Cyclopentadienyldichlorotitanium(III): A Free-Radical-like Reagent for Reducing –N=N– Multiple Bonds in Azo and Diazo Compounds

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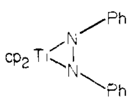
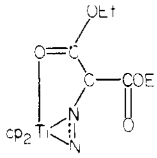
Abstract: Diphenyldiazomethane was reduced by [cpTiCl$_2$] (cp = η^5-C$_5$H$_5$) to a hydrazonido(2–) ligand to form [(cpTiCl$_2$)$_2$(μ-Ph$_2$C=NN)], which loses [cpTiCl$_3$] and evolves to a dinuclear complex, [(cpTiCl)$_2$(μ-Ph$_2$C=NN)$_2$], in which the two (cpTiCl) units are bridged by two hydrazonido(2–) ligands. Both hydrazonido ligands are η^2-N,N′ bonded to the same titanium atom in the solid state, with titanium–nitrogen bond distances ranging from 2.006 (6) to 2.178 (5) Å, while the second titanium is bonded at very short distances to the terminal nitrogens only, 1.860 (5) and 1.835 (6) Å. The ^{1}H NMR spectrum at –64 °C (CDCl$_3$) is in agreement with the solid-state structure showing the nonequivalence of the two cp rings, which become equivalent at room temperature because of the stereochemical nonrigidity of the hydrazonido ligand. [cpTiCl$_2$] reacted with azobenzene, forming a dimeric complex, [(cpTiCl)$_2$(μ-PhN)(μ-Ph$_2$N$_2$)], in which the phenylimido ligand forms from a –N=N– bond cleavage promoted by titanium(III). Phenylimido bridges the two titanium atoms at rather short distance Ti–N, 1.920 (4) Å, with nitrogen having sp^2 geometry, so that a multiple Ti–N interaction is involved. The molecular complexity of [cpTiCl$_2$], which may be a main point in determining its reactivity, was determined by an X-ray analysis carried out on the solid isolated from a THF solution, [cpTiCl$_2$(THF)$_{1.5}$]. It was found to be formed by the same number of pentacoordinate [cpTiCl$_2$(THF)$_2$] and tetracoordinate [cpTiCl$_2$(THF)] titanium(III) monomeric units. Crystallographic details for [cpTiCl$_2$(THF)$_2$][cpTiCl$_2$(THF)] are as follows: space group $P\bar{1}$ (triclinic), a = 11.139 (4), b = 13.641 (5), c = 9.398 (4) Å, α = 95.31 (3), β = 106.94 (2), γ = 98.51 (3)°, V = 1337.0 (9) Å^3, D_{calcd} = 1.451 g cm^{-3}, Z = 2. The final R factor is 4.9% for 2727 observed reflections. Crystallographic details for [(cpTiCl)$_2$(μ-Ph$_2$C=NN)$_2$] are as follows: space group $P2_1/c$ (monoclinic), a = 18.704 (2), b = 8.785 (1), c = 21.049 (2) Å, β = 100.57 (1)°, V = 3400.0 (6) Å^3, D_{calcd} = 1.339 g cm^{-3}, Z = 4. The final R factor is 5.4% for 2519 observed reflections. Crystallographic details for [(cpTiCl)$_2$(μ-PhN)(μ-Ph$_2$N$_2$)] are as follows: space group $C2/c$ (monoclinic), a = 14.041 (2), b = 12.743 (2), c = 15.875 (3) Å, β = 115.23 (2)°, V = 2569.5 (8) Å^3, D_{calcd} = 1.474 g cm^{-3}, Z = 4. The final R factor is 3.1% for 1035 observed reflections.

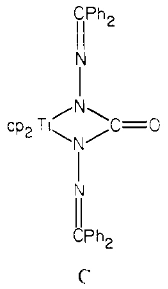
Titanium species in a low oxidation state have received much attention because of their powerful reducing properties toward organic functional groups[1] and small molecules like N$_2$[2] and CO.[3] The utilization of well-defined titanium complexes should serve to identify some fundamental steps in such complex reactions. The objective of this paper is to report our studies of the interaction of low-valent titanium complex, [cpTiCl$_2$] (cp = η^5-C$_5$H$_5$),[4] with azo and diazo compounds, which besides their own intrinsic interest as organic substrates also bear significant similarities with molecular nitrogen.[5-9] A further reason of interest comes from the fact that titanium(II) and titanium(III) complexes, generally, play a rather unique role in dinitrogen chemistry.[10] Moreover, some information on the interaction of titanocene unit with azo and diazo compounds is available.[8,11] Dicyclopentadienyltitanium(II), "cp$_2$Ti", a metallic carbene-like unit, used in the form of cpTi(CO)$_2$, adds to the –N=N– multiple bond of azobenzene (complex A)[11] and diethyl diazomalonate (complex B)[8] or it promotes the reaction of diphenyldiazomethane with carbon monoxide (complex C).[8]



A



B



C

It is well-known that [cpTiCl$_2$] is a powerful reducing agent toward organic substrates.[4,12] Its structure, which has never been clarified, has now been revealed by an X-ray structural analysis. [cpTiCl$_2$] acts as a free-radical-like species in its addition reactions to organic substrates,[12] as exemplified below for the titanium-promoted reductive coupling of ketones:[12a]

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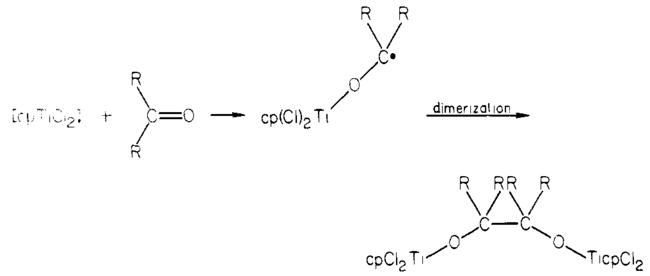

The reactivity of [cpTiCl$_2$] with diazo and azo compounds can be described as the consequence of a formal disproportionation to [cpTiCl$_3$] and [cpTiCl].

Reduction of diphenyldiazomethane to a hydrazonido(2-) ligand and the cleavage of the –N═N– bond in azobenzene to produce a phenylimido ligand have been achieved. The present results have been partially communicated.[13]

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. IR spectra were recorded with a Perkin-Elmer spectrophotometer. Magnetic susceptibility measurements were done by using a Faraday balance. ^{1}H NMR spectra were recorded with an E-360 (60 MHz) spectrophotometer and with a JEOL PS 100 NMR (90 MHz) spectrophotometer. The syntheses of diphenyldiazomethane[14] and cyclopentadienyldichlorotitanium(III), [cpTiCl$_2$](THF)$_{1.5}$,[4] were performed as described in the literature.

Synthesis of [cpTiCl$_2$](THF)$_{1.5}$ and [cpTiCl$_2$]. A THF (300 mL) solution of cpTiCl$_3$ (8.50 g, 38.75 mmol) was stirred with 4.0 g of Zn powder for 3 h. The final blue-green mixture was heated and filtered when hot and the mother liquor concentrated. By cooling to 0 °C overnight it gave sky-blue crystals (5.60 g of {[cpTiCl$_2$](THF)$_{1.5}$}),[4] which were filtered and washed twice with Et$_2$O (30 mL) to remove ZnCl$_2$. Tetrahydrofuran was removed by heating the solid at 100 °C for 30 min. The resulting pyrophoric mauve powder, hereinafter indicated as [cpTiCl$_2$],[4] was used in all reactions described.

Reaction of [cpTiCl$_2$] with Diphenyldiazomethane. A THF solution (50 mL) of [cpTiCl$_2$] (3.23 g, 17.55 mmol) was reacted with neat diphenyldiazomethane (1.80 g, 9.27 mmol). The color of the solution changed from sky-blue to deep red without any gas evolution. In a few minutes, a crystalline red-maroon solid (complex II) formed (1.10 g). The mother liquor was treated as described below. Anal. Calcd for [(cpTiCl$_2$)$_2$(Ph$_2$CN$_2$)]·(THF) II, C$_{27}$H$_{28}$Cl$_4$N$_2$OTi$_2$: C, 51.10; H, 4.42; N, 4.42; Cl, 22.40. Found: C, 50.84; H, 4.45; N, 4.36; Cl, 20.96. The IR spectrum does not show any band above 1600 cm^{-1}. ^{1}H NMR spectrum (τ, CDCl$_3$): 5.65 (10 H, s, cp); two multiplets centered at 2.38 and 2.83 (10 H, m, Ph); and two peaks for the THF molecule. To the filtered solution Et$_2$O (20 mL) was added until a solid started to crystallize. In a few hours a red-orange crystalline solid formed (IV), 0.60 g). Anal. Calcd for [(cpTiCl)$_2$(Ph$_2$CN$_2$)$_2$], C$_{36}$H$_{30}$N$_4$Cl$_2$Ti$_2$: C, 63.06; H, 4.38; N, 8.17; Cl, 20.73. Found: C, 63.47; H, 4.44; N, 8.21; Cl, 10.75. The IR spectrum (nujol) does not show any band above 1600 cm^{-1}. The ^{1}H NMR spectrum is temperature dependent. The spectrum (τ, CDCl$_3$) shows the following pattern: 4.38 (10 H, s, cp), 2.40 (16 H, m, Ph), and 1.86 (4 H, m, Ph) at 25 °C; 3.87 (10 H, brs, cp), 1.67 (16 H, m, Ph), 1.00 (4 H, m, Ph) at -30 °C; 4.45 (5 H, brs, cp), 3.45 (5 H, br s, cp), 1.80 (16 H, m, Ph), 1.17 (4 H, m, Ph) at -64 °C. The yield in complex IV can be improved if the intermediate complex II is not isolated. Conversion of II into IV is reported below. The direct synthesis of IV was carried out by heating a THF solution of I with diphenyldiazomethane until complex II dissolved. Complex IV crystallized from the resulting solution. The filtered solution was evaporated to dryness, giving a residue that was collected with toluene (20 mL) and heated. The suspension was filtered when hot, and then hexane was added (20 mL) to the resulting solution, from which [cpTiCl$_3$] crystallized as yellow solid (0.20 g).

Conversion of Complex II into Complex IV. Complex II [(cpTiCl$_2$)$_2$(Ph$_2$CN$_2$)·THF] (0.66 g) was suspended in THF (50 mL) and heated up to the boiling point of the solution. The solid dissolved in a few minutes, giving a red-maroon solution, from which, by addition of Et$_2$O (20 mL), complex IV crystallized as red-orange crystals (0.21 g).

Complex [cpTiCl$_3$] can be isolated from the mother liquor as described above.

Reaction of [cpTiCl$_2$] with Azobenzene. A THF solution (50 mL) of [cpTiCl$_2$] (3.06 g, 16.63 mmol) was treated with azobenzene (3.30 g, 18.13 mmol). The color of the solution changed from sky-blue to deep red-maroon. The solution on standing 12 h at room temperature and then cooled at 0 °C for 3 days gave a small amount of [(cpTiCl)$_3$(Ph$_2$N$_2$)$_2$] as red crystals. Anal. Calcd for C$_{39}$H$_{35}$Cl$_3$N$_4$Ti$_3$: C, 57.81; H, 4.32; Cl, 13.16; N, 6.92. Found: C, 57.81; H, 4.32; N, 6.91; Cl, 13.1. ^{1}H NMR spectrum (τ, CDCl$_3$): 3.65 (15 H, s, cp); 2.68 (20 H, m, Ph). The solution was evaporated to dryness and the residue dissolved by heating in toluene. The solution gave on standing at room temperature black-maroon crystals of [(cpTiCl)$_2$(μ-Ph$_2$N$_2$)(μ-PhN)] V (0.20 g). Anal. Calcd for C$_{28}$H$_{25}$N$_3$Cl$_2$Ti$_2$: C, 58.95; H, 4.39; N, 7.37; Cl, 12.46. Found: C, 59.36; H, 4.59; N, 7.83; Cl, 11.73. The mother liquor concentrated gave a mixture of deep yellow crystals of [cpTiCl$_3$] and of complex V. Due to the dimensions of the crystals, the two compounds can be easily separated and identified.

Reaction of [cpTiCl$_2$] with Benzo[*c*]cinnoline. Benzo[*c*]cinnoline (0.70 g, 3.88 mmol) was added to a THF solution of complex I (1.34 g, 7.28 mmol). The solution changed from sky-blue to red-maroon, forming yellow-maroon crystalline solid (0.70 g). Anal. Calcd for [(cpTiCl)$_2$(C$_{12}$H$_8$N$_2$)$_2$]·THF, C$_{38}$H$_{34}$N$_4$Cl$_2$OTi$_2$: C, 62.55; H, 4.66; N, 7.68; Cl, 9.74. Found: C, 61.99; H, 4.71; N, 7.43; Cl, 9.79. In a separate experiment complex XI refluxed for 4 h did not undergo any transformations. The ^{1}H NMR spectrum shows the presence of THF and the following peaks (τ, CDCl$_3$): 3.95 (10 H, s, cp); 2.72 (16 H, m, Ph).

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Extensive preliminary investigations employing rotation and Weissenberg photographs showed the crystals of the complexes IV and V to be monoclinic, with systematic absences consistent with the space groups $P2_1/c$ for IV and $C2/c$ (or Cc) for V. The lack of any systematic absences indicated the crystals of I to be triclinic. Crystal data and details of the parameters associated with data collections are given in Table I. Lattice constants came from a least-squares refinement of the 2θ values for 23 reflections having $2\theta >$ 26° for complex I and 20 reflections having $2\theta >$ 60° for complexes IV and V.

Data were collected at room temperature on a single-crystal diffractometer. The $\theta/2\theta$ scan method was used, and individual reflection profiles were analyzed as described by Lehmann and Larsen.[15] The structure amplitudes were obtained after the usual Lorentz and polarization reduction[16] and the absolute scale was established by Wilson's method.[17] No correction for absorption was applied ($\mu \cdot \bar{r}$ = 0.2, 0.7, and 0.4 for I, IV, and V, respectively) to complex I because of the small linear absorption coefficient (Table I) and to complexes IV and V because of the irregular shapes and the small sizes of the crystals used (Table I). These facts, particularly the last one, account also for the low number of observed data for IV and V.

Structure Solution and Refinement.[16] The structures were solved by the heavy-atom method and refined by full-matrix least-squares. The function minimized during the refinement was $\Sigma w|\Delta F|^2$. The weighting scheme used was $w = k/[\sigma^2(F_o) + |g|(F_o^2)]$; k is redetermined after each structure factor calculation and refined by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) \mid |g|(F_o^2)]/k$. The value for g was that giving the smallest variation of the mean value of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o. Anomalous scattering corrections were included in all structure factor calculations. Scattering factors for neutral atoms were taken from ref 18 for Ti, from ref 19 for Cl, O, N, C, and from ref 20 for H. There was no evidence for secondary extinction among the low angle reflections.

Final atomic coordinates are listed in Tables II, III, IV, SI, and ZV SII and thermal parameters are given in Tables SIII, SIV, and SV.[21]

Complex I. The 2519 reflections with $I > 2\sigma(I)$ were used in the structure solution and refinement. The structure was first refined isotropically down to R = 0.11 and then anisotropically for all non-hydrogen

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes I, IV, and V

	complex I, $C_{22}H_{34}Cl_4O_3Ti_2$	complex IV, $C_{36}H_{30}Cl_2N_4Ti_2$	complex V, $C_{28}H_{25}Cl_2N_3Ti_2$
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}(C_i^1$; No. 2)	$P2_1/c(C_{2h}^5$; No. 14)	$C2/c(C_{2h}^6$; No. 15)
a, Å	11.139 (4)	18.704 (2)	14.041 (2)
b, Å	13.641 (5)	8.785 (1)	12.743 (2)
c, Å	9.398 (4)	21.049 (2)	15.875 (3)
α, deg	95.31 (3)	90	90
β, deg	106.94 (2)	100.57 (1)	115.23 (2)
γ, deg	98.51 (3)	90	90
V, Å^3	1337.0 (9)	3400.0 (6)	2569.5 (8)
Z	2	4	4
D_{calcd}, g cm^{-3}	1.451	1.339	1.474
mol wt	584.1	685.4	570.2
cryst dimens, mm	0.27 × 0.48 × 0.40	0.22 × 0.26 × 0.29	0.09 × 0.10 × 0.30
linear absorption, cm^{-1}	10.15	57.38	74.61
diffractometer		Siemens AED	
scan type		$\theta/2\theta$	
scan speed		3-12° θ/min	
scan width		$(\theta-0.5°) - [\theta + (0.5 + \Delta\theta)]$ $(\Delta\theta = \lambda_{\alpha_2} - \lambda_{\alpha_1}/\lambda \tan\theta)$	
radiation	Nb-filtered Mo Kα (λ = 0.7107 Å)	Ni-filtered Cu Kα (λ = 1.5418 Å)	
2θ range, deg	6-52	6-120	6-110
std reflcn	$4\bar{5}1$	$\bar{2}\bar{4}1$	$1\bar{5}1$
		these were measured after every 50 reflections: no significant changes in intensity were observed	
unique total data	5193	4219	1585
unique obsd data ($I > 2\sigma$)	2727	2519	1035
no. of variables	280	332	210

Table II. Fractional Atomic Coordinates ×10^4 for Complex I

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
TI1	8570 (1)	3379 (1)	7449 (1)	C11	666 (7)	1476 (10)	4589 (10)
TI2	2581 (1)	2072 (1)	4079 (1)	C12	670 (8)	2451 (10)	4453 (15)
CL1	9934 (2)	4640 (1)	6921 (2)	C13	601 (8)	2601 (8)	3026 (20)
CL2	9789 (2)	2156 (2)	8216 (2)	C14	557 (7)	1661 (10)	2241 (8)
CL3	3845 (2)	3350 (1)	3324 (2)	C15	608 (7)	986 (6)	3245 (11)
CL4	3757 (2)	1019 (1)	5577 (2)	O16	3240 (4)	3132 (3)	6238 (4)
C1	6915 (9)	2851 (6)	8385 (14)	C17	3264 (7)	2833 (5)	7694 (7)
C2	6415 (7)	3376 (8)	7270 (9)	C18	3548 (13)	3752 (7)	8720 (10)
C3	7075 (12)	4348 (8)	7709 (15)	C19	3628 (8)	4618 (6)	7951 (9)
C4	7926 (11)	4389 (11)	9082 (17)	C20	3318 (7)	4226 (5)	6337 (7)
C5	7834 (11)	3454 (14)	9503 (10)	O21	2994 (4)	1155 (3)	2186 (4)
O6	7822 (4)	2683 (3)	5251 (4)	C22	2909 (8)	1469 (5)	733 (7)
C7	7451 (7)	3207 (5)	3930 (7)	C23	2794 (16)	632 (7)	−272 (10)
C8	6889 (9)	2381 (7)	2652 (8)	C24	3088 (11)	−220 (6)	540 (9)
C9	6696 (12)	1484 (7)	3183 (10)	C25	3056 (8)	95 (5)	2074 (8)
C10	7312 (7)	1604 (5)	4806 (7)				

Table III. Fractional Atomic Coordinates ×10^4 for Complex IV

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
TI	2248 (1)	1780 (1)	1858 (1)	C15	1576 (3)	−3029 (5)	−990 (2)
TI′	2529 (1)	1593 (1)	581 (1)	C16	1679 (3)	−2174 (5)	−422 (2)
CL	1552 (1)	3799 (3)	2082 (1)	C17	1215 (3)	−1182 (8)	537 (3)
CL′	3290 (1)	−539 (2)	577 (1)	C21	746 (2)	−1410 (5)	1027 (2)
N1	1768 (3)	946 (6)	1084 (2)	C22	267 (2)	−273 (5)	1148 (2)
N2	1678 (3)	−61 (6)	606 (2)	C23	−154 (2)	−486 (5)	1623 (2)
N1′	2909 (3)	2644 (6)	1421 (2)	C24	−96 (2)	−1835 (5)	1979 (2)
N2′	3488 (3)	2703 (6)	1130 (2)	C25	383 (2)	−2971 (5)	1859 (2)
C1	2291 (4)	969 (7)	2932 (2)	C26	804 (2)	−2758 (5)	1383 (2)
C2	3010 (4)	1338 (7)	2857 (2)	C11′	4209 (3)	3955 (6)	2049 (2)
C3	3214 (4)	316 (7)	2398 (2)	C12′	3719 (3)	5037 (6)	2197 (2)
C4	2620 (4)	−684 (7)	2190 (2)	C13′	3775 (3)	5556 (6)	2831 (2)
C5	2050 (4)	−280 (7)	2520 (2)	C14′	4321 (3)	4994 (6)	3317 (2)
C1′	2436 (8)	2082 (11)	−546 (3)	C15′	4811 (3)	3912 (6)	3169 (2)
C2′	2800 (8)	3341 (11)	−207 (3)	C16′	4756 (3)	3393 (6)	2535 (2)
C3′	2306 (8)	4071 (11)	132 (3)	C17′	4116 (3)	3308 (8)	1392 (3)
C4′	1637 (8)	3263 (11)	3 (3)	C21′	4707 (2)	3282 (6)	1012 (2)
C5′	1717 (8)	2034 (11)	−416 (3)	C22′	5310 (2)	4219 (6)	1207 (2)
C11	1147 (3)	−2167 (5)	−36 (2)	C23′	5880 (2)	4218 (6)	861 (2)
C12	511 (3)	−3016 (5)	−218 (2)	C24′	5846 (2)	3281 (6)	321 (2)
C13	408 (3)	−3871 (5)	−787 (2)	C25′	5242 (2)	2344 (6)	127 (2)
C14	940 (3)	−3878 (5)	−1173 (2)	C26′	4673 (2)	2345 (6)	472 (2)

Table IV. Fractional Atomic Coordinates $\times 10^4$ for Complex V

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
T1	1110 (1)	545 (1)	2846 (1)	C22	671 (4)	3243 (4)	3281 (4)
CL	1771 (1)	483 (1)	4465 (1)	C23	658 (4)	4323 (4)	3276 (4)
N1	206 (3)	−615 (3)	2161 (2)	C24	0 (0)	4863 (7)	2500 (0)
N2	0 (0)	1564 (4)	2500 (0)	H1	2700 (54)	1996 (54)	3483 (47)
C1	2567 (5)	1608 (7)	3039 (6)	H2	1473 (49)	2339 (51)	1978 (45)
C2	1835 (5)	1740 (5)	2146 (5)	H3	1194 (31)	608 (34)	1076 (28)
C3	1697 (5)	785 (5)	1684 (5)	H4	2474 (46)	−584 (47)	2148 (41)
C4	2378 (5)	51 (6)	2318 (6)	H5	3386 (42)	326 (43)	3729 (39)
C5	2920 (5)	562 (7)	3149 (6)	H12	799 (46)	−1167 (48)	916 (41)
C11	−146 (4)	−1451 (4)	1489 (3)	H13	329 (51)	−2406 (55)	−87 (47)
C12	290 (5)	−1559 (5)	873 (4)	H14	−1037 (49)	−3600 (51)	−137 (43)
C13	−46 (7)	−2368 (7)	226 (5)	H15	−1750 (46)	−3300 (49)	704 (42)
C14	−791 (7)	−3042 (6)	189 (5)	H16	−1340 (51)	−2020 (56)	1907 (47)
C15	−1247 (6)	−2917 (5)	776 (5)	H22	1154 (42)	2872 (42)	3875 (41)
C16	−941 (5)	−2136 (4)	1439 (4)	H23	1089 (39)	4668 (40)	3820 (36)
C21	0 (0)	2680 (5)	2500 (0)	H24	0 (0)	5476 (61)	2500 (0)

atoms to final R and R_w values of 0.049 and 0.053, respectively. All the hydrogen atoms were located in a difference map and introduced as fixed contributors with isotropic B fixed at 7.8 Å^2 prior the final refinement. The goodness of fit (GOF) was 2.4 and the values of k and g were 1.1760 and 0.001056, respectively. In the final cycle no parameter shifted by more than 0.1 its standard deviation. In the final difference map no peak was greater than 0.4 e Å^{-3}. The overdetermination ratio (NO:NV) was 2727:280 = 9.7:1 (NO = number of observations, NV = number of variables).

Complex IV. During the refinement the Ph and cp rings were treated as rigid groups. The refinement of the positional and anisotropic thermal parameters led to convergence with $R = 0.054$, $R_w = 0.056$, and GOF = 1.44 for the 2519 observed data ($k = 1.0000$, $g = 0.005967$, NO:NV = 2519:332 = 7.6:1). All the hydrogen atoms were located in a difference map and introduced in the final refinement as fixed contributors with $B = 6.3$ Å^2. In the last cycle the shift in each parameter does not exceed 0.2 times its standard deviation. The final difference map was featureless.

Complex V. E statistics calculated as a function of sin θ favor the centric case, $\langle |E^2 - 1| \rangle$ being equal to 0.98 ($\sim$0.97 is the theoretical value accepted for centrosymmetric structures). The $C2/c$ space group was then assumed and was confirmed by the successful solution of the structure. The approximate coordinates for the one independent titanium atom were derived from a Patterson map. The subsequent Fourier synthesis showed the complex to be a dimer having a crystallographic C_2 symmetry. The positional and anisotropic thermal parameter of the non-hydrogen atoms were refined to $R = 0.049$. At this point a difference map showed the positions of all the hydrogen atoms that were introduced in subsequent calculations and isotropically refined. The final R value was 0.031 for 1035 observed data. During the refinement unit weights were used since the introduction of the weighting scheme did not give satisfactory results in terms of analysis of variance and GOF. The NO:NV ratio was 1035:210 = 4.9:1. In the last cycle no parameter shifted by more than 0.4 its standard deviation. There were no peaks above the general background in the final difference map.

Results and Discussion

The present report concerns the reactivity of cyclopentadienyldichlorotitanium(III) with organic substrates bearing N–N multiple bonds. Before discussing this, it is necessary to define the nature of our starting complex, $[\mathrm{cpTiCl_2}]_n$. In spite of its utilization as a coupling agent of carbonyl functions,[12a] its structure was not previously defined because of experimental difficulties relating to its oxygen sensitivity and the presence in the crystals of very labile molecules of solvation.

The complex was synthesized by a conventional method and crystallized from THF, which is the solvent we used for its reaction with diazo and azo compounds. Solvated forms of $[\mathrm{cpTiCl_2}]_n$ in the solid state can therefore be related to its nature in solution. The problems to be solved were its molecular complexity and the coordination number achieved by titanium(III), both being strongly dependent on the solvent from which $[\mathrm{cpTiCl_2}]_n$ crystallizes.

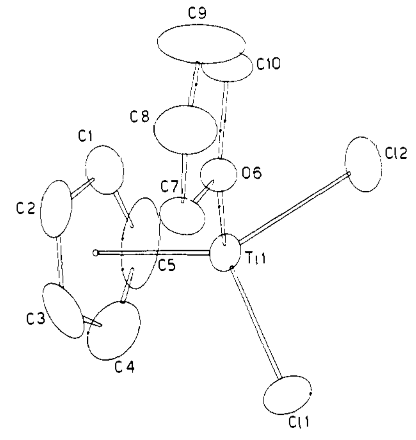


Figure 1. ORTEP drawing of the $[\mathrm{cpTi(Cl)_2(THF)}]$ molecule in complex 1 (30% probability ellipsoids).

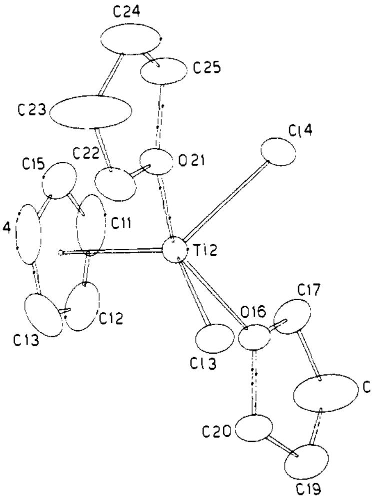


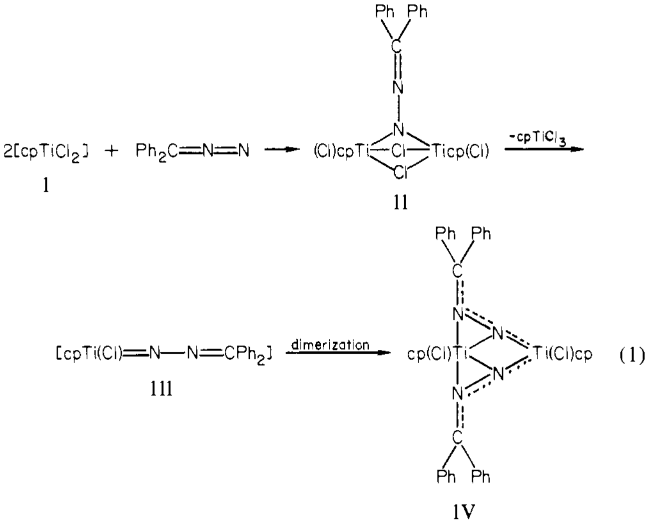
Figure 2. ORTEP drawing of the $[\mathrm{cpTi(Cl)_2(THF)_2}]$ molecule in complex 1 (30% probability ellipsoids).

Figures 1 and 2 show ORTEP views of the two monomers present in the asymmetric unit. The coordination geometry around each titanium can be described in a conventional way considering the cyclopentadienyl ring as a monodentate ligand. Titanium has a distorted tetrahedral coordination in molecule A (Figure 1), having the following set of bond angles [Cl1–Ti–Cl2, 105.6 (1)°; Cl2–Ti–O6, 93.7 (1)°; Cl1–Ti–O6, 94.4 (1)°]. Titanium achieves the pentacoordination in molecule B by bonding two THF molecules (Figure 2). The coordination polyhedron can be described as a trigonal bipyramid whose equatorial plane is defined by Ti2, Cl3, Cl4, cp2 (Table VIII). The two oxygen atoms from THF occupy the axial positions. Bond angles around titanium in the equatorial plane are close to the value of 120° (Table V) expected for a trigonal bipyramid. The greater distortion from the ideal polyhedron is associated with the O16–Ti2–O21 angle [151.0(2)°], which is significantly smaller than 180°. All bond distances within

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex 1

Ti1-cp1	2.014 (13)	Ti2-cp2	2.059 (8)
Ti1-Cl1	2.310 (2)	Ti2-Cl3	2.369 (2)
Ti1-Cl2	2.339 (3)	Ti2-Cl4	2.370 (2)
Ti1-O6	2.065 (4)	Ti2-O16	2.241 (4)
		Ti2-O21	2.275 (4)
O6-Ti1-cp1	113.6 (4)	O21-Ti2-cp2	105.0 (3)
Cl2-Ti1-cp1	121.5 (4)	O16-Ti2-cp2	104.0 (3)
Cl2-Ti1-O6	93.7 (1)	O16-Ti2-O21	151.0 (2)
Cl1-Ti1-cp1	121.5 (4)	Cl4-Ti2-cp2	120.5 (3)
Cl1-Ti1-O6	94.4 (1)	Cl4-Ti2-O21	83.1 (1)
Cl1-Ti1-Cl2	105.6 (1)	Cl4-Ti2-O16	83.3 (1)
Ti1-O6-C7	124.8 (4)	Cl3-Ti2-cp2	125.0 (3)
Ti1-O6-C10	124.3 (3)	Cl3-Ti2-cp2	125.0 (3)
C7-O6-C10	109.5 (4)	Cl3-Ti2-O21	80.4 (1)
Ti2-O16-C17	124.1 (4)	Cl3-Ti2-O16	82.3 (1)
Ti2-O16-C20	124.4 (3)	Cl3-Ti2-Cl4	114.5 (1)
C17-O16-C20	109.0 (4)	Ti2-O21-C22	124.1 (4)
		Ti2-O21-C25	125.9 (4)
		C22-O21-C25	108.3 (5)

the coordination polyhedron are significantly longer in molecule B than in molecule A, as a consequence of the increased coordination number of titanium. The largest difference was observed for the titanium–oxygen bonds varying from 2.065 (4) [Ti1–O6] to 2.241 (4) and to 2.275 (4) Å [Ti2–O21]. The structural parameters concerning the $cpTiCl_2$ fragment fall in the usual range.[22] All the reactions were performed with THF-free $[cpTiCl_2]$ I, dissolved in THF. Diphenyldiazomethane reacted at room temperature with a THF solution of $[cpTiCl_2]$, without losing N_2, as schematically exemplified in eq 1. Complex II



separated from the THF solution as red-maroon crystals containing a THF molecule *per* unit. The remaining solution contained complex IV and $[cpTiCl_3]$, which was recovered as described in the Experimental Section. A THF suspension of II converted on heating to a solution containing both IV and $[cpTiCl_3]$. This finding supports further the intermediacy of (II) in the formation of IV from I and diphenyldiazomethane. The elimination of $[cpTiCl_3]$ from II would generate a coordinatively unsaturated titanium complex, so that its conversion to IV is expected to occur. Diphenyldiazomethane is reduced by complex I to the corresponding diphenylhydrazonido(2−) ligand, which displays a terminal bonding mode in proposed intermediate III, while it bridges two titanium(IV) both in complexes II and IV. No special role can be envisaged for THF in complex II, whether coordinated to titanium or present as a crystallization solvate. Both complexes II and IV are diamagnetic, as can be deduced from the ^1H NMR spectra. The bonding mode of diphenyldiazomethane in complexes II and IV is probably very similar, as suggested by the resemblances in spectroscopic characteristics (absence of C=N band above 1600 cm^{-1}) with both nitrogen atoms involved in the solid state in bridging the two titanium atoms. This will be discussed on the basis of the structure of IV which was elucidated by an X-ray analysis.

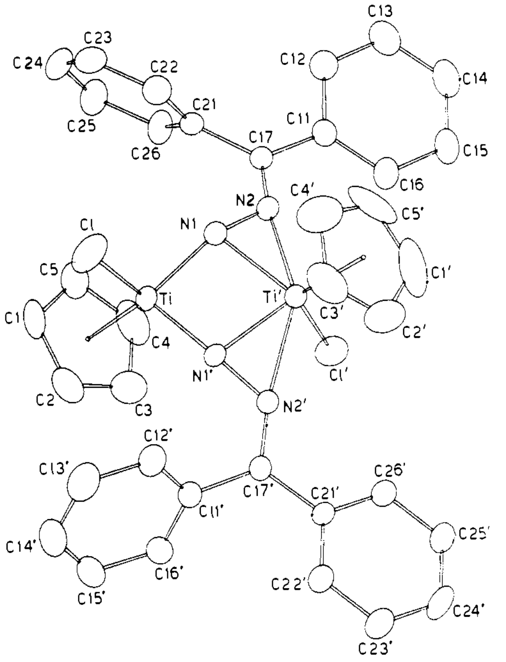


Figure 3. ORTEP drawing of complex IV (30% probability ellipsoids).

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex IV

Ti-cp	2.011 (5)	Ti′-cp′	2.054 (8)
Ti-Cl	2.300 (3)	Ti′-Cl′	2.353 (2)
Ti-N1	1.860 (5)	Ti′-N1	2.006 (6)
Ti-N1′	1.835 (6)	Ti′-N1′	2.006 (5)
N1-N2	1.327 (7)	Ti′-N2′	2.178 (5)
N1′-N2′	1.339 (8)	Ti′-N2	2.163 (6)
N2-C17	1.302 (8)	C17-C21	1.485 (9)
N2′-C17′	1.315 (8)	C17′-C11′	1.476 (8)
C17-C11	1.471 (8)	C17′-C21′	1.479 (8)
Ti-Ti′	2.837 (3)		
N1′-Ti-cp	117.1 (3)	N1-Ti′-N2	36.9 (2)
N1-Ti-cp	117.5 (2)	Cl′-Ti′-cp′	124.4 (2)
N1-Ti-N1′	89.2 (2)	Cl′-Ti′-N2′	85.3 (2)
Cl-Ti-cp	118.2 (2)	Cl′-Ti′-N1′	104.6 (2)
Cl-Ti-N1′	104.0 (2)	Cl′-Ti′-N1	105.3 (2)
Cl-Ti-N1	106.4 (2)	Cl′-Ti′-N2	85.0 (2)
N2′-Ti′-cp′	106.0 (3)	Ti′-N2-N1	65.1 (3)
N1′-Ti′-cp′	116.9 (3)	Ti′-N1-N2	78.0 (3)
N1′-Ti′-N2′	37.0 (2)	Ti-N1-N2	154.2 (4)
N1-Ti′-cp′	116.1 (4)	Ti-N1-Ti′	94.3 (2)
N1-Ti′-N2′	116.2 (2)	Ti-N1′-Ti′	95.1 (2)
N1-Ti′-N1′	80.6 (2)	Ti′-N1′-N2′	78.5 (3)
N2-Ti′-cp′	106.6 (3)	Ti-N1′-N2′	157.0 (4)
N2-Ti′-N2′	145.7 (2)	Ti′-N2′-N1′	64.5 (3)
N2-Ti′-N1′	115.5 (2)	Ti′-N2-C17	169.4 (4)
C17-N2-N1	125.3 (5)	Ti′-N2′-C17′	171.5 (4)
C11-C17-N2	119.5 (5)	C17′-N2′-N1′	124.0 (5)
C21-C17-N2	119.4 (5)	C11′-C17′-N2′	119.4 (5)
C11-C17-C21	121.1 (5)	C21′-C17′-N2′	117.8 (5)
		C11′-C17′-C21′	122.8 (5)

Figure 3 shows an ORTEP view of the dimeric complex IV, where two cpTiCl units are bridged by diphenylhydrazonido(2−) ligand. The structural parameters (Table VI) concerning such units are generally similar for both titanium atoms, though bond distances are slightly longer for the titanium having the higher coordination number: Ti–cp, 2.011 (5); Ti′–cp′, 2.054 (8); Ti–Cl, 2.300 (3); Ti′–Cl′, 2.353 (2). The bridging ligands are nonsymmetrically

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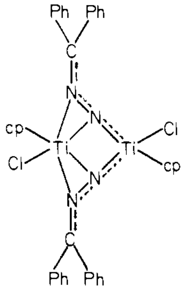
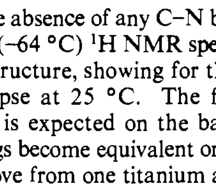
[22] Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169–174.

bonded to both titanium atoms. Titanium bonds only the terminal nitrogen of the hydrazonido ligands at very short distances [Ti–N1′, 1.835 (6); Ti–N1, 1.860(5)], which suggest the presence of a significant Ti–N double bond character.[8,13,24] Atom Ti′ is bonded to all four nitrogens at much longer distances ranging from 2.006 (5) to 2.178 (5) Å. The other parameters[25] which are instructive as to the bonding mode of the bridging ligands are as follows: (i) The N–N bond distances have significant multiple bond character, [N1–N2 1.327 (7) and N1′–N2′ 1.339 (8) Å]. (ii) The multiple bond character of the C17′–N2′ and C17–N2 units is 1.315 (8) and 1.302 (8) Å, respectively. (iii) The dihedral angle between plane 1 [Ti′, N1, N2, C17] and plane 2 [Ti′, N1′, N2′, C17′] (Table VIII) is 26.5 (8)°. Ti is 0.806(2) and 0.704(1) Å, respectively from these planes (Table VIII). (iv) The torsional angles C17–N2–N1–Ti and C17′–N2′–N1′–Ti are 102.9 (11) and 103.3 (11)°, respectively. (v) The bond angles around N2 and N2′ are C17–N2–N1 125.3(5) and C17′–N2′–N1′ 124.0(5)°, while those around N1 and N1′ are N2–N1–Ti 154.2(4) and N2′–N1′–Ti, 157.0(4)°. These features can be summarized in a structure as follows:



The hydrazonido(2−) ligand bridges the two titanium atoms in a fashion that is reminiscent of the bonding mode displayed by N_2 in the so-called titanocene–N_2 adduct clarified by Pez.[10a] Bridging bonding modes of diphenyldiazomethane have been found in a few complexes, namely $[cp_3Co_3(CO)(\mu_3\text{-}Ph_2CN_2)]$,[26] $[Fe_3(CO)_9(\mu_3\text{-}Ph_2CN_2)_2]$,[27] and $[cp_2Mo_2(CO)_4(\mu_2\text{-}Ph_2CN_2)]$.[28] The terminal nitrogen, however, in all these compounds is the only one involved in bonding the metal atoms. It would be useful to compare the related bond distances and angles of complex IV with those of the molybdenum complex $[cp_2Mo_2(CO)_4(\mu_2\text{-}Ph_2CN_2)]$[28]



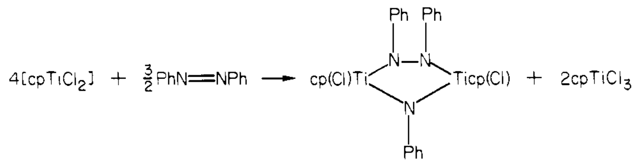
Such a comparison and the trend of bond distances in complex IV suggest an electronic delocalization over the Ti-N-N-C units. This would explain the absence of any C–N band above 1600 cm^{-1}. The low-temperature (−64 °C) ^{1}H NMR spectrum is in agreement with the solid-state structure, showing for the cp rings two broad singlets, which collapse at 25 °C. The fluxional behavior of hydrazonido ligands is expected on the basis of the solid-state structure. The cp rings become equivalent on the NMR time scale when N2 and N2′ move from one titanium atom to the other one.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex V[a]

Ti–cp1	2.040 (9)	Ti–N1′	2.363 (4)
Ti–Cl	2.332 (2)	N1–N1′	1.422 (6)
Ti–N1	1.950 (4)	N1–C11	1.438 (6)
Ti–N2	1.920 (4)	N2–C21	1.422 (8)
Ti–Ti′	2.829 (2)		
cp1–Ti–N1′	151.9 (3)	Ti–N2–C21	132.6 (1)
N2–Ti–N1′	83.3 (1)	Ti–N2–Ti′	94.9 (1)
N2–Ti–cp1	113.7 (2)	Ti–N1–N1′	87.5 (2)
N1–Ti–N1′	37.0 (2)	Ti′–N1–N1′	55.5 (2)
N1–Ti–cp1	116.2 (3)	Ti–N1–C11	155.7 (4)
N1–Ti–N2	95.6 (1)	Ti–N1–Ti′	81.4 (1)
Cl–Ti–N1′	85.8 (1)	N1′–N1–C11	116.1 (4)
Cl–Ti–cp1	110.0 (2)	Ti′–N1–C11	116.1 (3)
Cl–Ti–N2	103.4 (1)	N1–C11–C12	119.3 (5)
Cl–Ti–N1	116.6 (1)	N1–C11–C16	121.4 (5)
		N2–C21–C22	121.0 (4)

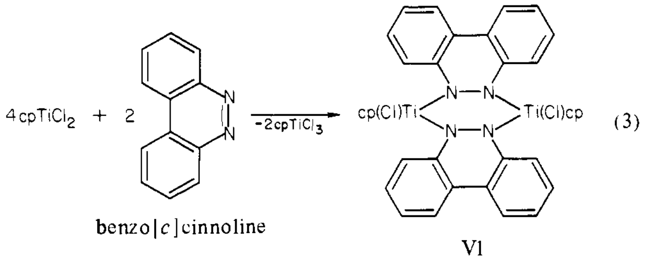
[a] ′ = $\bar{x}$, y, $1/2 - z$.

Complex I reacts as a two-electron reducing agent with substances containing nitrogen–nitrogen multiple bonds, that is, as a source of the hypothetical titanium(II) complex [cpTiCl]. Such a general behavior of complex I was also encountered in the reaction with azobenzene. Complex I reacts with azobenzene to form complex V as a major product of reaction 2. Complex V,



V (2)

whose structure was elucidated by an X-ray analysis, contains two [cpTiCl] units bridged both by an azobenzene molecule and by a phenylimido residue.[29] The genesis of phenylimido is interesting as well as intriguing. The –N=N– double bond cleavage is the key step involved in the conversion of N_2 molecule to ammonia.[30,31] While coupling of phenylimido to azobenzene is a common transformation,[29,32] the reverse reaction with nonactivated azo compounds is an unobserved transformation. The mechanism by which the –N=N– bond cleavage occurs is difficult to prove, in spite of the fact that an intermediate compound, $[(cpTiCl)_3(Ph_2N_2)_2]$ (see Experimental Section), has been isolated. The most plausible assumption concerns the formation of an azo compound in a preliminary step. Such a reaction should be followed by the attack on the metal-bonded N_2 unit from the free-radical-like [cpTiCl$_2$]. The proposed preliminary step in reaction 1 was simulated by replacing azobenzene with benzo[*c*]cinnoline.



benzo[*c*]cinnoline

VI

Complex VI was isolated as a maroon crystalline solid whose structure has been proposed on the basis of analytical and spectroscopic data. A determination of its structure was prevented

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[23] Titanium bond distances in related complexes can be found in: Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 792–800 and in ref 8 and 24.

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[25] C–N and N–N bond distances in related compounds can be found in ref 8, 23, 24, and in the following: Schramm, K. D., Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 2441–2448. Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, 99, 2108–2117.

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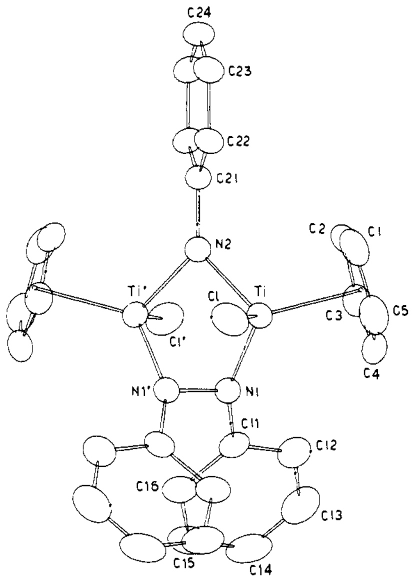
[31] Schrauzer, G. N.; Palmer, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 2659–2667 and references therein.

[32] Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279–293.



' = -x, y, ½-z

Figure 4. ORTEP drawing of complex V (30% probability ellipsoids).

Table VIII. Equations of Least-Squares Planes and, in Square Brackets, Distances (Å) from These Planes[a]

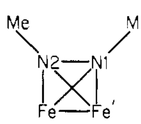
Complex I
plane through Ti2, Cl3, Cl4, cp2 (equatorial plane)
$0.2637x' - 0.5001y' - 0.8248z' = -3.7745$
[Ti2 −0.001(1), Cl3 0.000(2), Cl4 0.000(2), cp2 0.017(12), O16 −2.180(4), O21 2.192(4)]

Complex IV
(1) plane through Ti', N1, N2, C17
$-0.5711x' + 0.5983y' - 0.5620z' = -2.4111$
[Ti' 0.001(2), N1 −0.002(5), N2 0.016(5), C17 −0.014(6), Ti −0.806(2)]
(2) plane through Ti', N1', N2', C17'
$-0.2398x' + 0.8783y' - 0.4136z' = -0.3483$
[Ti' 0.000(1), N1' −0.001(5), N2' 0.007(5), C17' −0.008(7), Ti −0.704(1)]
dihedral angle 1∧2 = 26.5(8)°

Complex V
plane through Ti, C11, N1'
$-0.4984x' + 0.6255y' - 0.6003z' = -1.8357$
[N1 0.067(4)]

[a] The transformation matrix from fractional coordinates to orthogonal x', y', z' (Å) is (a $b \cos\gamma$ $c \cos\beta$//0 $b \sin\gamma$ $-c \sin\beta \cos\alpha$//0 0 $c \sin\beta \sin\alpha$).

by the low solubility and the low volatility of the complex. Complex VI could possibly also be a monomer. We did not observe any transformation of VI even boiling the reaction mixture. This is not surprising since the attack of the $-N_2-$ unit in VI either as a monomer or as a dimer by complex I is prevented by the steric hindrance of the groups bearing the azo function. We must add that $-N{=}N-$ bond cleavage in azo compounds was previously observed by using activated species like RN=NR, R = CF_3, in reaction with an iridium(I) complex[33] and R = $SiMe_3$ with a chromium(III) complex.[34] In neither instance is the mechanism of imido formation known. A poor relationship, however, can be found between reaction 3 and those promoted by the cited complexes, because of the difference in the substrate and in the chemical reactivity of the metal. Besides its origin, complex V deserves a detailed comment on its structure. A view of the molecular structure of the complex is shown in Figure 4; bond distances and angles are listed in Table VII. The molecule has a C_2 crystallographic symmetry; the two [cpTiCl][11] units are bridged by a phenylimido ligand. The coordination geometry around each titanium is close to being tetrahedral, considering the η-C_5H_5 ring as a monodentate ligand. Cl', N1 and Cl, N1' stay above and below, respectively, the plane defined by N2, Ti, and Ti'. The planar-trigonal arrangement of the groups around N2 along with the rather short Ti'–N2, and Ti–N2 distances [1.920(4) Å] suggest the existence of a Ti–N2 multiple bond interaction. Bridging alkylimido ligands have been recognized in various titanium complexes. The structural features of the Ti–N(R)–Ti unit[29] are very close to those found for the phenylimido unit in complex V. The azobenzene bridging bonding mode deserves detailed comment. The N1'–N1 bond distance [1.422(6)] is the longest so far encountered in metal-bonded azo compounds. The N–N bond distance has the following values in related azobenzene complexes: [$cp_2Ti(Ph_2N_2)$] [1.339 (8) Å];[24] [(t-$BuNC)_2Ni(Ph_2N_2)$] [1.385 (5) Å],[36] and $(PAr_3)_2Ni(Ph_2N_2)$ [Ar = p-tolyl; 1.371 (6) Å].[37] This suggests that such a bonding mode weakens considerably the N–N bond, and its subsequent cleavage may thus be plausible. The torsional angle Ti–N1–N1'–Ti' has the value of 81.3 (2)°. The Ti–N bond distances [Ti–N1, 1.950 (4); Ti–N1', 2.363 (4) Å] along with the Ti–Ti' distance [2.829 (2) Å] suggest that azobenzene could be considered as a symmetrical sawhorse ligand. However, such a bonding mode can be ruled out on the following grounds: (i) each titanium is tetrahedrally coordinated; (ii) the lone pair on the nitrogen does not have the geometrical requirement for interacting with titanium; (iii) the proximity of both nitrogen atoms to each titanium is mainly imposed by the bridging phenylimido; (iv) in doubly sawhorse azo units all metal–nitrogen distances are expected to be very close, as reported for [$Fe_2(CO)_6(Me_2N_2)$].[38]



Fe–N1, 1.873 (4) Å; Fe–N2, 1.882 (4) Å

Reaction 2 assumes importance in connection with the proposed formation of ammonia via the $-N{=}N-$ breaking of a diimide precursor in metal-promoted dinitrogen reduction. This seems to be a peculiar property of titanium(II) and titanium(III), promoting the reduction of $-N{=}N-$ fragments whether in N_2 or in organic substrates.

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Registry No. I, 87587-73-3; II, 87587-74-4; IV, 84897-93-8; V, 87587-75-5; VI, 87587-76-6; $cpTiCl_3$, 1270-98-0; $Ph_2C{=}N{=}N$, 883-40-9; PhN=NPh, 103-33-3; benzo[*c*]cinnoline, 230-17-1.

Supplementary Material Available: Listing of observed and calculated structure factors and coordinates for hydrogen atoms (Tables SI and SII), thermal parameters (Tables SIII, SIV, SV), and supplementary bond distances and angles (Table SVI) (52 pages). Ordering information is given on any current masthead page.

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