Titanium-Promoted Synthesis of a Carbohydrazido Ligand from Carbon Monoxide and Diphenyldiazomethane: Diazoalkane Coordination and Activation by Dicyclopentadienyltitanium(II) and -vanadium(II) Complexes[§]
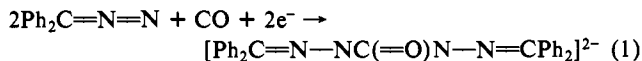
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Abstract: Vanadocene, Cp$_2$V (Cp = η^5-C$_5$H$_5$), reacts with diethyl diazomalonate, DEDM, and diphenyldiazomethane, DPDM, giving [Cp$_2$V(diazo)] complexes in which the diazo unit is η^2-N,N bonded to the metal. Titanocene dicarbonyl, Cp$_2$Ti(CO)$_2$, reacts with DEDM by losing carbon monoxide and giving [Cp$_2$Ti(DEDM)], in which the diazo ligand is η^3-N,N,O bonded to the metal through both nitrogen atoms and one oxygen of the ester groups. The complex has been spectroscopically and structurally characterized. Some relevant metrical parameters are as follows: Ti–N(1) = 1.980 (5) Å; Ti–N(2) = 2.219 (7) Å; Ti–O(1) = 2.247 (4) Å; C(12)–O(1) = 1.272 (7) Å; N(1)–N(2) = 1.214 (7) Å. This trend in bond distances suggests that the complex can be partially described as resulting from the 1,4 addition of the Cp$_2$Ti carbene-like unit to the EtOC-(=O)C(—N=N)COOEt diene-like structure. When the diazoalkane does not contain substituents having donor atoms, the "Cp$_2$Ti" unit promotes the reaction of CO with two diazoalkane molecules to produce a carbohydrazido ligand. When Cp$_2$Ti(CO)$_2$ was reacted with Ph$_2$CN$_2$, a trinuclear mixed valence titanium(III)–titanium(IV) complex was isolated, [(Cp$_2$Ti)$_3$-(Ph$_2$CN$_2$C(O)N$_2$CPh$_2$)$_2$], which contains two unpaired electrons per unit. Three "Cp$_2$Ti" units are bridged by two [Ph$_2$C=N—N*C(O)N*—N=CPh$_2$]$^{2-}$ ligands. Each ligand chelates a "Cp$_2$Ti" unit by using three N* atoms, while oxygen is engaged in bonding to the third Cp$_2$Ti unit. Some relevant structural parameters are as follows: Ti(2)–N(1) = 2.222 (5) Å; Ti(2)–N(2) = 2.210 (4) Å; N(1)–C(17) = 1.355 (8) Å; N(2)–C(17) = 1.351 (8) Å; N(1)–N(3) = 1.375 (8) Å; N(2)–N(4) = 1.394 (8) Å; C(17)–O(1) = 1.299 (7) Å; Ti(1)–O(1) = 1.930 (4) Å. C–N* and C–O bond distances show complete electron delocalization over the N$_2$CO unit bonding the two different titanium atoms. This is confirmed by the absence of any CO band above 1600 cm^{-1} in the IR spectrum. Crystallographic details for [Cp$_2$Ti(DEDM)]: space group $I4_1/a$ (tetragonal); a = 31.369 (3) Å; c = 7.760 (1) Å; Z = 16. The final R factor was 0.049 for 1551 observed reflections. Crystallographic details for [(Cp$_2$Ti)$_3$(Ph$_2$CN$_2$C(O)N$_2$CPh$_2$)$_2$]·3C$_7$H$_8$: space group $P2_12_12$ (orthorhombic); a = 27.667 (2) Å; b = 13.462 (1) Å; c = 11.846 (1) Å; Z = 2. The final R factor was 0.071 for 3301 observed reflections.

Diazoalkanes have been shown to be powerful tools in organometallic chemistry, as possible sources of reactive organic intermediates.[1] When diazoalkanes coordinate to a metal in their intact form, they can display bonding modes and a degree of activation related to those of a metal-bonded N$_2$ molecule.[2,3]

Because of the special role played by metals like titanium and vanadium in fixing dinitrogen[4] as well as in promoting molecular activation processes in which carbene-like species are involved,[5] we report the results obtained in the reaction between diazoalkanes and dicyclopentadienyltitanium and -vanadium compounds. We found that vanadocene is a rather versatile trapping reagent for various organic functional groups,[6] including the diazo unit >C=N=N.[7] Titanocene dicarbonyl, which is a source of the authentic "Cp$_2$Ti" unit,[8] reacts with a diazoalkane by either complexing it when it bears an additional functional group or promoting the reaction between diazoalkane and carbon monoxide as shown in eq 1. This reaction may represent a model study

$$2\text{Ph}_2\text{C}=\text{N}=\text{N} + \text{CO} + 2e^- \rightarrow$$
$$[\text{Ph}_2\text{C}=\text{N}—\text{NC}(=\text{O})\text{N}—\text{N}=\text{CPh}_2]^{2-} \quad (1)$$

for the metal-promoted formation of C–N bonds from carbon monoxide and metal-bonded N$_2$ molecules. The striking difference in the chemical behavior between the vanadocene and titanocene units[9] could be ascribed both to a different availability of the three metal orbitals not engaged in bonding the two η^5-C$_5$H$_5$ ligands[10] and to the different role played by the metal in transferring electrons to the molecule being activated.

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[§] Dedicated to Professor Lamberto Malatesta on the occasion of his 70th birthday.

Experimental Section

All the experimental operations were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Vanadocene, Cp$_2$V,[11] dicarbonyldicyclopentadienyltitanium, Cp$_2$Ti(CO)$_2$[12]

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diethyl diazomalonate (DEDM)[13] and diphenyldiazomethane (DPDM)[14] were prepared as described in the literature. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibility measurements were made with a Faraday balance. ^{1}H NMR spectra were carried out by using a Varian 60-MHz spectrometer.

Reaction of $Cp_2Ti(CO)_2$ with Diethyl Diazomalonate. A toluene solution (80 mL) of $Cp_2Ti(CO)_2$ (1.58 g, 6.75 mmol) was reacted with neat diethyl diazomalonate (DEDM 2.0 g, 10.75 mmol). The solution was left standing for 2 days and then heated to 70 °C for 20 min. By addition of *n*-hexane (25 mL), [$Cp_2Ti(DEDM)$] crystallized out as yellow-orange crystals (1.0 g, 41%). Anal. Calcd for [$Cp_2Ti(DEDM)$], $C_{17}H_{20}N_2O_4Ti$: C, 56.04; H, 5.49; N, 7.69. Found: C, 55.77; H, 5.98; N, 7.29. The crystals, the same as those used for the X-ray analysis, contain, before drying, some toluene (ca. 2 mol/titanium) which was verified by the NMR spectrum: ^{1}H NMR (C_6D_6, Me_4Si) two superposed triplets are centered at τ 8.95, two superposed quartets at τ 7.90, a singlet for Cp ligands is at τ 4.62; the IR (Nujol or THF solution) spectrum shows two strong bands at 1695 and 1640 cm^{-1}.

Reaction of Vanadocene with Diethyl Diazomalonate. To a toluene (50 mL) solution of vanadocene (1.80 g, 9.95 mmol) was added diethyl diazomalonate (2.80 g, 15.05 mmol) dissolved in toluene (25 mL). The solution became yellow in a few minutes. By the slow addition of *n*-hexane (50 mL) a black crystalline solid was obtained in a few hours (1.9 g, 52%). Anal. Calcd for [$Cp_2V(DEDM)$], $C_{17}H_{20}N_2O_4V$: C, 55.58; H, 5.45; N, 7.65. Found: C, 55.07; H, 5.60; N, 7.12. The IR spectrum (Nujol) displays two strong bands at 1670 and 1640 cm^{-1}. Depending on the crystallization rate the presence of some free diazo ligands can be found in the solid. The magnetic moment is 1.77 μ_B at 293 K.

Reaction of [$Cp_2V(DEDM)$] with O_2 and I_2. (a) A THF (3 mL) solution of [$Cp_2V(DEDM)$] displays two strong bands at 1640 and 1690 cm^{-1}. The reaction with oxygen generates new bands at 2130, 1775, 1735, and 1690 cm^{-1}, corresponding to those of the free diazo ligand. (b) [$Cp_2V(DEDM)$] dissolved in THF and reacted with a large excess of I_2 gave Cp_2VI_2 as deep black crystals.[6]

Reaction of $Cp_2Ti(CO)_2$ with Diphenyldiazomethane. To a toluene (25 mL) solution of $Cp_2Ti(CO)_2$ (1.89 g, 8.08 mmol) was added diphenyl-diazomethane (2.10 g, 10.82 mmol) dissolved in toluene (10 mL) at 0 °C. The final solution was allowed to rise to room temperature and was left standing for 2 days in vacuo. Slow evolution of carbon monoxide was observed (CO/Ti = 4/3). A deep blue compound crystallized out (1.5 g, 41%). Anal. Calcd for [($Cp_2Ti)_3(Ph_2CN_2C(O)N_2CPh_2)_2$], $C_{84}H_{70}N_8O_2Ti_3$: C, 73.79; H, 5.12; N, 8.20. Found: C, 73.88; H, 5.29; N, 6.37. X-ray analysis was performed on the toluene solvate crystals [($Cp_2Ti)_3(Ph_2CN_2C(O)N_2CPh_2)_2$]·$3C_7H_8$. The IR spectrum (Nujol) shows a strong >C=N band at 1700 cm^{-1} ($\chi_M{}^{corr}$ = 2698 × 10^{-6} cgsu. at 293 K).

Reaction of IV with 9,10-Phenanthrenequinone. Complex IV (0.55 g, 0.40 mmol) dissolved in THF (20 mL) was reacted with 9,10-phenanthrenequinone (0.90 g, 4.30 mmol). The final solution was left standing for several hours until a green microcrystalline solid separated from it. Anal. Calcd for [($Cp_2Ti)(Ph_2CN_2C(O)N_2CPh_2)$], $C_{37}H_{30}N_4OTi$: C, 74.74; H, 5.05; N, 9.42. Found: C, 73.95; H, 5.69; N, 9.59. The IR spectrum (Nujol) shows two strong bands at 1710 (C=N) and 1650 (C=O) cm^{-1}. Complex VI is diamagnetic.

Reaction of Vanadocene with Diphenyldiazomethane. A toluene (50 mL) solution of vanadocene (1.73 g, 9.56 mmol) was reacted with di-phenyldiazomethane (1.90 g, 9.79 mmol) dissolved in 25 mL of toluene. The color of the solution became deep red in a few minutes. When the solution was left overnight, a black solid crystallized from the solution (1.3 g, 36%). Since the solid burns in the air, any suitable analytical determination is prevented. The nitrogen content was determined by decomposing the complex with iodine: 0.551 g reacted with an excess of iodine in toluene gave 1.40 mmol of N_2 (95%). Complex VII has a magnetic moment of 1.73 μ_B at 293 K. [$Cp_2V(DPDM)$] did not react with carbon monoxide. Its reaction with O_2 makes free diphenyldiazo-methane (strong band at 2030 cm^{-1}), while the reaction with I_2 allowed the quantitative isolation of Cp_2VI_2.[6] When vanadocene is replaced by $Cp_2V(CO)$[15] in the reaction with Ph_2CN_2, carbon monoxide evolution was observed, while the final complex has the same IR spectrum of that obtained from Cp_2V, without any band above 1600 cm^{-1}.

X-ray Data Collection and Structure Refinement for $Cp_2Ti(DDEM)$. Preliminary X-ray examination (from rotation and Weissenberg photographs) showed a tetragonal unit cell. A summary of the crystal data and intensity data collection is given in Table I. Lattice constants came

Table I. Summary of Crystal Data and Intensity Collection

	II	IV
a, Å	31.369 (3)	27.667 (2)
b, Å	31.369 (3)	13.462 (1)
c, Å	7.760 (1)	11.846 (1)
Z	16	2
M	364.3	1643.7
calcd density, g/cm^3	1.266	1.233
space group	*I*4$_1$/*a*	*P*2$_1$2$_1$2
radiation	nickel-filtered Cu Kα (λ = 1.541 78)	niobium-filtered Mo Kα (λ = 0.710 69)
μ, mm^{-1}	3.87	0.31
scan type	θ-2θ	θ-2θ
scan range	±0.5° from peak center	
scan speeds	2.5–10° θ/min	
backgrounds	stationary crystal at ±0.5°	
2θ limits, deg	6–110	5–50
criterion for observn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	1551	3301
unique total data	2382	4315
cryst dimens, mm	0.10 × 0.14 × 0.37	0.42 × 0.50 × 0.81

from a least-squares refinement of the 2θ values of 24 reflections having 2θ > 80°.

Data were collected at room temperature by using a single-crystal Siemens AED automated diffractometer. The pulse height discriminator was set to accept 90% of the Cu Kα peak. One reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. For intensities and background the "five-point technique"[16] was used.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[17] No correction for absorption was applied ($\mu\bar{r}$ = 0.2).

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map.[18] The positions of all nonhydrogen atoms were revealed by the subsequent Fourier synthesis phased on the contribution of titanium. The full-matrix least-squares refinement was carried out first isotropically to R = 0.106 and then anisotropically to R = 0.073. At this point a difference map showed some disorder involving the C(17) methyl carbon. The structure was refined to converge down to R = 0.049 considering the C(17) atom statistically distributed over three positions with site occupation factors of 0.40 for C(17A) and 0.30 for C(17B) and C(17C), which were allow to vary isotropically. All the hydrogen atoms except those associated to C(16)–C(17) ethyl group were located in a ΔF map and refined isotropically in the last cycles. The final difference map showed two peaks at 0.55 e Å^{-3} (the general background was about 0.3 e Å^{-3}) to which no chemical meaning could be attributed. Attempts to refine their coordinates were completely unsuccessful, and the structure was considered to have converged at R = 0.049, no parameter shifting by more than 0.2 times its standard deviation in the last cycle.

The function minimized during least-squares refinement was $\sum w|\Delta F|$, and the reflections were weighted according to the scheme w^{-1} = [$\sigma^2(F_o)$ + 0.003$F_o{}^2$] based on counting statistics.[18] There was no evidence for secondary extinction among low-angle reflections. Among the unobserved reflections there were no serious discrepancies between F_o and F_c. The atomic scattering factors were those from ref 19 for Ti, those from ref 20 for O, N, and C, and those from ref 21 for H. The final atomic coordinates are listed in Table II. Thermal parameters are reported in Table III.[22]

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1920 *J. Am. Chem. Soc., Vol. 104, No. 7, 1982*

Gambarotta et al.

Table II. Atomic Coordinates ($\times 10^4$ for Nonhydrogen Atoms and $\times 10^3$ for Hydrogen Atoms), with Estimated Standard Deviations in Parentheses, for Complex II

	x/a	y/b	z/c		x/a	y/b	z/c
Ti	−428 (1)	1284 (1)	3313 (1)	C(15)	577 (2)	549 (2)	5884 (9)
O(1)	−568 (1)	800 (1)	5372 (5)	C(16)	1324 (3)	581 (3)	5463 (16)
O(2)	−280 (1)	295 (1)	7066 (5)	C(17A)	1560 (6)	807 (7)	6940 (29)
O(3)	637 (2)	260 (2)	6867 (7)	C(17B)	1638 (9)	894 (9)	5742 (45)
O(4)	899 (1)	750 (1)	5072 (6)	C(17C)	1611 (16)	754 (16)	4615 (65)
N(1)	114 (1)	1036 (1)	4152 (6)	H(1)	−1 (3)	97 (2)	25 (11)
N(2)	277 (2)	1269 (1)	3090 (7)	H(2)	−33 (3)	44 (3)	191 (11)
C(1)	−295 (2)	992 (2)	517 (8)	H(3)	−103 (2)	58 (2)	263 (10)
C(2)	−461 (2)	675 (2)	1515 (8)	H(4)	−123 (3)	145 (2)	133 (10)
C(3)	−880 (3)	780 (2)	1929 (9)	H(5)	−60 (2)	161 (3)	−44 (10)
C(4)	−973 (2)	1169 (3)	1183 (11)	H(6)	−117 (2)	181 (2)	373 (10)
C(5)	−615 (3)	1304 (2)	321 (10)	H(7)	−62 (2)	214 (2)	209 (11)
C(6)	−928 (2)	1823 (2)	4134 (9)	H(8)	4 (3)	211 (2)	365 (10)
C(7)	−615 (2)	2013 (2)	3128 (9)	H(9)	−9 (2)	167 (2)	647 (11)
C(8)	−229 (2)	1989 (2)	4054 (9)	H(10)	−86 (2)	150 (2)	662 (10)
C(9)	−311 (2)	1775 (2)	5596 (8)	H(131)	−82 (2)	50 (3)	836 (10)
C(10)	−746 (2)	1677 (2)	5652 (8)	H(132)	−90 (2)	15 (2)	637 (10)
C(11)	175 (2)	722 (2)	5356 (7)	H(141)	−49 (2)	−15 (2)	994 (12)
C(12)	−240 (2)	607 (2)	5939 (8)	H(142)	−60 (2)	−52 (3)	783 (10)
C(13)	−708 (2)	195 (2)	7619 (9)	H(143)	−97 (3)	−25 (2)	908 (10)
C(14)	−668 (2)	−209 (2)	8736 (9)				

X-ray Data Collection and Structure Refinement for [(Cp₂Ti)₃-(Ph₂CN₂C(O)N₂CPh₂)₂]·3C₇H₈.

X-ray Data Collection and Structure Refinement for [(Cp$_2$Ti)$_3$-(Ph$_2$CN$_2$C(O)N$_2$CPh$_2$)$_2$]·3C$_7$H$_8$. Preliminary X-ray examination of the crystals revealed an orthorhombic unit cell. A summary of crystal data and intensity data collection is given in Table I. Cell dimensions were obtained from a least-squares refinement of the 2θ values of 20 reflections having $2\theta > 34°$. Data were collected at room temperature by using a crystal mounted in a thin-walled glass capillary under nitrogen. Data collection and data reduction techniques have been described above. No correction for absorption was made ($\mu\bar{r} = 0.6$).

The structure was solved by the usual heavy-atom method.[18] From the three-dimensional Patterson map, approximate coordinates were obtained for the two independent titanium atoms, one of them lying on the twofold axis of the orthorhombic unit cell (space group $P2_12_12$, uniquely determined from systematic absences). Two successive Fourier syntheses yielded the positions of all nonhydrogen atoms in the complex. A difference Fourier map, calculated after isotropic refinement ($R = 0.118$), revealed the presence of two disordered independent toluene molecules. Disorder was solved by considering each molecule statistically distributed over two positions, which were isotropically refined with rigid-body constraint and site occupation factors of 0.6 (from C71 to C77) and 0.4 (from C61 to C67) for one molecule and 0.5 (from C81 to C87) for the other one statistically distributed around the twofold axis. All the other nonhydrogen atoms were refined anisotropically to converge in three full-matrix least-squares cycles to $R = 0.071$ ($R_w = 0.075$; $R_g = 0.096$) for 3301 observed reflections, using the rigid-body constraint for all the independent Cp and Ph rings. The hydrogen atoms were introduced as fixed contributors in calculated positions with isotropic thermal parameters fixed at $B = 7.9$ Å². The height of the most important peak in the final difference Fourier is about 0.4 e Å⁻³. Since the space group is *polar*, the chirality of the crystal was tested by inverting all coordinates (x, y, $z \rightarrow \bar{x}, \bar{y}, \bar{z}$) and refining to convergence once again. The resulting values ($R = 0.073$; $R_w = 0.075$; $R_g = 0.099$) allow one to conclude that the original assignment of crystal chirality is correct.

The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. During the final stage of refinement no parameter shifted by more than 0.6σ. Atomic scattering factors used were those indicated above.

The function minimized during all the least-squares calculations was $\sum w|\Delta F|^2$ where $w = 0.4578/\sigma^2(F) + 0.003F^2$.[18] The final atomic coordinates are listed in Tables IV and V.[22] Thermal parameters are reported in Table VI.[22]

Results

Titanocene dicarbonyl, Cp₂Ti(CO)₂ (Cp = η^5-C₅H₅), reacted with diethyl diazomalonate as reported in reaction 2. Compound

$$\text{Cp}_2\text{Ti(CO)}_2 + \text{R}_2\text{C}=\text{N}=\text{N} \rightarrow [\text{Cp}_2\text{Ti(DEDM)}] + 2\text{CO} \quad (2)$$

   I   DEDM   II

$$\text{R} = \text{CO}_2\text{Et}$$

II, obtained as yellow-orange crystals from a toluene solution, was found to be stable to heat and to air. Carbon monoxide is completely lost, while the diazo ligand is coordinated in its intact
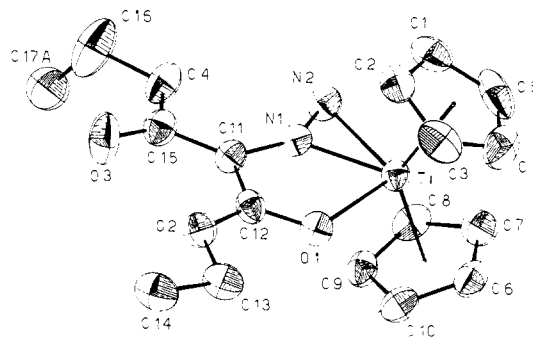

Figure 1. An ORTEP view of complex II, showing the labeling scheme. The thermal ellipsoids are drawn at the 40% probability level.

form. The IR spectrum displays two strong bands in solution as well as in the solid state in 1695 and 1640 cm⁻¹, while the H¹ NMR spectrum shows the presence of two nonequivalent ethyl groups. Analytical and spectroscopic data, including those from solution, agree with structure A, whose details have been confirmed

A
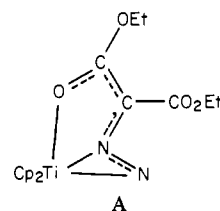
by an X-ray analysis. As depicted in Figure 1, the two bent Cp rings η^5 bonded to titanium make a cavity in the equatorial plane for the diazo ligand. The mutual orientation of the two rings is nearly eclipsed. Bond distances and angles for complex II are given in Table VII. All the parameters related to the [Cp₂Ti] unit fall in the usual range.[8,23] In the diazotitanium moiety the metal interacts with both N atoms and one oxygen from the ester groups: [Ti–N(1) = 1.980 (5) Å; Ti–N(2) = 2.219 (7) Å; Ti–O(1) = 2.247 (4) Å]. The significant asymmetry in the two Ti–N bond distances, higher than recently found in η^2-bonded diazoalkanes,[2] suggests that there is a contribution from the diazo–metal interaction different from the bonding mode exemplified in A.

(23) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454–9. Atwood, J. L.; Stone, K. E.; Alt, H.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367–75. Rausch, M. D.; Sikora, D. J.; Hrncir, D. C.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 3817–21.

Table VII. Bond Distances^a (Å) and Angles (Deg) for (Cp$_2$Ti)(DEDM)^b

Bond Distances

Ti-N(1)	1.980 (5)	C(1)-C(2)	1.364 (10)	C(6)-C(7)	1.389 (10)
Ti-O(1)	2.247 (4)	C(1)-C(5)	1.410 (12)	C(6)-C(10)	1.387 (9)
Ti-Cp(1)	2.077 (7)	C(2)-C(3)	1.393 (11)	C(7)-C(8)	1.410 (10)
Ti-Cp(2)	2.065 (7)	C(3)-C(4)	1.382 (11)	C(8)-C(9)	1.396 (9)
Ti-N(2)	2.219 (7)	C(4)-C(5)	1.374 (12)	C(9)-C(10)	1.399 (9)
		average	1.383 (9)	average	1.396 (6)
N(1)-N(2)	1.214 (7)	N(1)-C(11)	1.371 (7)		
C(11)-C(15)	1.433 (8)	C(11)-C(12)	1.425 (8)		
C(15)-O(3)	1.200 (8)	C(12)-O(1)	1.272 (7)		
C(15)-O(4)	1.347 (8)	C(12)-O(2)	1.318 (7)		
O(4)-C(16)	1.467 (9)	O(2)-C(13)	1.444 (8)		
C(16)-C(17A)	1.54 (2)	C(13)-C(14)	1.541 (9)		
C(16)-C(17B)	1.41 (3)	C(16)-C(17C)	1.24 (6)		

Bond Angles

N(1)-Ti-O(1)	70.6 (2)	C(2)-C(1)-C(5)	107.2 (6)	O(1)-C(12)-C(11)	120.6 (5)
N(1)-Ti-Cp(1)	112.1 (3)	C(1)-C(2)-C(3)	108.6 (6)	O(1)-C(12)-O(2)	120.4 (5)
N(1)-Ti-Cp(2)	111.9 (2)	C(2)-C(3)-C(4)	108.2 (7)	O(2)-C(12)-C(11)	119.0 (5)
O(1)-Ti-Cp(1)	102.7 (2)	C(3)-C(4)-C(5)	107.7 (7)	O(2)-C(13)-C(14)	105.7 (5)
O(1)-Ti-Cp(2)	103.0 (2)	C(4)-C(5)-C(1)	108.4 (6)	O(3)-C(15)-C(11)	127.3 (6)
Ti-N(1)-N(2)	84.4 (3)	average	108.0 (4)	O(3)-C(15)-O(4)	122.2 (6)
Ti-N(1)-C(11)	128.8 (4)	Cp(1)-Ti-Cp(2)	134.3 (3)	O(4)-C(15)-C(11)	110.4 (5)
N(2)-N(1)-C(11)	146.7 (5)	N(2)-Ti-N(1)	33.0 (2)	O(4)-C(16)-C(17A)	115.2 (1.0)
Ti-O(1)-C(12)	114.2 (4)	N(2)-Ti-O(1)	103.6 (2)	O(4)-C(16)-C(17B)	114.6 (1.3)
C(12)-O(2)-C(13)	116.5 (5)	N(2)-Ti-Cp(1)	104.6 (2)	O(4)-C(16)-C(17C)	113.1 (2.4)
C(15)-O(4)-C(16)	114.6 (6)	N(2)-Ti-Cp(2)	105.2 (2)	C(7)-C(6)-C(10)	109.2 (6)
N(1)-C(11)-C(12)	105.7 (5)			C(6)-C(7)-C(8)	107.3 (6)
N(1)-C(11)-C(15)	126.2 (5)			C(7)-C(8)-C(9)	107.7 (6)
C(12)-C(11)-C(15)	128.1 (5)			C(8)-C(9)-C(10)	108.2 (6)
				C(9)-C(10)-C(6)	107.6 (6)
				average	108.0 (4)

^{a} Bond distances involving hydrogens range from 0.82 to 1.22 Å and their esd's are in the interval 0.08–0.11 Å. ^{b} Cp1 and Cp2 are referred to the centroids of the rings C1–C5 and C6–C10, respectively. All the average values have been calculated by using the formulas $x_m = \Sigma w_i x_i / \Sigma w_i$, $\sigma_m = [1/(N-1)(\Sigma w_i x_i^2 / \Sigma w_i - x_m^2) + 1/\Sigma w_i]^{1/2}$, and $w_i = \sigma_i^{-2}$, where x_i are the individual observations and σ_i are their standard deviations.

Complex II may be viewed, in fact, as resulting from a 1,4 addition of the Cp$_2$Ti carbene-like unit to the unsaturated system (eq 3).
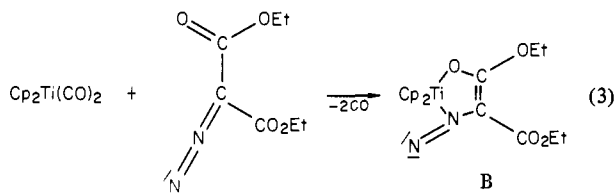
A bonding scheme, as given in B, can be considered as partially contributing to the description of the diazotitanium interaction, and it is based on the following bond distances: C(11)–C(12) = 1.425 (8) Å; C(11)–N(1) = 1.371 (7) Å; C(12)–O(1) = 1.272 (7) Å, the latter of which is significantly longer than the free C=O unit [C(15)–O(3) = 1.200 (8) Å]. Comparison of the geometry of this ligand is limited as the structure of the free molecule is unknown and the present structure is the first to be reported in which this ligand occurs. The N(2)–N(1)–C(11) angle [146.7 (5)°] is much larger than the expected value of 120° around N(1), while the N(1)–N(2) distance [1.214 (7) Å] is slightly shorter than the double bonds observed in HN=NH,[24] MeN=NMe,[25] and PhN=NPh[26] [1.238 (7), 1.254 (3), and 1.244 Å, respectively]. The presence of two nonequivalent ethyl groups in the ^{1}H NMR spectrum, together with the diamagnetism of complex II, shows that a structure like A or B remains even in solution. This bonding mode seems to be highly dependent on the presence of donor atoms on the diazo skeleton >C=N=N and on the presence of an available orbital on titanium(IV).

With vanadocene, only two orbitals are available on vanadium for bonding to the diazo unit, the third one remaining as non-

bonding with one unpaired electron, thus permitting evaluation of any stabilization effect due to a functional group on the diazo molecule. Vanadocene reacts very easily with a toluene solution of DEDM, giving a 1:1 adduct, which was isolated as a deep black crystalline solid very sensitive to the air (eq 4). Complex III has
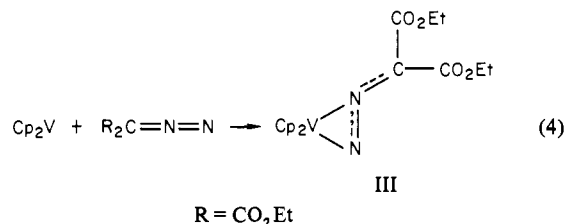
one unpaired electron (μ_{eff} = 1.77 μ_B at 293 K) and two strong bands in the IR spectrum at 1670 and 1640 cm^{-1}. Structures like A and B can be excluded on the basis of the electron configuration and of the very low tendency for vanadium to form metallacycles. Further support for the structure drawn for III comes from some preliminary crystallographic results on poor-quality crystals. Although the refinement of the structure did not succeed in giving a better fit than R = 29%, all the atoms of the complex were located by Patterson and Fourier syntheses. Their distribution indicates that the ligand does not chelate to the metal, but it interacts with the two N atoms. Although the atoms of the diazo ligand have been clearly defined, there is a major problem with the refinement of the Cp rings. The presence of the intact diazo moiety is further indicated in the reaction of O$_2$ with III which releases free DEDM, while the reaction with I$_2$ gave quantitatively Cp$_2$VI$_2$.[6]

The surprising role of an available orbital on titanium, besides the two involved in binding the N$_2$ unit, for promoting the activation of the diazo molecule was observed by employing a diazo molecule not having potentially coordinating substituents. This substitution, however, modifies, in addition, the metal to ligand electron-transfer process. Diethyl diazomalonate was replaced

(24) Trombetti, A. *Can. J. Phys.* **1968**, *46*, 1005–11.

(25) Chang, C. H.; Porter, R. F.; Brauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 5313–8.

(26) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 153–8.

Table VIII. Bond Distances (Å) and Angles (Deg) for $[(Cp_2Ti)_3(Ph_2CN_2C(O)N_2CPh_2)_2] \cdot 3C_7H_8{}^a$

Bond Distances					
Ti(1)-O(1)	1.930 (4)	C(17)-O(1)	1.299 (7)	N(4)-C(19)	1.269 (9)
Ti(2)-N(1)	2.222 (5)	C(17)-N(1)	1.355 (8)	C(18)-C(21)	1.489 (7)
Ti(2)-N(2)	2.210 (6)	C(17)-N(2)	1.351 (8)	C(18)-C(31)	1.517 (8)
Ti(1)-Cp(1)	2.064 (5)	N(1)-N(3)	1.375 (8)	C(19)-C(41)	1.520 (8)
Ti(2)-Cp(2)	2.060 (6)	N(2)-N(4)	1.394 (8)	C(19)-C(51)	1.493 (7)
Ti(2)-Cp(3)	2.056 (8)	N(3)-C(18)	1.306 (8)		

Bond Angles					
O(1)-Ti(1)-O(1)'	98.2 (2)	Ti(1)-O(1)-C(17)	149.2 (4)	C(17)-N(2)-N(4)	113.0 (5)
Cp(1)-Ti(1)-Cp(1)'	131.3 (2)	Ti(2)-N(1)-C(17)	94.1 (4)	N(1)-N(3)-C(18)	118.9 (5)
O(1)-Ti(1)-Cp(1)	106.4 (2)	Ti(2)-N(1)-N(3)	143.5 (4)	N(2)-N(4)-C(19)	119.3 (6)
O(1)-Ti(1)-Cp(1)'	105.0 (2)	Ti(2)-N(2)-C(17)	94.7 (4)	N(3)-C(18)-C(21)	127.7 (6)
Cp(2)-Ti(2)-Cp(3)	133.6 (3)	Ti(2)-N(2)-N(4)	144.4 (4)	N(3)-C(18)-C(31)	115.4 (5)
N(1)-Ti(2)-Cp(2)	114.3 (2)	O(1)-C(17)-N(1)	125.5 (5)	N(4)-C(19)-C(41)	126.2 (6)
N(1)-Ti(2)-Cp(3)	106.5 (3)	O(1)-C(17)-N(2)	123.9 (5)	N(4)-C(19)-C(51)	116.7 (6)
N(2)-Ti(2)-Cp(2)	106.4 (2)	N(1)-C(17)-N(2)	110.6 (5)	C(21)-C(18)-C(31)	116.8 (5)
N(2)-Ti(2)-Cp(3)	112.6 (3)	C(17)-N(1)-N(3)	112.0 (5)	C(41)-C(19)-C(51)	116.8 (5)
N(1)-Ti(2)-N(2)	60.3 (2)				

^{a} Cp1, Cp2, and Cp3 are referred to the centroids of the rings C1-C5, C6-C10, and C11-C15, respectively. Primed atoms at the symmetry related position $\bar{x}$, $\bar{y}$, and z.
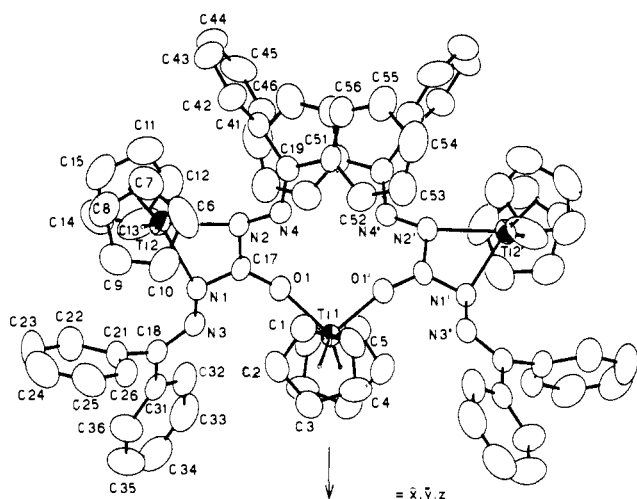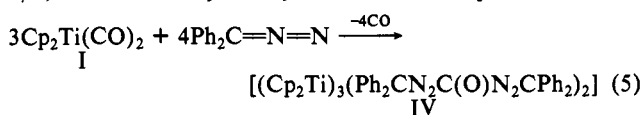

Figure 2. An ORTEP view of complex IV, showing the labeling scheme.

by diphenyldiazomethane, DPDM, in reaction 1. The reaction of $Cp_2Ti(CO)_2$ with DPDM was carried out at room temperature in toluene. The partial evolution of carbon monoxide (CO/Ti = 4/3) was followed by the crystallization of complex IV from the

$$3Cp_2Ti(CO)_2 + 4Ph_2C{=}N{=}N \xrightarrow{-4CO}$$
$$\underset{\text{I}}{}$$

$$[(Cp_2Ti)_3(Ph_2CN_2C(O)N_2CPh_2)_2] \quad (5)$$
$$\underset{\text{IV}}{}$$

solution as a deep blue solid containing toluene of crystallization. Compound IV has two unpaired electrons per unit ($\mu = 1.78\ \mu_B$ per titanium at 293 K) and the IR spectrum displays a strong C=N band at 1700 cm^{-1}.

Figure 2 shows a ORTEP drawing of the trinuclear complex, having a crystallographic C_2 symmetry. Two carbohydrazido ligands

$$[Ph_2C{=}N{-}NC({=}O)N{-}N{=}CPh_2]^{2-}$$
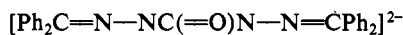
bridge the three Cp_2Ti units. Each ligand chelates a Cp_2iTi unit by using both N atoms, while oxygen atoms are engaged in bonding to the central Cp_2Ti unit. Structural parameters concerning all Cp_2Ti units fall in the usual range.[8] The Cp rings exhibit a staggered configuration around Ti(1), while they are neither staggered nor eclipsed around Ti(2). No significant new trend has been observed in the Ti-Cp, Ti-O, and Ti-N bond distances (Table VIII) in comparison with those of N analogous complexes.[27] Analysis of the bond distances and angles within

the skeleton of the organic moiety led us to propose the simplified picture for IV. All the N-N bond distances are very close to


IV
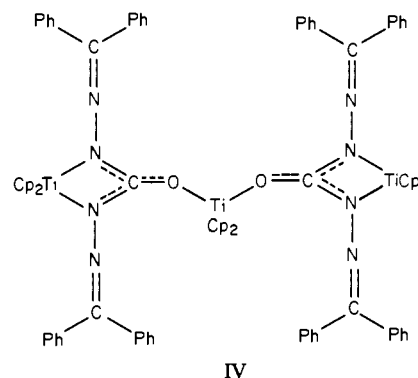
that of a single bond [N(1)-N(3) = 1.375 (8) Å; N(2)-N(4) = 1.394 (8) Å], while the C-O and C-N bonds involving the central carbon atom C(17) have significant double-bond character [C-(17)-N(1) = 1.355 (8) Å; C(17)-N(2) = 1.351 (8) Å; C(17)-O(1) = 1.299 (7) Å]. These parameters can be strictly related to those reported for the 1,5-diphenylcarbohydrazide, Ph-NH-NH-C(O)-NH-NHPh, molecule [N-N = 1.377 (8) Å; C-O, 1.235 (4) Å; C-N = 1.392 (3) Å].[28] This delocalization over all the N-C(O)-N units reduces the C-O bond order, with the consequent absence of any CO band at ca. 1600 cm^{-1} in the IR spectrum. The band appearing at 1700 cm^{-1} is due to the imino group >C=N. N(3), N(4), Ti(1), and Ti(2) are displaced [-0.454 (6), 0.604 (6), 0.955(1), and -0.206 (4) Å, respectively] from the perfect plane defined by C(17), O(1), N(1), and N(2). The assignment of a formal oxidation number to the titanium atoms must take into account both the structural data and the magnetic properties of IV. The most likely hypothesis, which is in agreement with the magnetic moment of 1.78 μ_B at 293 K for two Ti atoms per unit as well as for all the Cp rings η^5 bonded to the titanium atoms, requires that Ti(1) is titanium(IV), while Ti(2) is titanium(III).

The reaction of 9,10-phenanthrenequinone with the trinuclear complex IV affords the complexation of one of the three Cp_2Ti units[8] and gives the free unit VI, which is present in IV (eq 6). The different solubility of complexes V[8,27] and VI allows their partial separation. As expected, VI is diamagnetic and the IR spectrum shows that the CO group (ν_{CO} = 1650 cm^{-1}) is not further engaged in bonding to another metal center. Structural properties of the complexes IV and VI are very close to those reported for the titanocene–ureylene complexes, in spite of the

(27) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* 1979, 792–800 and references cited therein.

(28) De Ranter, C. J.; Blaton, N. M.; Peeters, O. M. *Acta Crystallogr., Sect. B* 1979, *B35*, 1295–7.

V

VI
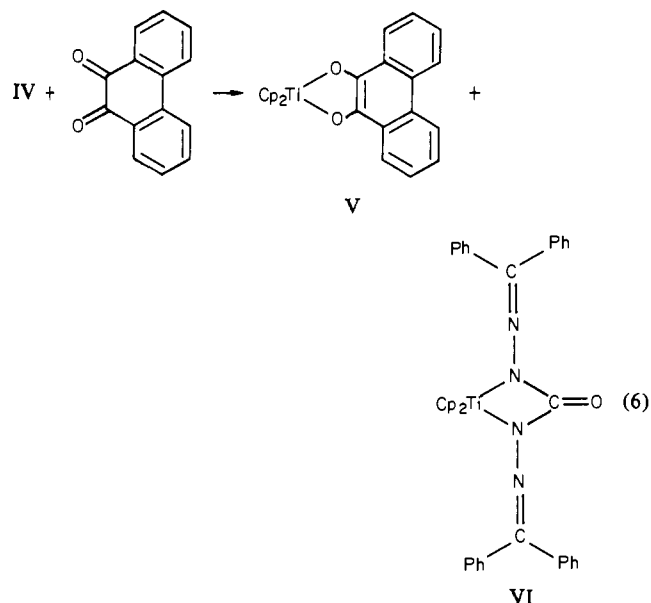
fact that in both cases their genesis and chemistry are poorly related to each other.[27] One of the most attractive result in this chemistry is the metal-assisted synthesis of a carbohydrazido derivative from CO and a diazoalkane. In order to relate this result to the presence of CO bonded to the metal, to the orbitals availability, and to the reducing power of the metal, we carried out reaction 7. Complex VII has been obtained by using either
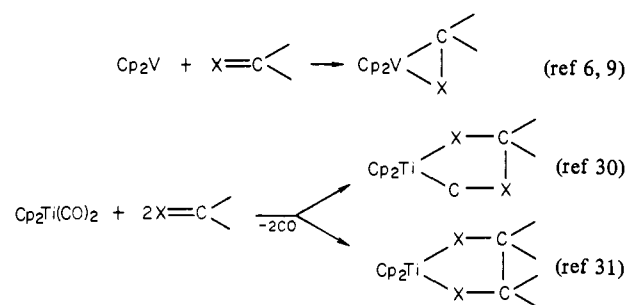

VII
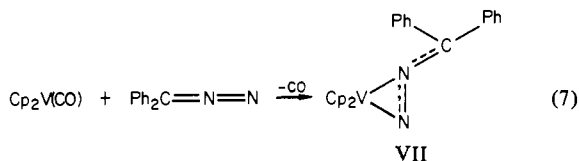
Cp$_2$V(CO)[15] or Cp$_2$V. Moreover, complex VII does not react with carbon monoxide. All these data confirm that the Cp$_2$V unit is unable to assist the reaction between two functional groups, namely, CO and Ph$_2$CN$_2$. Complex VII was obtained in the form of an extremely air-sensitive deep black crystalline solid, so that analytical determinations are very difficult. As expected, the magnetic moment of 1.73 μ_B at 293 K corresponds to that of a formal vanadium(IV) species. The presence of the intact diazo unit was proved by the reaction with O$_2$ giving free DPDM.

Discussion

Three aspects of the results obtained in the reaction between vanadocene and a titanocene source with diazoalkanes deserve attention: (a) the striking difference in chemical behavior of vanadocene vs. titanocene with diazoalkanes; (b) the bonding mode of a diazoalkane to early transition-metal "carbenes"; (c) the metal-assisted reaction between N$_2$ analogues such as diazoalkanes and carbon monoxide. The principal factor leading to the significant difference between the two employed models is that the three orbitals not engaged in coordinating to the two η^5-C$_5$H$_5$ units are made available in different ways for the coordinaton or the subsequent activation of functional groups and small molecules.[10] An additional factor that must be taken into account is the different reducing power of the two metals toward the diazo molecule being activated. Vanadocene reacts, usually, giving formally vanadium(IV) derivatives, containing one electron in a low-lying orbital not available for bonding to further donor atoms. Therefore two orbitals are available on vanadium for promoting molecular activation, while titanium, which has one electron less, has three orbitals for assisting the activation of the same functional groups. This would explain the fact that "Cp$_2$Ti" [from Cp$_2$Ti(CO)$_2$] promotes the dimerization of -C≡C-,[29] >C=O,[30] and >C=N–[31]

(29) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398-403.

Scheme I

functional groups, which give only 1:1 adducts when reacted with vanadocene,[6,9] keeping in mind that the change in the formal oxidation state is always the same for both model compounds. Each model fulfills a different role: the coordination of the group being activated is achieved by using vanadocene, while "Cp$_2$Ti" originating from Cp$_2$Ti(CO)$_2$ promotes a further "activation" of the substrate, i.e., its dimerization, as exemplified in Scheme I. The η^3-O,N,N' bonding mode of DEDM to titanium in complex II prevents any further "activation" of the diazo molecule. We can say that the metal needs to have a free orbital in order to bind to a further functional group, which can react with the first bonded substrate. The absence of any available orbital on the metal in the case of vanadocene causes the same kind of coordination using either DEDM or DPDM. Moreover, when Cp$_2$V is replaced with Cp$_2$V(CO) or the final complex VII is reacted with CO, no other product has been observed.

The η^2-bonding mode of a diazoalkane, while rather rare, was recently structurally clarified for the interaction of diazoalkanes with group 8 metals.[2] While the structure of II appears rather unique because of the coordination to the metal of an ester group, the trend observed in the M-N, N-N, and C-N bond distances for the metal-diazo skeleton resembles those observed for metals, with a much more marked asymmetry in the Ti-N bond distances, since titanium bonds closer the most electrophilic nitrogen [Ti-N(1) = 1.980 (5) Å; Ti-N(2) = 2.219 (7) Å].

The most interesting aspect of this chemistry is the activation of a diazo molecule occurring without the loss of the N$_2$ unit, in a reaction with carbon monoxide. This may represent a modeling study for an unexpected transformation of an N$_2$ metal-bonded molecule. The synthesis of the ligand carbohydrazido derivative dianion is exemplified in reaction 7, which represents a model

$$2Ph_2C=N=N + CO \xrightarrow{2e^-}$$
$$[Ph_2C=N-N-C(=O)-N-N=CPh_2]^{2-} \quad (8)$$
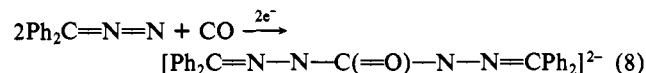
reaction for forming N-C bonds from N$_2$-like molecules and carbon monoxide. The route to establish a N-C bond from small molecules is an outstanding aspect in metal-promoted processes. Reaction 1 and the structure of II suggest that probable preliminary steps in reaction 4 can be exemplified as shown in eq 9.

D
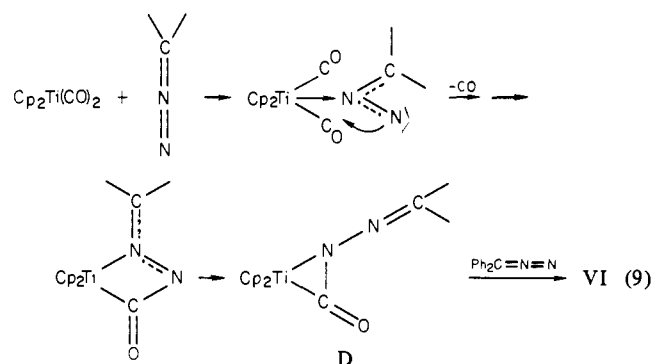
(30) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995-3002.
(31) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349-55.

A partial substitution of CO by the electrophilic reagent[29] is followed by an attack on CO by the nucleophilic N of the diazo unit. An η^2-C,N bonded unit, like that shown in D, may then insert another functional group, giving a larger metallacycle (complex VI). We feel that the formation of the trinuclear unit comes from the reaction of the preformed complex VI with $Cp_2Ti(CO)_2$ by a reaction similar to that observed in related titanium–ureylene complexes.[27] The proposed sequence indicates the preeminent role played by the presence of an available orbital on titanium in all the insertion steps depicted. This view seems to exclude that reaction 7 can be justified as arising from a fundamental one-electron reducing process of the diazo molecule requiring Ti(II) → Ti(III) oxidation, vs. the coordination of the diazo ligand to the metal involving a formal two-electron change in the oxidation state of the metal for both model complexes.

In conclusion, it would appear that vanadocene could be a highly versatile reagent for coordinating various functional groups, whereas titanocene, generated from $Cp_2Ti(CO)_2$, can promote the most elementary transformations of the same functional groups or small molecules.

Supplementary Material Available: Tables of thermal parameters for complexes II and IV (Tables III and VI) and fractional atomic coordinates for hydrogen atoms for complex IV (Tables IV and V) and listings of factor structures amplitudes for complexes II and IV (32 pages). Ordering information is given on any current masthead page.

Photochemical Addition of Tertiary Amines to Stilbene. Free-Radical and Electron-Transfer Mechanisms for Amine Oxidation

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received June 15, 1981

Abstract: Several amines of structure Me_2NCH_2R, where R = CH=CH$_2$, CO$_2$Et, C≡CCH$_3$, and C≡CH, but not Ph, react with the singlet state of *trans*-stilbene in hexane solution to yield adducts of structure $PhCH_2CHPhCHRNMe_2$. In acetonitrile solutions, these adducts are accompanied by variable amounts of adducts of structure $PhCH_2CHPhCH_2NMeCH_2R$. Both types of adduct are formed by cross combination of 1,2-diphenylethyl-α-aminoalkyl radical pairs. The mechanism of radical-pair formation is concluded to be solvent dependent. In nonpolar solvents, hydrogen atom transfer selectively yields a merostabilized α-aminoalkyl radical. In polar solvents, a sequential electron-transfer, proton-transfer mechanism yields both α-aminoalkyl radicals.

The abstraction of a hydrogen atom from tertiary amines can be effected chemically, electrochemically, photochemically, and enzymatically.[1] Several of these reactions are known to occur via one-electron oxidation to yield a planar aminium radical followed by deprotonation to yield an α-aminoalkyl radical (eq 1).[2] One characteristic of this mechanism is an increase in

$$R_2\overset{..}{N}CH_2R' \xrightarrow{-e} R_2\overset{+}{N}CH_2R' \xrightarrow{-H^+} R_2N\overset{.}{C}HR' \qquad (1)$$

reaction yield or rate with increasing solvent polarity. For example, singlet *trans*-stilbene and ethyldiisopropylamine form an unreactive fluorescent exciplex in nonpolar solvents (τ = 19 ns in hexane solution) but react efficiently to yield a diphenylethyl-α-aminoalkyl radical pair in polar solvents.[2,3] A second characteristic of this mechanism is stereoelectronic control of the deprotonation step.[4] For example, the reaction of singlet *trans*-stilbene with with ethyldimethylamine (1) yields 84% of adduct **a** and 16% of adduct **b** via the mechanism shown in Scheme I (R = CH$_3$).[1] The selective formation of the less substituted of two possible α-aminoalkyl radicals is consistent with a product-determining proton-transfer process but not with a simple hydrogen atom transfer process.

Amines processing π-electron-acceptor α-substituents are capable of forming exceptionally stable free radicals as a consequence of "merostabilization" (also known as "captodative stabilization").[5]
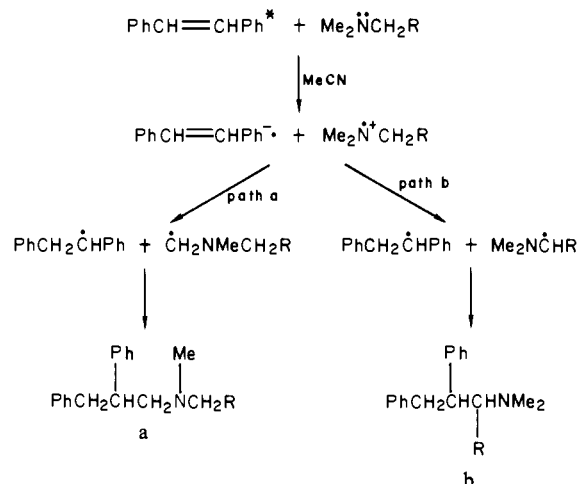
Scheme 1

Formation of merostabilized radicals from several α-substituted amines has been reported for hydrogen atom abstraction by *tert*-butoxy radicals[5] but not for electrochemical or photochemical oxidation of these amines. It thus appeared of interest to determine whether the reaction of singlet *trans*-stilbene with such amines yields the less substituted α-aminoalkyl radical, as observed for

(1) For leading references, see: Lewis, F. D.; Ho, T.-I.; Simpson, J. T. *J. Org. Chem.* **1981**, *46*, 1077–1082.
(2) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991–7996.
(3) Lewis, F. D.; Simpson, J. T. *J. Phys. Chem.* **1979**, *83*, 2015–2019.
(4) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243–274.

(5) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917–932.