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## Synthesis of New Fischer-type Carbene Complexes: Characterization and Reactions of Titanoxycarbene–Metal Complexes derived from $(\eta^5-C_5Me_5)_2Ti(C_2H_4)$ and Metal Carbonyls

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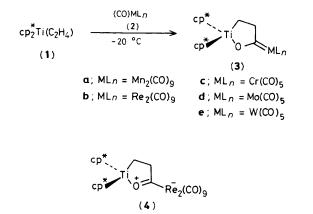
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Titanoxycarbene–metal carbonyl complexes have been synthesized by the reaction of  $(\eta^5-C_5Me_5)_2Ti(C_2H_4)$  and various metal carbonyls of group 6 and 7, and characterised by spectroscopic and X-ray crystallographic techniques; at elevated temperatures, 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,<sup>1a</sup> ( $\eta^2$ -aryne)zirconocene,<sup>1b</sup> or (dinitrogen)zirconocene<sup>2</sup> complexes and metal carbonyls. We have investigated the synthesis of new titanoxycarbene-metal complexes by the reaction of titanocene-ethylene complex (1) (cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) 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. <sup>1</sup>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



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

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 <sup>1</sup>H n.m.r. spectroscopy). The structures of (3a–e) are based on spectroscopic data.‡

(3b): m.p. 95–99 °C (decomp.); <sup>1</sup>H n.m.r.,  $\delta$  1.60 [t, J 7.1 Hz, C(5)H<sub>2</sub>], 1.78 (s, CMe), 4.02 [t, C(4)H<sub>2</sub>]; <sup>13</sup>C n.m.r.,  $\delta$  11.96 ( $J_{C-H}$  127 Hz, CMe), 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.); <sup>1</sup>H n.m.r.,  $\delta$  1.62 [t, J 6.9 Hz,

(3c): m.p. 98—103 °C (decomp.); <sup>1</sup>H n.m.r.,  $\delta$  1.62 [t, J 6.9 Hz, C(5)H<sub>2</sub>], 1.78 (s, CMe), 4.35 [t, C(4)H<sub>2</sub>]; <sup>13</sup>C n.m.r.,  $\delta$  11.99 (J<sub>C-H</sub> 127 Hz, CMe), 67.44 [J<sub>C-H</sub> 129 Hz, C(5)], 81.01 [J<sub>C-H</sub> 124 Hz, C(4)], 220.19, 225.2 (broad, CO), 349.79 [C(3)]. (3d): <sup>1</sup>H n.m.r.  $\delta$  1.65 [t, J 7.0 Hz, C(5)H<sub>2</sub>], 1.78 (s, CMe), 4.20 [t, ..., C(4)], 2.25.2 (broad, CO), 2.25 (broad, CO), 2.

(3d): <sup>1</sup>H n.m.r.  $\delta$  1.65 [t, J 7.0 Hz, C(5)H<sub>2</sub>], 1.78 (s, CMe), 4.20 [t, C(4)H<sub>2</sub>]; <sup>13</sup>C n.m.r.,  $\delta$  12.09 ( $J_{C-H}$  128 Hz, CMe), 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.); <sup>1</sup>H n.m.r., δ 1.60 [t, *J* 7.1 Hz, C(5)H<sub>2</sub>], 1.78 (s, CMe), 4.10 [t, C(4)H<sub>2</sub>]; <sup>13</sup>C n.m.r., δ 12.02 ( $J_{C-H}$  127 Hz, *CMe*), 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)].

<sup>‡</sup> All n.m.r. spectra were recorded on a JEOL GX400 spectrometer in [<sup>2</sup>H<sub>8</sub>]toluene at -30 °C using solvent absorptions at  $\delta$  2.31 and  $\delta_c$  137.70 as internal standards. <sup>13</sup>C N.m.r. absorptions due to sp<sup>2</sup> carbon atoms of the cyclopentadienyl ligands were not recorded because of overlap with those due to the aromatic carbon atoms of the solvent.

<sup>(3</sup>a): m.p. 115—118 °C (decomp.); <sup>1</sup>H n.m.r.,  $\delta$  1.53 [t, J 6.8 Hz, C(5)H<sub>2</sub>], 1.74 (s, CMe), 4.20 [t, C(4)H<sub>2</sub>]; <sup>13</sup>C n.m.r.,  $\delta$  11.93 (J<sub>C-H</sub> 127 Hz, CMe), 65.99 [J<sub>C-H</sub> 130 Hz, C(5)], 80.34 [J<sub>C-H</sub> 124 Hz, C(4)], 218.58, 225.60, 226.45 (CO), 333.97 [C(3)].

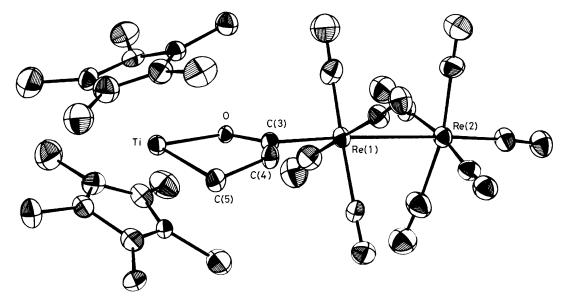


Figure 1. An ORTEP drawing of the molecular structure of (3b). Selected bond distances: Re(1)-Re(2) 3.057(2), Re(1)-C(3) 2.12(3), Ti-O(2) 2.02(2), Ti-C(5) 2.25(2), O(2)-C(3) 1.26(3), C(3)-C(4) 1.57(4), C(4)-C(5) 1.52(4) Å; angles: Re(2)-Re(1)-C(3) 176.7(7). Re(1)-C(3)-O(2) 125(2). Re-C(3)-C(4) 118(2), 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),  $C(3)-C(4)-C(5) 110(2)^{\circ}$ .

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  $\text{Re}_2(\text{CO})_{10}$  by conventional 'Fischer-type' methods where the carbene is *cis* to the Re–Re bond.<sup>3</sup> 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.<sup>1</sup>

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

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.

When the complexes (3a-e) in  $[{}^{2}H_{8}]$ 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.<sup>5</sup> This suggests that these complexes have chemical properties characteristic of metallacyclopentanes<sup>6</sup>-8 and oxametallacyclopentanes<sup>9</sup> of group 4 transition metals.

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<sup>§</sup> Crystal data for (**3b**): monoclinic, space group P2/a, a = 30.401(1), b = 9.251(1), c = 27.561(5) Å;  $\beta = 105.73(1)^{\circ}$ , U = 7460(2) Å<sup>3</sup>,  $D_c = 1.86$  g cm<sup>-3</sup>, M = 1044.98, Z = 8 (two independent molecules). Crystal of  $0.21 \times 0.32 \times 0.53$  mm was sealed in a thin-walled capillary tube under argon. Diffraction data were collected at  $-40^{\circ}$ C with monochromated Mo- $K_{\alpha}$  radiation,  $2\theta_{max} = 50^{\circ}$ . Intensities were corrected for absorption ( $\mu = 71.14 \text{ cm}^{-1}$ ). 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.

<sup>¶</sup> The half lives of (**3a**), (**3b**), (**3c**), and (**3e**) in  $[{}^{2}H_{8}]$ toluene are 116 (30 °C), 223 (30 °C), 73 (0 °C), and 64 min (30 °C), respectively.