Structure and Bonding of Heterobimetallic Fischer Carbene Complexes

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Heterobimetallic Fischer carbene complexes $(CO)_5CrC(OM')(R)$ [M' = $Ti(O$-i-$Pr)_3$, R = n-Bu (3); R = 2-furyl (4); R = $C(Me)CH_2$ (5); M' = $TiCp_2Cl$, R = $C(Me)CH_2$ (6)] are readily synthesized by metalation of pentacarbonylchromium acylate intermediates. X-ray crystallographic determinations have been performed at −120 °C for these compounds, as well as for the acylate precursor [NMe$_4$][$(CO)_5CrC(O)$-$(CMeCH_2)$] (7). Structures of 3–5 are the first to be reported of bimetallic carbene systems in which the Lewis acidic metal contains only oxygen ligands. The heterobimetallic complexes display unusually short Cr–C(carbene) and O–C(carbene) bond distances, with respect to standard alkoxycarbene analogues. 3 is monoclinic, $P2_1/n$, with $a = 12.694$ (2) Å, $b = 14.409$ (3) Å, $c = 13.552(3)$ Å, $\beta = 96.12$ (2)°, and $R = 0.044$. 4 is monoclinic, $P2_1/n$, with $a = 12.431$ (4) Å, $b = 10.775$ (2) Å, $c = 17.476$ (6) Å, $\beta = 95.17$ (3)°, and $R = 0.046$. 5 is triclinic, $P\bar{1}$, with $a = 9.555$ (2) Å, $b = 11.135$ (3) Å, $c = 12.613$ (4) Å, $\alpha = 108.33$ (2)°, $\beta = 110.73$ (2)°, $\gamma = 97.51$ (2)°, and $R = 0.038$. 6 is monoclinic, $P2_1/n$, with $a = 12.369$ (3) Å, $b = 12.964$ (3) Å, $c = 12.993$ (4) Å, $\beta = 107.47$ (2)°, and $R = 0.031$. 7 is orthorhombic, $Pnma$, with $a = 11.603$ (3) Å, $b = 9.327$ (3) Å, $c = 14.993$ (7) Å, and $R = 0.039$. The relevance of structural and spectroscopic data to bonding in these systems is discussed: the substitution of an O-bound electron-deficient metal for an O-alkyl group of a Fischer alkoxycarbene complex appears to increase π-electron delocalization across the carbenoxy unit in such a way as to strengthen both M–C(carbene) and O–C(carbene) interactions.

Introduction

Fischer carbene complexes have received much attention for their versatile C–C bond-forming transformations.[1] Our efforts are directed toward an exploration of the chemistry of bimetallic systems in which the carbene heteroatom is bound to a second, electron-deficient, metal. Such complexes offer the opportunity to control carbene reactivity by steric and electronic variations of the Lewis acidic component. In addition, carbenoxy compounds bearing early- and late-transition elements may be relevant to the CO-activation event of the Fischer–Tropsch reaction, which is catalyzed by electron-rich metals and metal–oxide cocatasyts.[2,3]

To provide a foundation for understanding reactivity in comparison with simple alkoxycarbene complexes, we have undertaken structural studies of a series of such bimetallic compounds involving chromium and titanium. The bimetallic carbene moiety 1 can be regarded as a resonance form of the O-metalated metalloacyl fragment 2, as shown in Figure 1.[1a,4] An understanding of the bonding in bimetallic carbene structures as it relates to these two extremes is desired.

Here we report the syntheses and solid-state structures of four carbene complexes containing Cr(0) and Ti(IV) fragments, including the first bimetallic species in which the Lewis acidic metal bears only oxygen ligands. We describe a shortening of the carbene carbon–oxygen bond

distance in the oxymetallacarbene fragment upon substitution of an alkyl group by the electron-deficient metal center, with metal–carbene bond distances essentially unchanged. In addition, the first X-ray crystal structure of a pentacarbonylchromium acyl anion is described.

Results

Crystal Structures. The series $(CO)_5CrC[OTi(O$-i-$Pr)_3][R]$ (3, R = n-Bu; 4, R = 2-furyl; 5, R = $CMeCH_2$) are depicted by ORTEP diagrams in Figures 2–4. The complex $(CO)_5CrC(OTiCp_2Cl)(CMeCH_2)$ (6) is shown in Figure 5. Table I lists crystallographic data for all structures, Tables II–VI show atom coordinates, and Table VII summarizes the important bond distances and angles. In each structure the carbene carbon is labeled C(1) and the carbenoxy oxygen atom is designated O(1).

Complexes 3–5 are each centrosymmetric dimers bridged by titanium isopropoxide groups; for the most part, the monomeric units are described to avoid confusion. The titanium centers are of variable coordination geometry: roughly trigonal-bipyramidal, octahedral, and square-pyramidal, respectively. Complex 6 is a monomeric structure bearing a $TiCp_2Cl$ fragment in place of the $Ti(O$-i-$Pr)_3$ group 5. Ti–O–C bond angles are in the range of 133–164° for 3–5 and 173.2 (2)° for 6, characteristic of titanium(IV) alkoxides.

The complexes $(CO)_5CrC(OEt)(Me)$ (8)[5] and $(CO)_5Cr(OMe)(Ph)$ (9)[6] are the best structures of simple alkoxycarbenes available in the literature for purposes of comparison (Table VII).[8] The structure of the 2-propenyl-

(1) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, Deerfield Beach, FL, 1983. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; JAI Press: Greenwich, CT, 1988; Vol. 1, pp 209–393. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587–608. (d) Schubert, U. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, England, 1982; p 233.

(2) (a) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: Orlando, FL, 1984. (b) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 8, Chapter 50, pp 40–62. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103.

(3) Homogeneous catalysis of the Fischer–Tropsch reaction invariably proceeds in the presence of Lewis acidic metals, particularly aluminum hydrides[30] or halides.[31] It has long been suggested that the role of metal oxide additives is to coordinate to the oxygen atom of bound CO and thereby facilitate CO bond cleavage.[2b,32]

(4) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261–286.

(5) Schubert, U. In ref 1a, p 94.

(6) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 642–647.

(7) Anslyn, E. V.; Santarsiero, B. D.; Grubbs, R. H. *Organometallics* **1988**, *7*, 2137–2145.

(8) The (*E*)-2-butenyl complex $(CO)_5Cr(OMe)(E$-$C(Me)$=CHMe)[33] is an alkoxycarbene structure that can also be used for comparison. However, it has two very unusual bond distances that make it an exceptional case. The M–C(1) bond is unusually short (2.006(5) Å), and the olefinic bond distance is extremely small (1.238 (10) Å), closer to a typical C≡C triple bond (1.20 Å) than a C=C double bond (1.33 Å). The C(1)–O(1) bond distance is unremarkable (1.301 (6) Å). The olefin moiety is oriented perpendicular to the carbene plane, as in structure 6, but the origin of the short C=C bond is unknown. We have repeated this X-ray structure, with essentially the same results. No other pentacarbonylchromium carbene structures bearing one alkoxy and one innocent carbon substituent at the carbene carbon have been subjected to X-ray analysis.
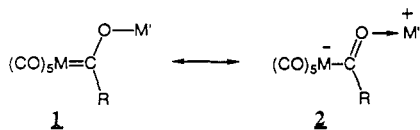
Figure 1. Carbene and acyl resonance forms of heterobimetallic Fischer carbene complexes.
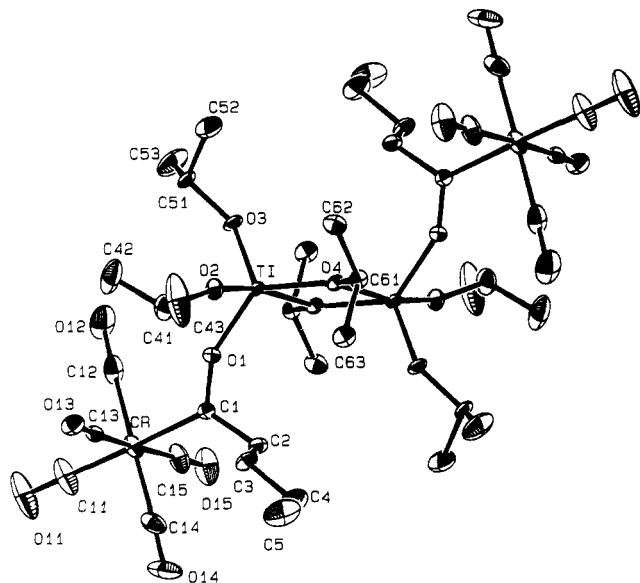
Figure 2. ORTEP diagram of {(CO)$_5$CrC[OTi(O-i-Pr)$_3$][n-Bu]}$_2$ (3) with numbering scheme.
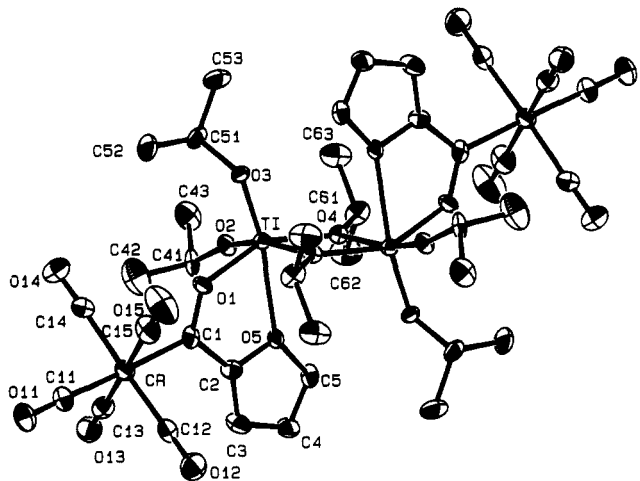
Figure 3. ORTEP diagram of {(CO)$_5$CrC[OTi(O-i-Pr)$_3$][2-furyl]}$_2$ (4) with numbering scheme.

Figure 4. ORTEP diagram of {(CO)$_5$CrC[OTi(O-i-Pr)$_3$][CMeCH$_2$]}$_2$ (5) with numbering scheme.
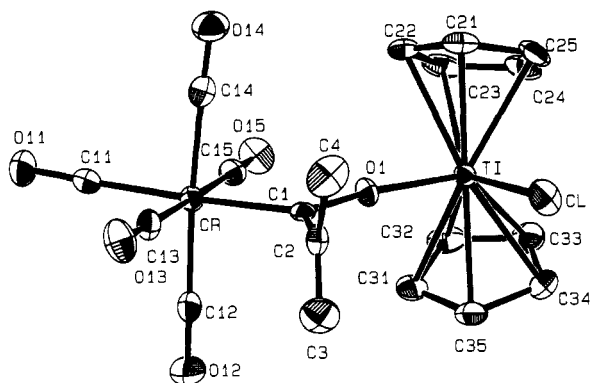
Figure 5. ORTEP diagram of (CO)$_5$CrC[OTiCp$_2$Cl][CMeCH$_2$] (6) with numbering scheme.
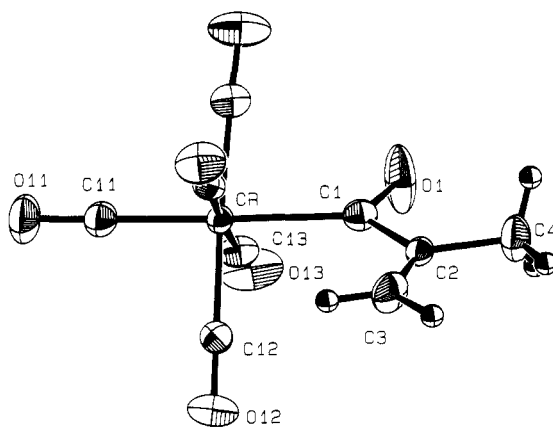
Figure 6. ORTEP diagram of [Me$_4$N][(CO)$_5$CrC(O)(CMeCH$_2$)] (7) with numbering scheme (cation not shown).

substituted chromium acylate complex [NMe$_4$][(CO)$_5$Cr-(COCMe=CH$_2$)] (7) has also been obtained (Figure 6, Table VII) as a representative of the "acyl" resonance form. Although (CO)$_5$Cr–acylate complexes have long been employed as carbene complex precursors,[9,1a] 7 appears to be the first crystal structure of such a compound to be reported.[10] The complex anion exhibits mirror plane symmetry with the carbene and propenyl groups located on the plane. The Cr–C(1) bond distance of 7 (2.147 (5) Å)

is significantly longer, and the C(1)–O(1) distance (1.234 (5) Å) significantly shorter, than the carbene complexes discussed here. Of standard Fischer carbene systems, only those bearing two π-donating heteroatoms at the carbene carbon have longer Cr–C(1) bond distances,[11] and none have shorter C(1)–O(1) bonds.

(9) Fischer, E. O.; Maasbol, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580–581.

(10) Related acylate structures are as follows. (a) [NMe$_4$][Cp-(CO)$_2$MnC(O)Ph]: Hädicke, E.; Hoppe, W. *Acta Crystallogr., Sect. B* **1971**, *B27*, 760–768. (b) (CO)$_3$Mo(PhCOLi)[Ph$_2$P(OCH$_2$CH$_2$)$_3$OPPh$_2$]: Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941–5943.

(11) Examples are as follows. (a) (CO)$_5$CrC(NEt$_2$)$_2$, 2.190 (7) Å: Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 444–445. (b) (CO)$_5$CrC(NEt$_2$)SePh, 2.171 (8) Å: Fischer, E. O.; Himmelreich, D.; Cai, R.; Fischer, H.; Schubert, U.; Zimmer-Gasser, B. *Chem. Ber.* **1981**, *114*, 3209–3219.

Table I. Crystallographic Data for 3-7

	3	4	5	6	7
formula	$C_{38}H_{60}Cr_2O_{18}Ti_2$	$C_{38}H_{48}Cr_2O_{20}Ti_2$	$C_{36}H_{54}Cr_2O_{18}Ti_2$	$C_{19}H_{15}ClCrO_6Ti$	$C_{13}H_{17}CrNO_6$
fw	1004.67	1024.58	974.60	474.67	335.28
cryst size, mm	0.35 × 0.19 × 0.12	0.17 × 0.12 × 0.05	0.3 × 0.22 × 0.20	0.4 × 0.32 × 0.31	0.48 × 0.27 × 0.12
cryst system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
a, Å	12.634 (2)	12.431 (4)	9.555 (2)	12.369 (3)	11.603 (3)
b, Å	14.409 (3)	10.775 (2)	11.135 (3)	12.964 (3)	9.327 (3)
c, Å	13.552 (3)	17.476 (6)	12.613 (4)	12.993 (4)	14.993 (7)
α, deg	90	90	108.33 (2)	90	90
β, deg	96.12 (2)	95.17 (3)	110.73 (2)	107.47 (2)	90
γ, deg	90	90	97.51 (2)	90	90
V, Å³	2465 (2)	2331 (1)	1146.7 (5)	1987.4 (9)	1623 (2)
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$Pnma$
Z	2	2	1	4	4
d_{calcd}, g cm⁻³	1.35	1.46	1.41	1.53	1.37
μ(Mo Kα), cm⁻¹	7.9	8.4	8.5	11.0	7.1
diffractometer	Enraf-Nonius CAD4	Rigaku AFC6S	Siemens R3m/V	Rigaku AFC6S	Rigaku AFC6S
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 73)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
transm factors	0.78–1.00	0.88–1.00	0.86–1.00	0.89–1.00	0.87–1.00
temp, °C	−120	−120	−120	−120	−120
2θ range, deg	4–50	4–46	3.5–55	4–50	4–50
no. of unique data measd	4517	3196	5267	3557	1645
no. of unique reflcns with $I > 3\sigma(I)$	3053	1575	4615	2616	1120
no. of params	272	280	264	253	150
R	0.044	0.046	0.038	0.031	0.039
R_w	0.054	0.052	0.051	0.045	0.047
GOF	1.62	1.39	1.28	1.48	1.88
highest resid in final ΔF map, e Å⁻³	0.49	0.46	0.90	0.51	0.31

Table II. Positional Parameters for 3

atom	x	y	z
Cr	0.67497 (6)	0.42371 (4)	−0.35995 (4)
Ti	0.48130 (5)	0.40954 (4)	−0.06976 (4)
O(1)	0.5664 (2)	0.4199 (2)	−0.1798 (2)
O(2)	0.5053 (2)	0.2895 (2)	−0.0619 (2)
O(3)	0.3456 (2)	0.4168 (2)	−0.1159 (2)
O(4)	0.5094 (2)	0.4441 (2)	0.0672 (2)
O(11)	0.6971 (5)	0.4035 (3)	−0.5787 (3)
O(12)	0.4355 (3)	0.4129 (3)	−0.3982 (3)
O(13)	0.6844 (2)	0.2167 (2)	−0.3181 (2)
O(14)	0.9142 (3)	0.4313 (2)	−0.3156 (3)
O(15)	0.6711 (3)	0.6343 (2)	−0.3779 (2)
C(1)	0.6537 (3)	0.4384 (2)	−0.2137 (3)
C(2)	0.7397 (3)	0.4666 (3)	−0.1332 (3)
C(3)	0.7965 (3)	0.3798 (3)	−0.0902 (3)
C(4)	0.8900 (4)	0.4030 (3)	−0.0153 (4)
C(5)	0.9407 (4)	0.3167 (4)	0.0334 (4)
C(11)	0.6895 (5)	0.4111 (3)	−0.4957 (3)
C(12)	0.5265 (4)	0.4174 (3)	−0.3853 (3)
C(13)	0.6802 (3)	0.2942 (3)	−0.3363 (3)
C(14)	0.8240 (4)	0.4290 (3)	−0.3315 (4)
C(15)	0.6715 (4)	0.5547 (3)	−0.3714 (3)
C(41)	0.5412 (4)	0.2024 (3)	−0.0986 (3)
C(42)	0.4635 (5)	0.1695 (4)	−0.1801 (5)
C(43)	0.5631 (8)	0.1372 (4)	−0.0171 (4)
C(51)	0.2601 (3)	0.3608 (3)	−0.1621 (3)
C(52)	0.1962 (4)	0.3289 (4)	−0.0830 (4)
C(53)	0.1976 (4)	0.4182 (4)	−0.2401 (4)
C(61)	0.5407 (3)	0.3915 (2)	0.1580 (2)
C(62)	0.4582 (3)	0.3192 (3)	0.1735 (3)
C(63)	0.6509 (3)	0.3517 (3)	0.1533 (3)

Table III. Positional Parameters for 4

atom	x	y	z
Cr	−0.0385 (1)	0.1415 (1)	0.32319 (7)
Ti	0.0649 (1)	0.0971 (1)	0.05720 (8)
O(1)	0.0401 (4)	0.1006 (5)	0.1696 (3)
O(2)	0.0954 (4)	0.2571 (4)	0.0559 (3)
O(3)	0.1988 (4)	0.0381 (5)	0.0665 (3)
O(4)	0.0101 (4)	0.0748 (4)	−0.0513 (3)
O(5)	−0.1155 (4)	0.1663 (5)	0.0745 (3)
O(11)	−0.0338 (5)	0.1481 (6)	0.4964 (3)
O(12)	−0.2712 (5)	0.0521 (6)	0.3154 (4)
O(13)	−0.0991 (5)	0.4140 (6)	0.3181 (3)
O(14)	0.1978 (5)	0.2134 (6)	0.3355 (4)
O(15)	0.0315 (6)	−0.1291 (7)	0.3218 (4)
C(1)	−0.0387 (6)	0.1408 (7)	0.2061 (4)
C(2)	−0.1294 (6)	0.1830 (7)	0.1525 (4)
C(3)	−0.2271 (7)	0.2376 (8)	0.1580 (5)
C(4)	−0.2776 (7)	0.2553 (8)	0.0820 (5)
C(5)	−0.2078 (7)	0.2093 (7)	0.0333 (4)
C(11)	−0.0350 (7)	0.1440 (8)	0.4304 (5)
C(12)	−0.1843 (8)	0.0881 (8)	0.3172 (4)
C(13)	−0.0773 (7)	0.3083 (9)	0.3205 (5)
C(14)	0.1085 (7)	0.1857 (8)	0.3297 (5)
C(15)	0.0056 (8)	−0.027 (1)	0.3224 (5)
C(41)	0.1015 (7)	0.3878 (7)	0.0722 (4)
C(42)	0.126 (1)	0.406 (1)	0.1561 (5)
C(43)	0.1889 (8)	0.4456 (8)	0.0283 (5)
C(51)	0.3027 (6)	0.0929 (8)	0.0878 (5)
C(52)	0.3280 (7)	0.077 (1)	0.1721 (5)
C(53)	0.3848 (7)	0.0359 (9)	0.0413 (5)
C(61)	0.0334 (7)	0.1485 (8)	−0.1175 (4)
C(62)	−0.0198 (7)	0.2701 (9)	−0.1180 (5)
C(63)	0.1534 (7)	0.1520 (8)	−0.1238 (5)

Spectroscopy. Titanium alkoxide complexes participate in rapid ligand-exchange processes, which affect the NMR spectra of the carbene compounds reported here. ¹H and ¹³C NMR spectra of 3–5 at room temperature show a single set of isopropoxide resonances, which broaden but do not resolve to separate signals upon cooling to −40 °C.[12] The carbene carbon signals of the furyl complex 4 (304.8

(12) Solid-state CP-MAS ¹³C NMR spectroscopy at 25 °C of complex 3 shows three sets of isopropoxide groups, as expected for the X-ray structure. Neither variable-temperature solution-phase nor solid-phase NMR spectroscopy of any titanoxycarbene complex shows evidence of isomerization about the C(1)–O(1) bond, suggesting that the configuration shown in the crystal structures is strongly favored.

ppm) and the TiCp₂Cl complex 6 (357.2 ppm) are visible at ambient temperature; in contrast, lower temperature is required for the carbene resonance of compounds 3 (362.0 ppm) and 5 (351.6 ppm) to be resolved. This difference is presumably due to the diminished ability of 4 and 6 to engage in associative ligand exchange at titanium.

The addition of 3 equiv of isopropyl alcohol per titanium atom to the *n*-butyl complex 3 gives rise to exchange of free alcohol with bound isopropoxide, *without* substitution of the titanium carbenoxy ligand (to give a hydroxycarbene complex) or attack of alcohol at the carbene carbon (to give an isopropoxycarbene complex). In addition, molecular

Table IV. Positional Parameters for 5

atom	x	y	z
Cr	0.2690 (1)	0.7369 (1)	0.5334 (1)
Ti	0.0785 (1)	0.6478 (1)	0.1024 (1)
O(1)	0.1183 (2)	0.6510 (1)	0.2654 (1)
O(2)	0.0223 (2)	0.7952 (2)	0.1379 (2)
O(3)	0.2581 (2)	0.6964 (2)	0.0962 (2)
O(4)	−0.0839 (2)	0.5490 (1)	−0.0611 (1)
O(11)	0.5360 (3)	0.8370 (2)	0.7857 (2)
O(12)	0.0645 (2)	0.6465 (2)	0.6457 (2)
O(13)	0.1960 (3)	1.0010 (2)	0.5876 (2)
O(14)	0.4915 (2)	0.8195 (2)	0.4297 (2)
O(15)	0.3235 (2)	0.4648 (2)	0.4705 (2)
C(1)	0.0883 (2)	0.6724 (2)	0.3601 (2)
C(2)	−0.0831 (3)	0.6413 (2)	0.3265 (2)
C(3)	−0.1389 (3)	0.7073 (3)	0.4032 (2)
C(4)	−0.1887 (3)	0.5402 (3)	0.2008 (2)
C(11)	0.4356 (3)	0.7985 (2)	0.6892 (2)
C(12)	0.1376 (3)	0.6796 (2)	0.6002 (2)
C(13)	0.2245 (3)	0.9023 (2)	0.5670 (2)
C(14)	0.4066 (3)	0.7893 (3)	0.4674 (2)
C(15)	0.3025 (3)	0.5653 (3)	0.4923 (2)
C(41)	0.0101 (3)	0.9125 (2)	0.2181 (2)
C(42)	0.1728 (3)	1.0025 (3)	0.3032 (3)
C(43)	−0.0905 (3)	0.9762 (2)	0.1446 (3)
C(51)	0.3784 (3)	0.8051 (2)	0.1186 (2)
C(52)	0.5249 (3)	0.7616 (4)	0.1413 (3)
C(53)	0.3301 (4)	0.8468 (3)	0.0120 (3)
C(61)	−0.2055 (3)	0.5858 (2)	−0.1439 (2)
C(62)	−0.3277 (3)	0.6052 (3)	−0.0980 (3)
C(63)	−0.1349 (3)	0.7004 (2)	−0.1652 (2)

Table V. Positional Parameters for 6

atom	x	y	z
Cr	0.16150 (4)	0.23001 (4)	0.13247 (4)
Ti	−0.15632 (4)	0.13405 (4)	0.23893 (4)
Cl	−0.24718 (7)	0.27066 (6)	0.30141 (7)
O(1)	−0.0407 (2)	0.2191 (2)	0.2109 (2)
O(11)	0.3765 (2)	0.1738 (2)	0.0795 (2)
O(12)	0.0227 (2)	0.2536 (2)	−0.1037 (2)
O(13)	0.2464 (2)	0.4510 (2)	0.1402 (2)
O(14)	0.2805 (2)	0.1975 (2)	0.3707 (2)
O(15)	0.0845 (2)	0.0065 (2)	0.1226 (2)
C(1)	0.0271 (2)	0.2772 (2)	0.1815 (2)
C(2)	0.0048 (2)	0.3891 (2)	0.1972 (2)
C(3)	−0.0531 (3)	0.4467 (3)	0.1157 (3)
C(4)	0.0533 (3)	0.4282 (3)	0.3097 (3)
C(11)	0.2941 (3)	0.1930 (3)	0.0977 (2)
C(12)	0.0748 (3)	0.2459 (3)	−0.0156 (3)
C(13)	0.2124 (3)	0.3686 (3)	0.1383 (2)
C(14)	0.2377 (3)	0.2109 (2)	0.2806 (3)
C(15)	0.1125 (3)	0.0906 (3)	0.1258 (2)
C(21)	−0.0392 (3)	0.1274 (3)	0.4215 (2)
C(22)	0.0127 (3)	0.0658 (3)	0.3616 (3)
C(23)	−0.0603 (3)	−0.0169 (2)	0.3177 (2)
C(24)	−0.1563 (3)	−0.0079 (3)	0.3532 (2)
C(25)	−0.1431 (3)	0.0798 (3)	0.4173 (2)
C(31)	−0.1919 (3)	0.1179 (3)	0.0490 (2)
C(32)	−0.2076 (3)	0.0210 (2)	0.0895 (2)
C(33)	−0.3016 (3)	0.0278 (3)	0.1293 (3)
C(34)	−0.3424 (3)	0.1291 (3)	0.1140 (3)
C(35)	−0.2730 (3)	0.1854 (3)	0.0663 (2)

Table VI. Positional Parameters for 7

atom	x	y	z
Cr	0.14043 (6)	0.25	0.03213 (4)
O(1)	0.3919 (3)	0.25	0.0011 (2)
O(11)	−0.1088 (2)	0.25	−0.0241 (3)
O(12)	0.0879 (2)	0.0149 (3)	0.1652 (2)
O(13)	0.2098 (3)	0.0218 (3)	−0.1020 (2)
N	0.1173 (3)	0.25	0.6487 (2)
C(1N)	0.2194 (6)	0.25	0.7100 (4)
C(1)	0.3214 (4)	0.25	0.0626 (3)
C(2N)	0.1240 (4)	0.3783 (4)	0.5903 (4)
C(2)	0.3780 (4)	0.25	0.1536 (3)
C(3N)	0.0084 (6)	0.25	0.6994 (5)
C(3)	0.3183 (5)	0.25	0.2287 (3)
C(4)	0.5077 (5)	0.25	0.1547 (4)
C(11)	−0.0114 (4)	0.25	−0.0029 (3)
C(12)	0.1089 (2)	0.1051 (4)	0.1158 (2)
C(13)	0.1822 (3)	0.1073 (4)	−0.0510 (2)
H(1NA)	0.209 (4)	0.168 (4)	0.741 (3)
H(1NB)	0.290 (6)	0.25	0.671 (4)
H(2NA)	0.053 (3)	0.378 (4)	0.555 (2)
H(2NB)	0.124 (4)	0.449 (6)	0.634 (3)
H(2NC)	0.204 (4)	0.377 (5)	0.549 (3)
H(3NA)	−0.049 (6)	0.25	0.655 (4)
H(3A)	0.360 (4)	0.25	0.288 (4)
H(3B)	0.234 (5)	0.25	0.228 (3)
H(3NB)	0.016 (4)	0.330 (5)	0.736 (3)
H(4A)	0.539 (3)	0.166 (4)	0.125 (2)
H(4B)	0.533 (5)	0.25	0.214 (4)

The lowest energy band of the electronic spectra of pentacarbonyltungsten carbene complexes has been assigned to a M → carbene ($\pi \rightarrow \pi^*$) MLCT charge-transfer transition.[14,15a] Assuming the same assignment for chromium systems, this band is broadened and shifted to lower energy when a titanoxy substituent is present, as shown in Table VIII. Only complexes having extended π interactions with the carbene carbon display low-energy MLCT bands at wavelengths longer than 400 nm.[15]

Reactions. The reactions of these and similar bimetallic carbene complexes with dienes, olefins, and alkynes are under investigation and will be reported separately. We have observed Diels–Alder reactions with dienes, cyclopropanation reactions of allylic alcohols, and insertion/benzannulation processes with alkynes, in some cases with unusual stereochemical consequences. However, heterobimetallic carbene complexes are generally less stable in solution than their methoxycarbene analogues. Thus, decomposition to the extent of 50% occurs in CH_2Cl_2 solution at room temperature under N_2 atmosphere in 26 h for 3, 11 h for 4, and 90 min for 5, whereas $(CO)_5CrC$-$(OMe)(CMeCH_2)$ is stable for several days. Interestingly, $(CO)_5CrC[OTi(O\text{-}i\text{-}Pr)_3][CH_3]$ (11) shows very little decomposition under the same conditions. Complex 6 is also stable at room temperature for several days. All bimetallic complexes reported here are stable in solution at −30 °C for periods exceeding 1 week and indefinitely at −30 °C in the solid state.

Discussion

Titanium. A feature of interest in the structures of complexes 3–5 is the presence of bridging isopropoxide ligands, which are rarely found in this type of interaction

weight determination of $(CO)_5CrC[OTi(O\text{-}i\text{-}Pr)_3][Me]$ (11, the methyl analogue of 3) by the Signer method[13] in CH_2Cl_2 shows an average molecularity of 1.5 ± 0.2 in solution. These data suggest that titanium isopropoxide ligand exchange and monomer–dimer equilibration are occurring in solution at rapid rates on the NMR time scale for $-OTi(O\text{-}i\text{-}Pr)_3$ complexes.

(13) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 94–96. Complexes 3–5 are not sufficiently stable at room temperature in solution for a molecular weight measurement to be made by this method, which requires approximately 7 days.

(14) Foley, H. C.; Stubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1983, 105, 3064–3073.

(15) (a) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* 1988, 110, 8413–8421. (b) Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* 1970, 9, 32–39.

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(17) Prepared as in ref 33; electronic spectrum obtained in this work (hexane).

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complexes 3-10

	3	4	5	6	7	8[a]	9[b]	10[c]
Cr–C(1)	2.040 (4)	2.046 (8)	2.072 (2)	2.045 (3)	2.147 (5)	2.053 (1)	2.04 (3)	2.089 (6)
C(1)–O(1)	1.272 (4)	1.290 (9)	1.284 (3)	1.268 (3)	1.232 (6)	1.314 (1)	1.33 (2)	1.269 (7)
C(1)–C(2)	1.514 (5)	1.47 (1)	1.500 (3)	1.502 (4)	1.517 (6)	1.511 (1)	1.47 (4)	1.528 (10)
C(2)–C(3)	1.527 (5)	1.36 (1)	1.335 (4)	1.317 (5)	1.322 (7)	n/a	n/a	n/a
Ti–O(1)	1.938 (2)	2.016 (5)	1.942 (2)	1.926 (2)	n/a		n/a	2.007 (4)
Ti–O(2)	1.758 (2)	1.766 (5)	1.767 (2)	n/a	n/a		n/a	n/a
Ti–O(3)	1.772 (2)	1.776 (5)	1.767 (2)	n/a	n/a		n/a	n/a
Ti–O(4)	1.918 (2)	1.970 (5)	1.933 (1)	n/a	n/a		n/a	n/a
Ti–O(4)'	2.113 (2)	2.073 (5)	2.100 (2)	n/a	n/a		n/a	n/a
Ti–O(5)	n/a	2.408 (5)	n/a	n/a	n/a		n/a	n/a
Cr–C(11)	1.878 (5)	1.871 (9)	1.877 (2)	1.890 (3)	1.838 (5)		1.87 (3)	1.844 (7)
Cr–C(12)	1.881 (5)	1.90 (1)	1.889 (3)	1.912 (3)	1.880 (3)		1.86 (3)	1.880 (7)
Cr–C(13)	1.893 (4)	1.86 (1)	1.896 (3)	1.899 (3)	1.887 (4)		1.91 (2)	1.897 (7)
Cr–C(14)	1.892 (6)	1.88 (1)	1.909 (3)	1.889 (3)	n/a		1.89 (3)	1.876 (7)
Cr–C(15)	1.894 (5)	1.90 (1)	1.917 (3)	1.900 (3)	n/a		1.89 (2)	1.892 (7)
Ti–Cl	n/a	n/a	n/a	2.368 (1)	n/a		n/a	2.347 (2)
Ti–O(1)–C(1)	150.7 (2)	132.7 (5)	153.3 (2)	173.2 (2)	n/a		n/a	158.3 (4)
Ti–O(2)–C(41)	153.5 (3)	164.1 (5)	154.8 (2)	n/a	n/a		n/a	n/a
Ti–O(3)–C(51)	141.2 (2)	133.6 (5)	145.7 (2)	n/a	n/a		n/a	n/a
O(2)–Ti–O(4)'	166.5 (1)	165.5 (2)	163.3 (1)	n/a	n/a		n/a	n/a
O(1)–Ti–O(2)	90.9 (1)	92.6 (2)	90.7 (1)	n/a	n/a		n/a	n/a
O(2)–Ti–O(3)	103.6 (1)	98.6 (2)	103.4 (1)	n/a	n/a		n/a	n/a
O(2)–Ti–O(4)	100.5 (1)	99.3 (2)	99.5 (1)	n/a	n/a		n/a	n/a
O(3)–Ti–O(4)	113.6 (1)	106.5 (2)	110.7 (1)	n/a	n/a		n/a	n/a
O(1)–Ti–O(4)	131.6 (1)	150.4 (2)	135.3 (1)	n/a	n/a		n/a	n/a
O(1)–Ti–O(3)	109.0 (1)	98.2 (2)	108.9 (1)	n/a	n/a		n/a	n/a
O(2)–Ti–O(5)	n/a	84.4 (2)	n/a	n/a	n/a		n/a	n/a
O(4)–Ti–O(5)	n/a	85.1 (2)	n/a	n/a	n/a		n/a	n/a
O(1)–Ti–O(5)	n/a	69.2 (2)	n/a	n/a	n/a		n/a	n/a
O(3)–Ti–O(5)	n/a	167.3 (2)	n/a	n/a	n/a		n/a	n/a
O(1)–Ti–Cl	n/a	n/a	n/a	95.30 (7)	n/a		n/a	97.2 (1)
Cr–C(1)–O(1)	122.6 (2)	124.2 (5)	119.8 (2)	126.1 (2)	119.3 (3)		134 (2)	129.2 (5)
Cr–C(1)–C(2)	124.6 (3)	124.6 (6)	127.9 (2)	122.0 (2)	127.9 (3)		122 (1)	119.4 (5)
O(1)–C(1)–C(2)	112.6 (3)	111.2 (6)	112.2 (2)	111.6 (2)	112.7 (4)		104 (2)	111.3 (5)
OC–Cr–C(1)–C(2)[a]	12.3 (3)	39.9 (7)	18.7 (3)	4.2 (2)	46.0 (1)			
Cr–C(1)–O(1)–Ti	177.6 (3)	–176.3 (3)	146.5 (3)	–103 (2)	n/a			
Cr–C(1)–C(2)–C(3)	–89.4 (3)	5 (1)	32.7 (3)	85.4 (3)	0			

[a] Reference 5. [b] Reference 6. [c] See Discussion; ref 7.

Table VIII. MLCT Bands in Chromium Carbene Complexes (CO)₅Cr[C(R¹)(R²)]

R¹	R²	λmax (MLCT), nm	log ε	ref
Me	OMe	376	3.85	15
n-Bu	OTi(O-i-Pr)₃	412	3.86	complex 3
2-furyl	OEt	460	4.20	16
2-furyl	OTi(O-i-Pr)₃	510	4.20	complex 4
CMeCH₂	OMe	396	3.95	17
CMeCH₂	OTi(O-i-Pr)₃	440	3.54	complex 5
CMeCH₂	OTiCp₂Cl	424	3.98	complex 6

due to the resulting steric congestion around both titanium centers.[18] In each case reported here, the planar four-membered Ti₂O₂ ring is skewed, with the longer bridging Ti–O bond (Ti–O(4)') oriented trans to a nonbridging isopropoxide ligand (Ti–O(2)), demonstrating a trans influence of the π-donating terminal alkoxide. Spectroscopic and molecular weight measurements (vide supra) confirm that the bridging interaction is easily broken in solution, giving rise to rapid monomer–dimer equilibration.

While the Ti–O(2) and Ti–O(3) bond distances in complexes 3–5 are unremarkable, the Ti–O(1) bonds in 3–6 are much longer than those of typical terminal titanium(IV) alkoxides and are in the same range as the bridging Ti–

O-i-Pr interactions [Ti–O(4) and Ti–O(4)']. This supports the notion that O(1)→C(1) π donation occurs at the expense of O(1)→Ti π donation, suggesting that sterically unfavorable isopropoxide bridges are formed in the solid state to maximize the available ligand electron density at each Ti(IV) center. In the monomeric form, then, the Ti(O-i-Pr)₃ substituents of the n-butyl complex 3 and the 2-propenyl structure 5 are likely to be relatively strong Lewis acidic centers. The Ti–O(1) bond of the furyl complex 4 (2.016 (5) Å) is even longer than that of 3 (1.938 (2) Å) and 5 (1.942 (2) Å), which may reflect the reduced Lewis acidity of a six-coordinate compared to a five-coordinate Ti(IV) center.

Chromium. Bonding in Fischer carbene systems is often evaluated in terms of competitive π donation by the metal and the heteroatom substituent(s) to the carbene p orbital; for monoalkoxycarbene complexes these are described as "carbene" and "acyl" resonance forms. As examples of these two extremes, we use the alkoxycarbene complexes 8[5,8] and 9[6] and the acylate complex 7.

The C(1)–O(1) bond distance in each of the titanoxycarbene complexes 3–6 is shorter than that in 8 and 9. This strengthened C–O interaction suggests that the "acyl" resonance structure 2 (Figure 1) is an important contributor to the bonding in these species, as has been noted by Erker for a series of zirconoxycarbene complexes.[19] This view is supported by the Ti–O(1) bond distances discussed above.

(18) For example, Ti(O-i-Pr)₄ exists largely as a monomer in solution: (a) Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 113–126. (b) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978; Chapter 4. (c) Bradley, D. C.; Mehrotra, R. C.; Wardlaw, W. *J. Chem. Soc.* **1952**, 5020–5023.

(19) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397–412 and references therein.
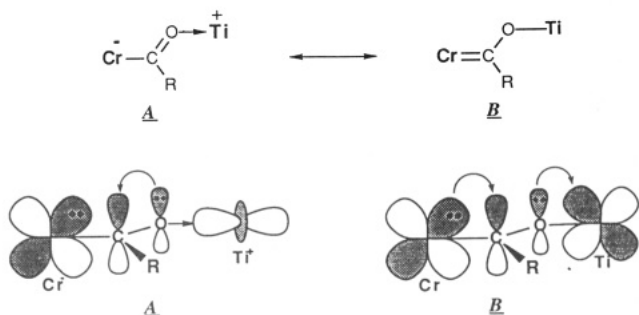
Figure 7. Orbital interactions in acyl (A) and carbene (B) resonance forms of titanoxycarbene complexes.

The 2-propenyl complex **5** shows the longest Cr–C(1) bond of the carbene structures reported here (2.072 (2) Å), perhaps due to the partial π conjugation of the olefinic group with the carbene fragment (Cr=(1)—C(2)=C(3) dihedral angle = 32.7 (3)°) in the manner of other Fischer carbene complexes.[4,20a] The crystal structure of $(CO)_5CrC(OTiCp_2Cl)(CMeCH_2)$ **(6)**, in which TiCp$_2$Cl appears in place of Ti(O-i-Pr)$_3$ in **5**, shows the 2-propenyl moiety to adopt a perpendicular orientation with respect to the carbene plane [Cr=C(1)—C(2)=C(3) dihedral angle = 85.4 (3)°]. The absence of π conjugation of Cr=C(1) and C(2)=C(3) bonds in **6** is consistent with the shortening of the Cr=C(1) bond (2.045 (3) Å in **6** vs 2.072 (2) Å in **5**). The C(2)–C(3) bond distance is slightly longer in **5** than in **6**, also consistent with greater vinylcarbene conjugation in the former, but the C(1)–C(2) distances are not affected.

The inverse relationship between C(1)–heteroatom and M–C(1) bond distances in Fischer carbene complexes has been well established, providing evidence for the aforementioned "competition" between acyl and carbene resonance forms.[4,20] However, we observe that the Cr–C(1) bond distances of structures **3** (2.040 (4) Å), **4** (2.046 (8) Å), **5** (2.072 (2) Å), and **6** (2.045 (3) Å) are very near to those of the alkoxycarbene complexes **8** (2.053 (1) Å) and **9** (2.04 (3) Å), whereas the C(1)–O(1) bonds of **3**–**6** are considerably shortened. The simple picture of competitive π donation of metal and heteroatom to the carbene carbon must therefore be modified for such heterobimetallic complexes. Apparently, significant carbenoid character remains in these systems, as their participation in reactions characteristic of Fischer carbene complexes (such as benzannulation and cyclopropanation) would indicate.[21]

We suggest that π delocalization in the M–C–O–M' unit is increased for titanoxycarbene complexes by virtue of the π acidity of the d^0 metal center, illustrated by the two resonance structures in Figure 7. O(1)→C(1) π donation

occurs in the acyl resonance form A, which is enhanced relative to alkoxycarbene complexes.[4,22] The loss of Cr–C(1) double-bond character in acyl form A is balanced by increased Cr→C(1) π donation in the carbene resonance form B, resulting in unchanged Cr–C(1) distances for titanoxycarbene complexes that have shortened C(1)–O(1) bonds. In B, O(1)→Ti pπ → dπ donation can be expected to be important, as has been noted for d^0 metal alkoxide complexes in which large C–O–Ti bond angles are observed.[23] No such interaction is possible for alkoxycarbene structures. The combination of A and B suggests that π-electron density may be delocalized over the titanoxycarbene moiety to a greater extent than in alkoxycarbene systems. This is consistent with the observed shift of the MLCT band in the electronic spectrum to lower energy for the bimetallic complexes.

A report has appeared of a complex related to **6**, containing η^5-C$_5$Me$_5$ (Cp*) ligands {(CO)$_5$CrC(OTiCp*$_2$Cl)(Me)} **(10)** in Table VII}, in which the large C$_{carbene}$–O–Ti bond angle (158.3°) has been attributed to steric effects and not π-bonding contributions.[7] Our results suggest that electronic factors may indeed play a role, since **6** contains a much *less* sterically encumbering titanium center than **10** and shows a *larger* C(1)–O(1)–Ti bond angle (173.2 (2)°). Steric interactions involving the 2-propenyl group of **6** should be minimized by its perpendicular orientation with respect to the carbene plane.

A comparison of structures **6** and **10** shows the former to have a shorter Ti–O(1) bond distance (1.926 (2) Å vs 2.007 (4) Å) and a longer Ti–Cl bond (2.368 (1) Å vs 2.347 (2) Å). Therefore, O(1)→Ti π donation occurs to a greater extent in **6** than in **10**, presumably because TiCp$_2$Cl is more electron-deficient than TiCp*$_2$Cl. This may contribute to the shorter Cr–C(1) distance in **6** (2.045 (3) Å) compared to **10** (2.089 (6) Å). In addition, the π-accepting LUMO of the Cp$_2$TiCl fragment is the a$_1$ orbital, which lies in the plane bisecting the Cp–Ti–Cp angle.[24] The nearly linear C(1)–O(1)–Ti bond angle in **6** suggests sp hybridization at O(1), allowing O(1)–Ti and O(1)–C(1) π overlap to occur using both p orbitals of O(1). The presence of an sp-hybridized substituent at the carbene carbon has been shown to result in a shortened Cr–C(1) bond in the case of $(CO)_5CrC(OEt)(C≡CPh)$ [Cr–C(1) = 2.00 (2) Å, C(1)–O(1) = 1.32 (2) Å].[25]

With these results we suggest that metal–carbon double-bond character in bimetallic Fischer carbene complexes can be enhanced by two factors: (1) the presence of strongly electron-withdrawing ligands on the Lewis acidic center to destabilize the acyl resonance form, and (2) an accepting orbital of proper symmetry to overlap with the carbenoxy π system to enhance M=C π bonding in the "carbene" resonance description. Structure–reactivity correlations are in progress to test these predictions.

(20) Bond distances in selected bimetallic complexes of the general form M=C(R^1)(R^2) are as follows. (a) M = (CO)$_5$Cr, R^1 = OEt, R^2 = NMe$_2$: Cr=C = 2.133 (4) Å, C–O = 1.346 (5) Å [Huttner, G.; Krieg, B. *Chem. Ber.* **1972**, *105*, 67–81], compared to structures **7** and **9**. (b) M = (CO)$_5$Cr, R^1/R^2 = –CH$_2$-allyl–ZrCp$_2$O–: Cr=C = 2.063 (4) Å, C–O = 1.254 (5) Å [Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649–7650], compared to structures **7** and **9**. (c) M = (CO)$_5$Re(CO)$_4$Re, R^1/R^2 = –CH$_2$–CH$_2$–TiCp$_2$O–: Re=C = 2.12 (3) Å, C–O = 1.26 (3) Å [Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145–1146], compared to M = (CO)$_5$Re(CO)$_4$Re, R^1 = OMe, R^2 = Me: Re=C = 2.094 (7) Å, C–O = 1.299 (8) Å [Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053–3059]. (d) M = (CO)$_5$Cr, R^1 = OTi-(η^5-C$_5$Me$_5$)$_2$Cl, R^2 = Me: Cr=C = 2.089 (6) Å, C–O = 1.269 (7) Å,[7] compared to structures **7** and **9**. (e) In the following case, a siloxycarbene complex having a C–O bond distance *not* reduced relative to alkoxycarbene complexes has a short Cr=C bond. M = (CO)$_5$Cr, R^1 = OSi(SiMe$_3$)$_3$, R^2 = 2-furyl: Cr=C = 2.033 (7) Å, C–O = 1.321 (9) Å [Schubert, U.; Wiener, M.; Köhler, F. H. *Chem. Ber.* **1979**, *112*, 708–716].

(21) Indeed, even chromium acylate complexes retain enough carbenoid character to engage in insertion chemistry with alkynes,[34] but similar reactions of bimetallic carbene species occur at a much greater rate.

(22) The relative contribution of the acyl resonance form is greater for a titanoxycarbene structure than, for example, a methoxycarbene complex because a titanium(IV) alkoxide or cyclopentadienyl fragment can accommodate a positive charge more easily than a methyl group (CH$_3$$^+$ is less favorable than (RO)$_3$Ti$^+$). The same principle is illustrated by the structure of (CO)$_5$Cr=C(Me)ORe(CO)$_5$,[35] in which the presence of a (CO)$_5$Re$^+$ unit bound to the carbenoxy oxygen atom gives rise to a short C(1)–O(1) bond of 1.26 (1) Å. The Cr–C(1) bond distance is 2.08 (1) Å, longer than in the titanoxycarbene carbene systems, since the (CO)$_5$Re unit is a poorer π acceptor from oxygen than is Ti(IV).

(23) (a) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977–983. (b) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014. (c) Curtis, M. D.; Thanedar, S.; Bulter, W. M. *Organometallics* **1984**, *3*, 1855–1859. (d) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.

(24) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(25) Huttner, G.; Lorenz, H. *Chem. Ber.* **1975**, *108*, 1864–1870.

Experimental Section

General Methods. All manipulations were performed in a dry nitrogen atmosphere using standard glovebox and Schlenk techniques. $Cr(CO)_6$ and Cp_2TiCl_2 were purchased from Strem Chemical Co. and used as received. Ti(O-*i*-Pr)$_4$ and TiBr$_4$ were obtained from Aldrich Chemical Co.; the former was vacuum distilled, and the latter sublimed. CH_2Cl_2 was purified by distillation from P_4O_{10}, diethyl ether by distillation from LiAlH$_4$, and THF by distillation from Na–benzophenone ketyl. NMR spectra were recorded on a GE GN-300 instrument (300 MHz ^{1}H, 75.52 MHz ^{13}C), referenced to residual protons in the solvent. UV–vis spectra were obtained with a Hewlett-Packard Model 8452A diode-array spectrophotometer in hexane solution using quartz cells filled under nitrogen in the drybox. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Syntheses. Acylate complexes [(CO)$_5$Cr(COR)][NMe$_4$] (R = *n*-Bu, 2-propenyl, 2-furyl) were prepared from $Cr(CO)_6$ and the appropriate lithium reagent by the Fischer method[1,9] and were recrystallized from CH_2Cl_2. Ti(O-*i*-Pr)$_3$Br was prepared by mixing Ti(O-*i*-Pr)$_4$ and TiBr$_4$ in a 3:1 molar ratio in CH_2Cl_2 solution, followed by evaporation of solvent to provide a pale yellow solid, stable at room temperature when stored in the absence of air.

Complexes 3–5 and 11 were prepared by addition of an equimolar solution of Ti(O-*i*-Pr)$_3$Br to a CH_2Cl_2 solution of the acylate precursor in the drybox at room temperature. Cooling the deep red solutions briefly to –30 °C followed by filtration removed approximately 95% of the byproduct Me$_4$NBr. Evaporation of the filtrate afforded the desired complexes in quantitative yield. Further purification and preparation of single crystals was achieved by recrystallization from CH_2Cl_2 or CH_2Cl_2/Et$_2$O mixtures at –30 °C. X-ray analyses were performed in a dry nitrogen cold stream at –120 °C on crystals that were mounted quickly in air on glass fibers tipped with silicone grease.

Data for (CO)$_5$CrC[OTi(O-*i*-Pr)$_3$][*n*-Bu] (3): ^{1}H NMR (CDCl$_3$, δ) 4.72 (m, 3 H), 3.14 (t, 2 H), 1.48 (m, 2 H), 1.34 (d, 18 H), 0.92 (t, 3 H); ^{13}C NMR (75.6 MHz, CDCl$_3$, –20 °C, 0.12 M, δ) 362.0, 224.1, 217.8, 83.9 (br), 66.8, 27.3, 25.3 (br), 22.4, 13.8; IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}) 2055, 1978, 1933; UV (λ_{max}, hexane, nm) 234 (log ϵ 4.63), 348 (w), 412 (log ϵ 3.86). Anal. Calcd for [C$_{19}$H$_{30}$CrO$_9$Ti]$_2$: C, 45.4; H, 6.0. Found: C, 44.4; H, 6.0.

Data for (CO)$_5$CrC[OTi(O-*i*-Pr)$_3$][2-furyl] (4): ^{1}H NMR (CDCl$_3$, δ) 7.84 (s, 1 H), 7.51 (dd, *J* = 2, 13 Hz, 1 H), 6.52 (m, 1 H), 5.01 (br m, 3 H), 1.32 (br d, 18 H); ^{13}C NMR (75.6 MHz, CDCl$_3$, δ) 304.8, 224.4, 218.5, 161.4, 143.6 (br), 123.8, 113.8, 83.0 (br), 25.0, 24.8, 23.9; IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}) 2052, 1975, 1933; UV (λ_{max}, hexane, nm) 232 (log ϵ 4.81), 338 (w), 510 (br, log ϵ 4.20). Anal. Calcd for [C$_{19}$H$_{24}$CrO$_{10}$Ti]$_2$: C, 44.5; H, 4.7. Found: C, 43.2; H, 4.7.

Data for (CO)$_5$CrC[OTi(O-*i*-Pr)$_3$][C(CH$_3$)CH$_2$] (5): ^{1}H NMR (CDCl$_3$, δ) 5.48 (br s, 1 H), 5.32 (br s, 1 H), 4.70 (m, 3 H), 1.83 (s, 3 H), 1.33 (d, *J* = 6.7 Hz, 18 H); ^{13}C NMR (75.6 MHz, CDCl$_3$, –20 °C, 0.13 M, δ) 351.6, 225.2, 218.5, 159.6, 121.9, 84.3 (br), 26.0 (br), 20.1; IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}) 2054, 1978, 1934; UV (λ_{max}, hexane, nm) 232 (log ϵ 4.85), 284 (shoulder), 440 (br, log ϵ 3.54). Anal. Calcd for [C$_{18}$H$_{28}$CrO$_9$Ti]$_2$: C, 44.5; H, 5.4. Found: C, 44.2; H, 5.5.

Data for (CO)$_5$CrC[OTi(O-*i*-Pr)$_3$][CH$_3$] (11): ^{1}H NMR (CDCl$_3$, δ) 4.85 (m, 3 H), 2.77 (s, 3 H), 1.36 (d, *J* = 7 Hz, 18 H); ^{13}C NMR (75.6 MHz, CDCl$_3$, –20 °C, 0.15 M, δ) 355.1, 225.0, 218.3, 83.8 (br), 54.3, 25.5 (br); IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}) 2054, 1973, 1931. Anal. Calcd for [C$_{16}$H$_{24}$CrO$_9$Ti]$_2$: C, 41.8; H, 5.3. Found: C, 41.4; H, 5.3.

Compound 6 was prepared in a similar manner, requiring addition of a solution of Cp$_2$TiCl$_2$ to a stirred solution of the acylate precursor over several minutes to avoid the formation of disubstituted products. Filtration and recrystallization provided the red complex in 90–95% yield. For (CO)$_5$CrC(OTiCp$_2$Cl)-(CMeCH$_2$) (6): ^{1}H NMR (CDCl$_3$, δ) 6.51 (s, 10 H), 4.94 (d, *J* =

1.5 Hz, 1 H), 4.81 (d, *J* = 1.5 Hz, 1 H), 1.76 (s, 3 H); ^{13}C NMR (75.6 MHz, CDCl$_3$, δ) 357.2, 224.3, 217.5, 160.2, 118.5, 109.8, 18.2; IR (ν_{CO}, CH$_2$Cl$_2$, cm^{-1}) 2052, 1975, 1931; UV (λ_{max}, CH$_2$Cl$_2$, nm) 246 (log ϵ 4.64), 340 (w), 424 (ϵ 3.98). Anal. Calcd for [C$_{19}$H$_{15}$ClCrO$_6$Ti]$_2$: C, 48.1; H, 3.2. Found: C, 47.8; H, 3.3.

X-ray Crystallography. All X-ray experiments were carried out at –120 °C. Pertinent details of the data collections and structure determinations are listed in Table I. Crystals of 3–7 were mounted on glass fibers and quickly transferred to the cold N$_2$ stream of the diffractometers. Unit cells were determined using the setting angles of 25 high-angle reflections.

The intensities of three standard reflections were monitored during each data collection, showing neither significant decay nor instrument instability. Empirical absorption corrections were applied based on the ψ scans of several reflections. Only very small crystals of 4 could be obtained; the crystal selected diffracted weakly, as there were no significant intensities observed in the region above 2θ of 46°.

All calculations were performed using a VAXstation 3520 computer. The crystallographic software package TEXSAN 5.0[26] was applied for crystals 3, 4, 6, and 7. The structures were solved by direct methods programs SIR[27] (structures 4 and 6) and MITHRIL[28] (structures 3 and 7). Structure 5 was solved by direct methods in SHELXTL PLUS.[29]

Full-matrix least-squares refinement with anisotropic thermal displacement parameters for all non-ydrogen atoms was carried out for each of the structures. Most of the hydrogen atoms were found in difference Fourier maps. The remaining H atoms were placed in calculated positions (C–H = 1.0 Å). The H atoms were treated as fixed contributors to the structure factors (structures 3–6). In the case of structure 7, the H atoms were refined with isotropic thermal displacement parameters. The final difference maps were featureless with the highest peaks listed in Table I.

Supplementary Material Available: Complete tables of bond distances and angles, thermal parameters, and calculated H atom positions (19 pages); listings of calculated and observed structure factors (77 pages). Ordering information is given on any current masthead page.

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