Early-transition-metal ketenimine complexes

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Table SI. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^4$) (one third trace of the diagonalized matrix), with e.s.d.'s in parentheses for the complex **3**.

Atom	X/a	Y/b	Z/c	Ueq
Ti	0.0(0)	3168.6(6)	2500.0(0)	450(4)
C1	662(4)	3259(3)	1289(3)	729(20)
C2	1391(3)	3309(4)	1973(4)	740(20)
C3	1439(4)	2442(6)	2380(3)	869(23)
C4	796(5)	1854(4)	1968(5)	917(26)
C5	281(4)	2328(5)	1308(4)	877(23)
C6	495(7)	4028(5)	616(4)	1413(39)
C7	2114(5)	4098(5)	2119(6)	1349(37)
C8	2201(6)	2145(8)	3086(5)	1794(50)
C9	775(8)	750(5)	2046(9)	2340(82)
C10	-451(6)	1910(7)	628(6)	1718(47)
N1	467(5)	4449(5)	3005(5)	415(26)
C11	1203(7)	4918(8)	3536(6)	426(30)
C12	1535(10)	5838(9)	3420(9)	591(41)
C13	2253(17)	6135(18)	3939(25)	559(55)
C14	2700(13)	5709(11)	4658(13)	620(50)
C15	2384(19)	4796(12)	4786(16)	634(49)
C16	1660(22)	4373(14)	4218(15)	517(46)
C17	3479(8)	6140(9)	5265(7)	902(46)
C18	-218(7)	4681(6)	2391(9)	411(46)
C19	-677(5)	5476(5)	2047(4)	447(25)
C20	-1471(8)	5441(10)	1381(7)	475(37)
C21	-2029(15)	6285(20)	1054(24)	532(49)
C22	-2771(14)	6141(11)	424(11)	680(46)
C23	-3021(11)	5298(12)	72(9)	835(55)
C24	-2501(20)	4497(13)	333(16)	736(62)
C25	-1735(24)	4578(14)	954(16)	613(62)
C26	-397(5)	6464(5)	2343(5)	476(25)
C27	-57(8)	7126(8)	1814(7)	614(38)
C28	244(10)	8053(9)	2115(11)	740(46)
C29	228(10)	8323(8)	2872(10)	801(46)
C30	-133(11)	7718(9)	3380(10)	867(55)
C31	-426(8)	6767(7)	3124(6)	592(35)

Table SII. Atomic coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^4$) with e.s.d.'s in parentheses for the hydrogen atoms of the complex **3**.

Atom	X/a	Y/b	Z/c	U
H6A	-34(7)	3856(5)	211(4)	2120(0)
H6B	1016(7)	4067(5)	365(4)	2120(0)
H6C	396(7)	4643(5)	850(4)	2120(0)
H7A	1919(5)	4630(5)	1755(6)	2024(0)
H7B	2679(5)	3846(5)	2019(6)	2024(0)
H7C	2200(5)	4318(5)	2675(6)	2024(0)
H8A	2571(6)	2699(8)	3277(5)	2691(0)
H8B	2571(6)	1659(8)	2903(5)	2691(0)
H8C	1943(6)	1891(8)	3523(5)	2691(0)
H9A	244(8)	500(5)	1684(9)	3511(0)
H9B	756(8)	578(5)	2599(9)	3511(0)
H9C	1313(8)	480(5)	1904(9)	3511(0)
H10A	-693(6)	2413(7)	250(6)	2577(0)
H10B	-933(6)	1640(7)	859(6)	2577(0)
H10C	-189(6)	1413(7)	347(6)	2577(0)
H12	1253(10)	6226(9)	2987(9)	1048(103)
H13	2501(17)	6716(18)	3806(25)	1048(103)
H15	2652(19)	4454(12)	5253(16)	1048(103)
H16	1484(22)	3739(14)	4291(15)	1048(103)
H17A	3611(8)	6774(9)	5086(7)	1048(103)
H17B	4008(8)	5737(9)	5306(7)	1048(103)
H17C	3315(8)	6184(9)	5790(7)	1048(103)
H21	-1883(15)	6900(20)	1266(24)	1048(103)
H22	-3124(14)	6678(11)	231(11)	1048(103)
H23	-3538(11)	5250(12)	-343(9)	1048(103)
H24	-2663(20)	3899(13)	92(16)	1048(103)
H25	-1376(24)	4031(14)	1097(16)	1048(103)
H27	-35(8)	6948(8)	1282(7)	1048(103)
H28	458(10)	8484(9)	1771(11)	1048(103)
H29	462(10)	8922(8)	3062(10)	1048(103)
H30	-186(11)	7933(9)	3896(10)	1048(103)
H31	-636(8)	6351(7)	3483(6)	1048(103)

Table SIII. Anisotropic displacement parameters Uij ($x10^4$ $Å^2$) for the non-hydrogen atoms of the complex **3**. The anisotropic thermal parameters are in the form:

$$\exp(-2\pi^2(U_{11}h^2a^{*2}+...+2U_{12}hka^*b^*))$$

Atom	U11	U22	U33	U23	U13	U12
Ti	534(7)	338(5)	513(7)	0(0)	187(5)	0(0)
C1	1096(40)	643(28)	554(28)	108(23)	414(28)	187(28)
C2	710(31)	785(32)	879(35)	-320(28)	521(28)	-181(26)
C3	792(37)	1198(43)	730(35)	206(35)	417(30)	421(36)
C4	1158(46)	481(25)	1407(52)	167(34)	954(42)	174(31)
C5	746(34)	1004(39)	963(42)	-605(36)	366(31)	-163(32)
C6	2110(85)	1419(58)	942(46)	620(44)	856(53)	712(59)
C7	1223(52)	1398(55)	1725(74)	-780(55)	1000(53)	-613(46)
C8	1260(59)	3144(123)	1037(54)	442(71)	371(48)	1343(74)
C9	3533(148)	505(34)	4014(171)	263(59)	3190(146)	373(56)
C10	1135(57)	2268(95)	1778(78)	-1360(74)	362(56)	-457(60)
N1	445(44)	296(35)	523(46)	79(31)	144(37)	23(29)
C11	491(53)	409(47)	408(47)	76(43)	159(40)	89(43)
C12	591(60)	405(55)	792(86)	159(54)	175(57)	-98(56)
C13	628(106)	421(84)	729(76)	10(83)	375(92)	28(69)
C14	463(72)	600(83)	805(92)	-249(92)	147(60)	-101(81)
C15	730(90)	690(82)	504(69)	10(87)	179(59)	-10(99)
C16	589(68)	384(72)	582(88)	229(57)	128(65)	-23(67)
C17	765(71)	1114(86)	816(74)	-68(69)	138(60)	-361(66)
C18	488(87)	332(34)	414(90)	-62(46)	96(78)	-124(33)
C19	578(46)	410(35)	384(39)	69(32)	172(35)	-32(35)
C20	561(62)	444(64)	416(59)	133(56)	91(47)	-9(67)
C21	542(99)	441(68)	659(68)	150(60)	230(96)	-60(68)
C22	672(76)	770(81)	549(73)	209(84)	13(59)	172(88)
C23	704(94)	923(90)	811(91)	10(74)	-4(68)	-153(79)
C24	783(109)	700(85)	612(109)	-22(81)	-120(84)	-127(86)
C25	830(102)	366(73)	625(122)	-98(69)	103(93)	30(81)
C26	587(45)	351(31)	498(44)	55(33)	131(39)	28(31)
C27	781(77)	477(54)	563(51)	63(48)	92(56)	-8(54)
C28	763(84)	357(60)	1033(76)	134(66)	29(94)	-52(56)
C29	921(95)	358(54)	1042(69)	-7(56)	9(84)	-130(52)
C30	1265(111)	451(64)	927(85)	-284(64)	318(90)	-14(71)
C31	797(73)	481(50)	518(44)	-77(44)	179(53)	26(49)

Table SIV. Bond distances (Å) and angles (deg) with e.s.d.'s in parentheses for **3**.

Ti	- C1	2.431(6)	C11	- C16	1.420(25)
Ti	- C2	2.429(6)	C12	- C13	1.303(31)
Ti	- C3	2.422(7)	C13	- C14	1.382(40)
Ti	- C4	2.439(7)	C14	- C15	1.379(25)
Ti	- C5	2.416(7)	C14	- C17	1.503(21)
Ti	- N1	2.024(7)	C15	- C16	1.413(35)
Ti	- C18	2.119(9)	C18	- C19	1.360(12)
Ti	- CE1	2.124(7)	C19	- C20	1.454(13)
C1	- C2	1.412(7)	C19	- C26	1.485(10)
C1	- C5	1.411(8)	C20	- C21	1.474(29)
C1	- C6	1.531(9)	C20	- C25	1.404(25)
C2	- C3	1.374(9)	C21	- C22	1.381(33)
C2	- C7	1.521(9)	C22	- C23	1.324(23)
C3	- C4	1.338(9)	C23	- C24	1.373(27)
C3	- C8	1.520(10)	C24	- C25	1.385(38)
C4	- C5	1.375(9)	C26	- C27	1.436(15)
C4	- C9	1.533(8)	C26	- C31	1.379(14)
C5	- C10	1.522(10)	C27	- C28	1.417(17)
N1	- C11	1.421(11)	C28	- C29	1.323(25)
N1	- C18	1.334(13)	C29	- C30	1.378(22)
C11	- C12	1.393(16)	C30	- C31	1.425(17)

CE1	-Ti	-CE1'	139.6(2)
C18	-Ti	-CE1'	106.5(3)
C18	-Ti	-CE1	113.4(3)
N1	-Ti	-CE1'	105.9(3)
N1	-Ti	-CE1	109.3(3)
N1	-Ti	-C18	37.5(3)
C5	-Ti	-C18	117.0(3)
C5	-Ti	-N1	131.4(3)
C4	-Ti	-C18	141.5(3)
C4	-Ti	-N1	130.6(2)
C4	-Ti	-C5	32.9(2)
C3	-Ti	-C18	121.8(3)
C3	-Ti	-N1	99.2(3)
C3	-Ti	-C5	54.9(2)
C3	-Ti	-C4	32.0(2)
C2	-Ti	-C18	91.0(3)
C2	-Ti	-N1	80.3(3)
C2	-Ti	-C5	55.5(2)
C2	-Ti	-C4	53.7(2)
C2	-Ti	-C3	32.9(2)
C1	-Ti	-C18	87.7(4)
C1	-Ti	-N1	97.9(3)
C1	-Ti	-C5	33.8(2)
C1	-Ti	-C4	54.7(2)
C1	-Ti	-C3	55.4(2)
C1	-Ti	-C2	33.8(2)
Ti	-C1	-C6	127.8(4)
Ti	-C1	-C5	72.5(3)
Ti	-C1	-C2	73.0(3)
C5	-C1	-C6	130.1(5)
C2	-C1	-C6	122.9(5)
C2	-C1	-C5	106.0(5)
Ti	-C2	-C1	73.2(3)
C1	-C2	-C7	124.9(5)
C1	-C2	-C3	108.1(5)
Ti	-C2	-C7	129.3(4)
Ti	-C2	-C3	73.3(4)
C3	-C2	-C7	125.7(6)

Ti	-C3	-C2	73.8(4)
C2	-C3	-C8	125.0(6)
C2	-C3	-C4	108.4(6)
Ti	-C3	-C8	126.0(5)
Ti	-C3	-C4	74.8(4)
C4	-C3	-C8	125.6(7)
Ti	-C4	-C3	73.3(4)
C3	-C4	-C9	125.9(6)
C3	-C4	-C5	110.5(7)
Ti	-C4	-C9	133.7(4)
Ti	-C4	-C5	72.6(4)
C5	-C4	-C9	121.7(6)
C1	-C5	-C4	106.8(5)
Ti	-C5	-C4	74.5(4)
Ti	-C5	-C1	73.7(3)
C4	-C5	-C10	128.1(7)
C1	-C5	-C10	124.2(6)
Ti	-C5	-C10	125.3(5)
Ti	-N1	-C18	75.1(5)
Ti	-N1	-C11	144.8(6)
C11	-N1	-C18	138.2(9)
N1	-C11	-C16	116.3(13)
N1	-C11	-C12	125.7(10)
C12	-C11	-C16	118.0(12)
C11	-C12	-C13	117.7(15)
C12	-C13	-C14	129.1(28)
C13	-C14	-C17	126.0(21)
C13	-C14	-C15	113.8(18)
C15	-C14	-C17	120.2(15)
C14	-C15	-C16	121.0(18)
C11	-C16	-C15	119.8(22)
Ti	-C18	-N1	67.4(5)
N1	-C18	-C19	139.7(10)
Ti	-C18	-C19	152.8(7)
C18	-C19	-C26	121.3(7)
C18	-C19	-C20	124.1(9)
C20	-C19	-C26	114.7(8)
C19	-C20	-C25	121.2(14)
C19	-C20	-C21	124.7(14)
C21	-C20	-C25	114.0(16)
C20	-C21	-C22	118.3(21)
C21	-C22	-C23	125.1(19)
C22	-C23	-C24	118.7(16)
C23	-C24	-C25	120.1(22)
C20	-C25	-C24	123.6(20)
C19	-C26	-C31	122.3(7)
C19	-C26	-C27	119.5(8)
C27	-C26	-C31	118.2(8)
C26	-C27	-C28	119.1(10)
C27	-C28	-C29	121.8(13)
C28	-C29	-C30	120.2(15)
C29	-C30	-C31	120.7(11)
C26	-C31	-C30	119.8(10)

CE1 is the centroid of the Cp* ring
' = -x, y, 1/2-z

TABLE SV

Experimental Data for the X-ray Diffraction Study of Compound $Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2(C,N)\text{-}TolN{=}C{=}CPh_2)$

formula	$C_{41}H_{47}NTi$
fw	601.70
crystal system	monoclinic
space group	*C*2/*c*
diffractometer	Philips PW 1100
radiation	(Mo-Kα), λ = 0.71073 Å
monochromator	graphite
temp, K	293
a, Å	14.969(5)
b, Å	13.830(5)
c, Å	16.703(5)
β, deg	101.78(2)
V, Å^3	3385(2)
Z	4
reflns for lattice | number	32
parameters | θ range, deg	8-18
D_{calcd}, g cm^{-3}	1.181
F(000)	1288
cryst dimens, mm	0.15 x 0.23 x 0.35
μ (Mo-Kα), cm^{-1}	2.81
scan speed, deg min^{-1}	3-9.6
scan width, deg	1.20 + 0.34 tan θ
scan mode	θ/2θ
2θ range, deg	6-54
std refln	one monitored every 100
decay	none
reflns measd, range *h*,*k*,*l*	$-19\le h\le 18$, $-17\le k\le 17$, $0\le l\le 21$
unique total data	3694
unique total data with [$F_o^2 \ge -\sigma(F_o^2)$]	3586
unique obsd data [$F_o \ge 4\sigma(F_o)$]	1824
structure solution	direct methods: SIR92
structure refinement	SHELXL-93 (full-matrix least-squares on F^2

function minimized	$\Sigma w[F_o^2-F_c^2]^2$
no. of params	296
no. of params restraints	80
max shift/esd dev	-0.240
mean shift/esd dev	0.018
max/min resid. electron dens., e/Å^3	0.59/-0.62
goodness of fit[a]	0.952
*R*1[b]	0.0791
*wR*2[c]	0.1998
weighting scheme, *a*, *b*[d]	0.1604, 0.0000

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[a] GOOF = $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$

[b] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

[d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$