.96 (J_{C-H} 127 Hz, C*Me*), 66.35 [J_{C-H} 128 Hz, C(5)], 85.02 [J_{C-H} 124 Hz, C(4)], 199.04, 200.95 (CO), 289.76 [C(3)].

(**3c**): m.p. 98—103 °C (decomp.); ^{1}H n.m.r., δ 1.62 [t, *J* 6.9 Hz, C(5)H_2], 1.78 (s, CMe), 4.35 [t, C(4)H_2]; ^{13}C n.m.r., δ 11.99 (J_{C-H} 127 Hz, C*Me*), 67.44 [J_{C-H} 129 Hz, C(5)], 81.01 [J_{C-H} 124 Hz, C(4)], 220.19, 225.2 (broad, CO), 349.79 [C(3)].

(**3d**): ^{1}H n.m.r. δ 1.65 [t, *J* 7.0 Hz, C(5)H_2], 1.78 (s, CMe), 4.20 [t, C(4)H_2]; ^{13}C n.m.r., δ 12.09 (J_{C-H} 128 Hz, C*Me*), 67.87 [J_{C-H} 129 Hz, C(5)], 82.10 [J_{C-H} 122 Hz, C(4)], 209.30 (CO), 344.94 [C(3)].

(**3e**): m.p. 106—110 °C (decomp.); ^{1}H n.m.r., δ 1.60 [t, *J* 7.1 Hz, C(5)H_2], 1.78 (s, CMe), 4.10 [t, C(4)H_2]; ^{13}C n.m.r., δ 12.02 (J_{C-H} 127 Hz, C*Me*), 67.56 [J_{C-H} 127 Hz, C(5)], 83.59 [J_{C-H} 124 Hz, C(4)], 201.07 (J_{C-W} 125 Hz), 205.2 (broad, CO), 328.36 [C(3)].

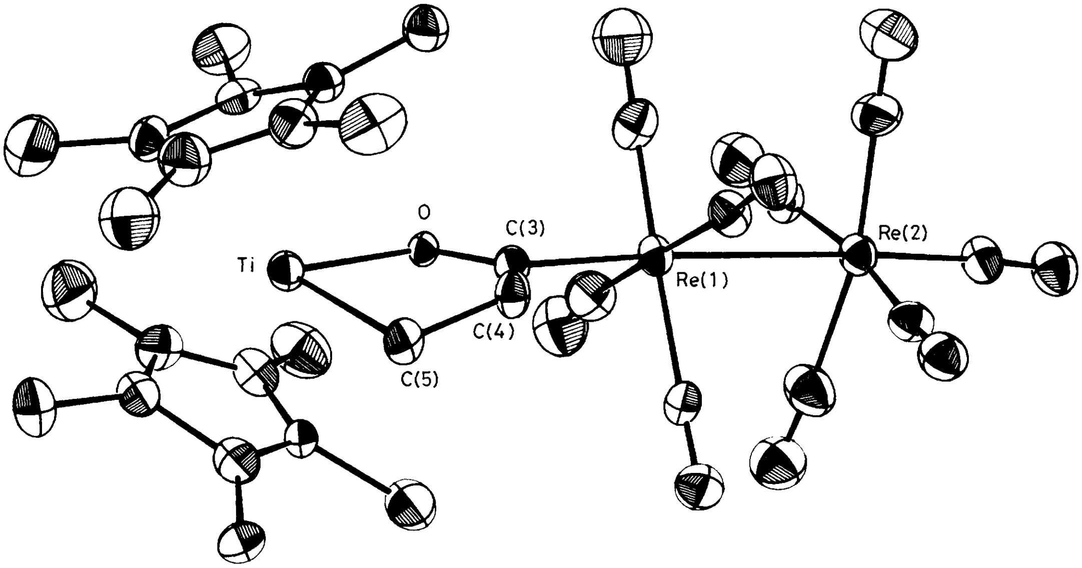

Figure 1. An ORTEP drawing of the molecular structure of (**3b**). Selected bond distances: Re(1)–Re(2) 3.057(2), Re(1)–C(3) 2.12(3), Ti–O(2) 2.02(2), Ti–C(5) 2.25(2), O(2)–C(3) 1.26(3), C(3)–C(4) 1.57(4), C(4)–C(5) 1.52(4) Å; angles: Re(2)–Re(1)–C(3) 176.7(7). Re(1)–C(3)–O(2) 125(2). Re–C(3)–C(4) 118(2), O(2)–Ti–C(5) 79.1(9), Ti–O(2)–C(3) 122(2). Ti–C(5)–C(4) 106(2), O(2)–C(3)–C(4) 117(2), C(3)–C(4)–C(5) 110(2)°.

The molecular structure of (**3b**) was further established by single-crystal *X*-ray diffraction.§ Two molecules of (**3b**) with different conformations of the metallacyclic five-membered ring are crystallographically independent and make an enantiomorphic pair. The molecular structure of one of the two molecules is shown in Figure 1.

The carbenic ligand is *trans* to the Re–Re bond which contrasts with the complexes derived from $Re_2(CO)_{10}$ by conventional 'Fischer-type' methods where the carbene is *cis* to the Re–Re bond.[3] The C(3)–O bond distance in (**3b**) is considerably shorter than that of a usual C–O single bond, while the Ti–O bond is long. This shows that there is an important contribution from the dipolar resonance structure (**4**), as previously reported for zirconoxy-carbene–metal complexes.[1]

Since the compound (**1**) can be viewed as a titanacyclopropane complex,[4,5] the present reaction can be considered to proceed by a pericyclic $[2_s + 2_s]$-type reaction.[4] This can also be envisaged as a four-electron insertion process (migratory insertion) into a strained Ti–C σ bond. The observed reactivity of metal carbonyls toward (**1**) can be ascribed to the remarkable oxophilic nature of titanium.

When the complexes (**3a**—**e**) in $[^2H_8]$toluene were kept at 0—30 °C, quantitative formation of ethylene and the corresponding metal carbonyls (**2a**—**e**) was observed, which indicates that the C(3)–C(4) bond of the oxatitanacyclopentane ring was selectively cleaved during the thermolysis.¶ The fate of the titanocene moiety has not been established. Such fission of a C(carbenic)–C bond is unusual for Fischer-type carbene complexes.[5] This suggests that these complexes have chemical properties characteristic of metallacyclopentanes[6—8] and oxametallacyclopentanes[9] of group 4 transition metals.

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§ *Crystal data for* (**3b**): monoclinic, space group $P2/a$, a = 30.401(1), b = 9.251(1), c = 27.561(5) Å; β = 105.73(1)°, U = 7460(2) Å^3, D_c = 1.86 g cm^{-3}, M = 1044.98, Z = 8 (two independent molecules). Crystal of 0.21 × 0.32 × 0.53 mm was sealed in a thin-walled capillary tube under argon. Diffraction data were collected at −40 °C with monochromated Mo-K_α radiation, $2\theta_{max}$ = 50°. Intensities were corrected for absorption (μ = 71.14 cm^{-1}). Unique 6715 reflections with $|F_o|>3\sigma(F_o)$ were used for the structure determination. The final conventional residual was R = 0.069 and R_w = 0.082 for 866 variables.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

¶ The half lives of (**3a**), (**3b**), (**3c**), and (**3e**) in $[^2H_8]$toluene are 116 (30 °C), 223 (30 °C), 73 (0 °C), and 64 min (30 °C), respectively.