Azo-complexes of Bis(cyclopentadienyl)-titanium and -vanadium; Model Systems for N–N Multiple Bond Activation ‡

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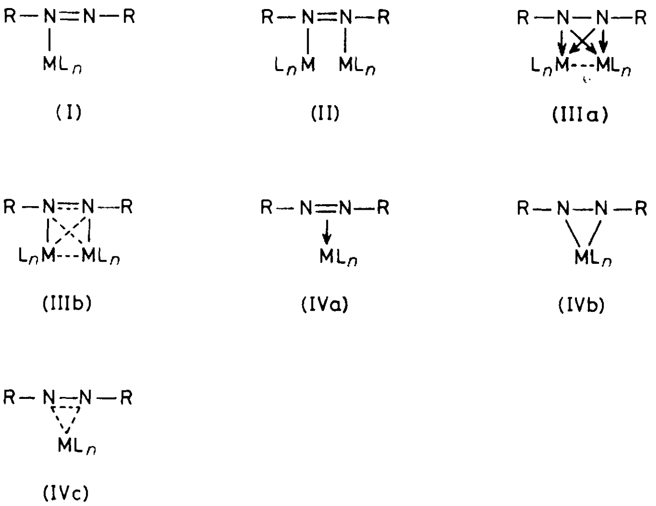
Azobenzenebis(η^5-cyclopentadienyl)-titanium and -vanadium and some titanium and vanadium analogues have been synthesized from [Ti(CO)$_2$(cp)$_2$] and [V(cp)$_2$] (cp = η^5-C_5H_5) respectively. In the mononuclear structure of [Ti(cp)$_2$(PhN=NPh)] the conformation and bond data of the *cis*-azobenzene ligand differ considerably from those of the free molecule. The complex consists of a Ti(cp)$_2$ moiety bridged in an edge-on fashion to the azo-group with the most significant bond data being: N–N 1.339(8), N–C 1.395(10), Ti–N 1.968(6), Ti–cp(centroid) 2.077 Å, N–Ti–N 39.8(5), and cp–Ti–cp 133.0°. The metal–nitrogen and –azo bonding characteristics are evaluated in connection with related compounds. A quantitative *ab initio* molecular orbital treatment of the related model complex [TiCl$_2$(MeN=NMe)] is consistent with the main conformational data and indicates strong interaction of of the azo-group and the metal. Formation of the complex gives rise to a lowering of the N–N bond order and an increase of the titanium oxidation state.

Molecular activation processes by transition metals can be extended to a large range of organic molecules. Amongst them organic substrates containing C–C and N–N multiple bonds deserve special attention. The obvious relationship of the latter with the N_2 molecule makes their activation particularly interesting.

Organometallic complexes containing a co-ordinated azo-grouping have recently attracted considerable attention. The two nitrogen lone pairs and the N=N π-bond provide a rich variety of co-ordination modes of the azo-grouping, as shown in Scheme 1. Obviously, the co-ordination type is quite sensitive to the nature of the metal centre. In fact, acidic metals interact with the non-bonding electrons of the nitrogen atoms and basic metals with the π electrons of the azo-group.



Scheme 1. Some co-ordination modes of azo-compounds

Table 1. Analytical data

Complex	Analysis [a] (%) C	H	N	Yield (%)	*M* [a,b]
(1) [Ti(cp)$_2$(PhN=NPh)]	73.0	5.4	7.9	56	375
	(73.3)	(5.6)	(7.8)		(360)
(2) [Ti(cp)$_2${N$_2$(C$_6$H$_4$Me-*p*)$_2$}]	75.9	6.1	6.95	67	
	(74.2)	(6.2)	(7.2)		
(4) [V(cp)$_2$(PhN=NPh)]	72.8	5.3	7.8	85	350
	(72.7)	(5.5)	(7.7)		(363)
(3) [Ti(cp)$_2$(N$_2$C$_{12}$H$_8$)]	73.4	4.5	7.53	57	
	(73.7)	(5.0)	(7.8)		
(5) [V(cp)$_2$(N$_2$C$_{12}$H$_8$)]	72.5	5.0	7.25	57	
	(73.1)	(5.0)	(7.8)		

[a] Calculated values in parentheses. [b] By cryoscopy in C_6H_6.

It is well known that the most efficient systems in nitrogen activation are the low-valent Group 4 elements, especially when used in bis-cyclopentadienyl derivatives.[1-3] This report describes the formation of such azobenzene–titanium and -vanadium complexes. Structural and electronic properties of [Ti(cp)$_2$(PhN=NPh)] (cp = η^5-C_5H_5) and related compounds are discussed.

Experimental

Materials.—Commercial azo-reagents were recrystallized before use. The complexes [Ti(CO)$_2$(cp)$_2$], [{TiCl(cp)$_2$}$_2$], [V(cp)$_2$], and [V(CO)(cp)$_2$] were prepared as described elsewhere.[4-7]

Analytical Techniques.—Carbon monoxide absorptions and evolutions were measured volumetrically. Microanalyses are reported in Table 1. Infrared spectra of Nujol mulls were recorded on Perkin-Elmer 283 and 337 spectrophotometers. Proton n.m.r. spectra were recorded on a Varian EM-360 spectrometer with SiMe$_4$ as internal standard. Magnetic susceptibility measurements were carried out with a Faraday balance. Three-dimensional *X*-ray data (2 402 measured reflections) were collected on a Picker FACS 1 diffractometer.

Preparations.—Unless otherwise stated, all reactions were carried out in a purified nitrogen atmosphere. Solvents were rendered water- and oxygen-free by standard procedures.

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‡ *Non-S.I. units employed:* B.M. = 0.927×10^{-23} A m^2; eV ≈ 1.60×10^{-19} J; cal = 4.184 J.

Azobenzenebis(η^5-*cyclopentadienyl*)*titanium* (1).—A heptane solution (100 cm^3) of [$Ti(CO)_2(cp)_2$] (1.3 g, 5.55 mmol) was treated with solid azobenzene (1.0 g, 5.55 mmol) at room temperature. After standing for 3 d black crystals of [$Ti(cp)_2$(PhN=NPh)] were obtained and washed with heptane (yield *ca.* 56%). Treatment of [$Ti(CO)_2(cp)_2$] (0.12 g, 0.51 mmol) with azobenzene (0.5 g, 2.74 mmol) in heptane (25 cm^3) at 30 °C gave 0.85 mmol of CO.

Reaction of (1) *with iodine.* Admixture of toluene solutions of (1) (0.45 g, 1.25 mmol in 25 cm^3) and iodine (0.7 g, 2.76 mmol) gave a black-violet precipitate of [$TiI_2(cp)_2$] (0.51 g, 1.18 mmol). After treatment with aqueous sodium thiosulphate and chromatography on silica gel with heptane elution, azobenzene (2.0 g, 1.1 mmol, m.p. 68—70 °C) was recovered.

Hydrolysis of (1). (*a*) Complex (1) (0.22 g, 0.61 mmol) was dissolved in toluene and treated with some drops of concentrated aqueous HCl. Red crystals of [$TiCl_2(cp)_2$] were obtained on standing (0.12 g, 0.49 mmol). (*b*) A benzene solution of (1) (0.44 g, 1.22 mmol, in 20 cm^3) was treated with 3 cm^3 of a 2 : 1 ethanol–water mixture. After stirring for 24 h, and concentration of the benzene phase to 5 cm^3, chromatography over silica gel with benzene as an eluant gave hydrazobenzene (0.18 g, 0.98 mmol; m.p. 134—136 °C) and azobenzene (0.035 g, m.p. 67—71 °C).

Bis(η^5-*cyclopentadienyl*)-*4,4'-dimethylazobenzenetitanium* (2).—A heptane solution (200 cm^3) containing [$Ti(CO)_2(cp)_2$] (2.1 g, 8.97 mmol) and 4,4'-dimethylazobenzene (1.7 g, 8.02 mmol) was heated at 60 °C and then left standing for 4 d. The deep black solution was then concentrated to 20—30 cm^3 and black crystals of complex (2) obtained (67%).

Reaction Between Azobenzene and Bis[*chlorobis*(η^5-*cyclopentadienyl*)*titanium*(III)].—[{$TiCl(cp)_2$}$_2$] (1.49 g, 3.49 mmol) was suspended in toluene (100 cm^3) and treated with azobenzene (1.3 g, 7.1 mmol). After stirring for 24 h a deep brown solution with a microcrystalline red solid was obtained. The mixture was concentrated to 20 cm^3, heptane added (50 cm^3), and the red solid filtered off; it was shown to be [$TiCl_2(cp)_2$] (0.8 g, 3.21 mmol). After cooling the solution to −78 °C, black crystals of [$Ti(cp)_2$(PhN=NPh)] (1) were obtained (0.5 g, 1.39 mmol).

Benzo[c]*cinnolinebis*(η^5-*cyclopentadienyl*)*titanium* (3).—Solid benzo[*c*]cinnoline (0.65 g, 0.36 mmol) was added to a toluene solution (50 cm^3) of [$Ti(CO)_2(cp)_2$] (0.835 g, 3.57 mmol). The colour changed rapidly from red-maroon to black and CO evolution was observed. The solution was kept for 3 d at room temperature and finally the i.r. spectrum showed the presence of [$Ti(CO)_2(cp)_2$] only as traces. After evaporation to dryness, the residue was dissolved in heptane and recrystallized on cooling (yield *ca.* 57%).

Azobenzenebis(η^5-*cyclopentadienyl*)*vanadium* (4).—Solid azobenzene (3.0 g, 1.65 mmol) was added to a 100-cm^3 solution of [$V(cp)_2$] (3.0 g, 1.66 mmol). The colour of the solution changed in 1 h from deep violet to black-brown. The solution was concentrated to 40 cm^3, heptane added (200 cm^3) and a black microcrystalline solid obtained. After filtration and washing with heptane, [$V(cp)_2$(PhN=NPh)] (4) was isolated in 85% yield.

Oxidation of (4). (*a*) Admixture of a toluene solution of iodine (2.0 g, 7.9 mmol, in 50 cm^3) with a toluene solution of (4) (1.2 g, 3.3 mmol, in 30 cm^3) immediately gave a deep violet crystalline solid, which was filtered off. After treatment with aqueous sodium thiosulphate and evaporation to dryness, extraction of the residue with pentane (50 cm^3) gave pure azobenzene (97%; m.p. 68—69 °C). (*b*) A benzene solution of (4) (0.205 g, 0.6 mmol, in 5 cm^3) was kept in a dry oxygen atmosphere. The colour of the solution changed at once. After chromatography over silica gel with pentane as an eluant, pure azobenzene (m.p. 65—68 °C) was recovered.

Hydrolysis of (4). (*a*) A 50-cm^3 solution of (4) (1.2 g, 3.31 mmol) in $CHCl_3$ was treated with dry HCl. The complex [$VCl_2(cp)_2$] formed immediately; after cooling to −78 °C and recrystallization from $CHCl_3$ saturated with HCl, a 90% yield was obtained. (*b*) A benzene solution (20 cm^3) of (4) (0.28 g, 0.77 mmol) was stirred with 1.5 cm^3 of a 2 : 1 ethanol–water mixture. After 1 h the benzenic phase was concentrated to 3 cm^3 and silica-gel chromatography, with benzene as an eluant, led to hydrazobenzene as the main product (77%, m.p. 124—125 °C) together with some traces of azobenzene.

Benzo[c]*cinnolinebis*(η^5-*cyclopentadienyl*)*vanadium* (5).—Benzo[*c*]cinnoline (0.89 g, 4.95 mmol) was dissolved in toluene (20 cm^3) containing [$V(cp)_2$] (0.85 g, 4.7 mmol). The colour of the solution rapidly became deep violet and a black-violet crystalline solid was obtained (57%) by addition of heptane.

Reaction of (4) *with* $CH_3O_2CC{\equiv}CCO_2CH_3$.—Complex (4) (0.59 g, 1.6 mmol) in 25 cm^3 of benzene was reacted with $CH_3O_2CC{\equiv}CCO_2CH_3$ (0.3 cm^3, 2.1 mmol). During heating for 2 h at 50—60 °C, the colour changed from black-maroon to deep green. The solution was concentrated to 5 cm^3 and addition of heptane (20 cm^3) gave green crystals of [$V(cp)_2(CH_3O_2CC{\equiv}CCO_2CH_3)$] (6) (*ca.* 84%), which was compared with an authentic sample.[8] Azobenzene (m.p. 65—68 °C) was obtained in 86% yield by silica-gel chromatography with heptane of the filtered toluene–heptane fraction.

Reaction of Carbonylbis(η^5-*cyclopentadienyl*)*vanadium with Azobenzene.*—[$V(CO)(cp)_2$] (0.23 g, 1.1 mmol) was dissolved in toluene (10 cm^3) and reacted with solid azobenzene (0.25 1.37 mmol). Carbon monoxide evolution took place and complex (1) obtained in 50% yield after addition of heptane.

Calculations.—The calculations were of the LCCGO-SCF-MO (linear combination contracted gaussian orbital–self consistent field–molecular orbital) *ab initio* type, using the UNIVAC version of the IBMOL package,[9] implemented and improved at ' G. Donegani ' Research Laboratories for a UNIVAC 1100/20 computer.

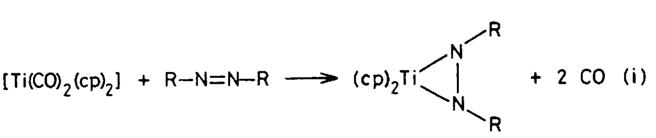
A gaussian basis set of minimal type, of quality equivalent to a single-zeta Slater basis set, was used [ref. 10(*a*) for H, C, and N; ref. 10(*b*) for Ti and Cl]. Titanium has been described with 11 *s*, 5 *p*, and 2 *d*-type gaussian contracted in 4(*s*)-, 2(*p*)- and 1(*d*)-type functions. The contraction scheme may be specified as [(5 + 2 + 2 + 2)/*s*; (3 + 2)/*p*; (2)/*d*]. Similarly, Cl has been described with [(5 + 2 + 2)/*s*; (3 + 2)/*p*] functions, C and N with [(5 + 2)/*s*; (3)/*p*] and H with [(3)/*s*] functions. Only in the case of azomethane was a reference calculation made with an enlarged basis set, namely [(5 + 2 + 1)/*s*; (3 + 1)/*p*] for C and N, and [(4 + 1)/*s*] for H.

Results and Discussion

Azobenzene can be used as a model molecule for N_2, at least as far as the change in reactivity of the former on co-ordination to a transition metal and the bonding mode of the azo-group to the metal are concerned.[11]

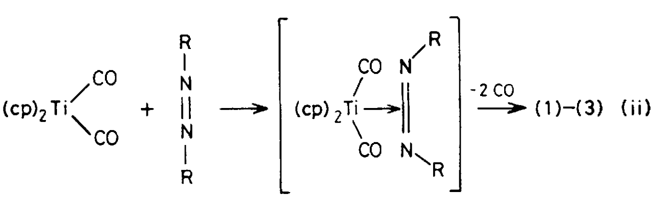
The choice of dicarbonylbis(η^5-cyclopentadienyl)titanium(II), [$Ti(CO)_2(cp)_2$], and vanadocene, [$V(cp)_2$], for studying the interaction of the N_2 unsaturated system, was based on their known carbene-like behaviour in addition to a multiple bond having electrophilic character.[12–14]

Titanium–Azo-complexes.—Dicarbonylbis(η^5-cyclopentadienyl)titanium(II) reacts at room temperature in hydrocarbon solutions with molecules containing the reactive azo-unit. Under loss of carbon monoxide, a black-maroon crystalline solid is formed according to equation (i). The products are monomeric in benzene and diamagnetic, as inferred from n.m.r. spectra. Spectroscopic data do not give significant information besides the presence of a Ti(cp)$_2$ unit (n.m.r.) and a considerable bathochromic shift of the N=N stretching vibration in the i.r. spectrum. However, details about the attachment mode of the azo-unit are deduced from the reactivity of compounds (1)—(3). Oxidation with I_2 or O_2 gives the starting azo-compound, thus excluding an *ortho*-metallation process involving the phenyl substituent or the presence of a 2-(phenylazo)phenyl ligand, as described by refs. 15 and 16. Bonding mode (I) is ruled out on the basis of hydrolysis with substances containing active protons, which form quantitatively hydrazobenzene from the azobenzene complexes.



(1; R = Ph)
(2; R = C_6H_4Me-*p*)
(3; Where R–N=N–R represents benzo[*c*]cinnoline)

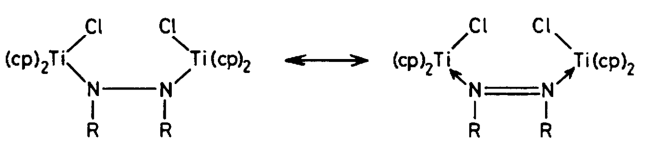
Occurrence of reaction (i) is then interpreted through a first step consisting of an interaction between the nucleophilic d^2-[Ti(CO)$_2$(cp)$_2$] with the electrophilic azo-compound [equation (ii)]. Loss of CO is a consequence of the decreasing electron density at the metal. Clearly, azobenzene is a weaker σ-donor and π-acceptor than CO.



Since dinitrogen fixation has been accomplished by many titanium(III) bis-cyclopentadienyl derivatives,[17] the reaction with azobenzene was extended to [{TiCl(cp)$_2$}$_2$], which is electronically very similar to the alkyl derivatives. Reaction (iii) in toluene solution is slow, but yields [TiCl$_2$(cp)$_2$] and (1)

$$[\{TiCl(cp)_2\}_2] + Ph{-}N{=}N{-}Ph \longrightarrow [TiCl_2(cp)_2] + [Ti(cp)_2(PhN{=}NPh)] \quad \text{(iii)}$$

almost quantitatively. Formation of (1) and [TiCl$_2$(cp)$_2$] proceeds probably through the following binuclear system resulting either from monoelectronic oxidation of the free radical-like Ti^{III} by the unsaturated system and successive ligand redistribution, or from interaction of Ti^{III} with the nitrogen lone pairs followed by a redox process combined with ligand redistribution. The nature of the substituents on the azo-linkage does not seem to have appreciable influence on the chemical properties of the azo-adducts. Scarcity of structural information on ligands η^2-co-ordinated to titanium makes the structure of (1) particularly interesting (see later).

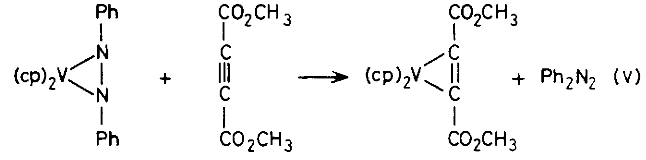


Vanadium–Azo-complexes.—Reactions of vanadocene, [V(cp)$_2$], in hydrocarbon solutions with molecules containing an azo-linkage parallel that reported for titanium and lead to black-maroon solids which are well soluble in benzene and are monomeric (Table 1). The magnetic moment of (4) at 292 K ($\mu_{eff.}$ = 1.77 B.M.) corresponds to that expected for a diamagnetically diluted system. Instead of [V(cp)$_2$], [V(CO)(cp)$_2$] can be used in reaction (iv). Azobenzene is recovered by oxidation of (4) with O_2 or I_2. Hydrolytic displacements with HCl and aqueous ethanol give [VCl$_2$(cp)$_2$] and hydrazobenzene respectively, supporting the presence of the V(cp)$_2$ unit and attachment of the N–N system to the metal through π-interaction.

$$[V(cp)_2] + R{-}N{=}N{-}R \longrightarrow [V(cp)_2(R{-}N{=}N{-}R)] \quad \text{(iv)}$$

(4; R = Ph)
(5; where R–N=N–R represents benzo[*c*]cinnoline)

Addition of R–N=N–R is reminiscent of the addition of other π-acids to vanadium(II). The π-acid strength of the azo-compound can be related to that of ligands displaced by or replacing it. The formal equivalence between azobenzene and π-acids is evident from the exchange between Ph$_2$N$_2$ and $CH_3O_2CC{\equiv}CCO_2CH_3$ [equation (v)].



(4) (6)

Clearly, V^{II} and Ti^{II} show similar metal–azo-bonding features. The expected one-electron delocalization on the Ph$_2$N$_2$ unit by the free radical-like d^1-V^{IV} seems to have no significant effect on the activation of the co-ordinated N–N unit, *e.g.* by free radical reagents.

Molecular Structure of cis-*Azobenzenebis*(η^5-*cyclopentadienyl*)*titanium* (1).—The bonding mode of the azobenzene ligand may be derived from the previously reported [18] crystal structure of [Ti(cp)$_2$(PhN=NPh)] [space group $P2_12_12_1$; a = 18.034(10), b = 8.904(4), c = 11.426(7) Å, and Z = 4], where bonding data are given. Here only the azo and metal-nitrogen bonding are critically evaluated.

The molecular structure of complex (1) provides the first bonding data for an edge-on *cis*-azobenzene complex. In fact no structural data have been reported for the *cis*-azobenzene ligands in [PtCl$_2$(PhN=NPh)] and [Pd$_2$Cl$_6$(PhN=NPh)$_3$].[19] Co-ordination induces both geometrical and conformational differences in the ligand.[18] In contrast to electron-rich metal

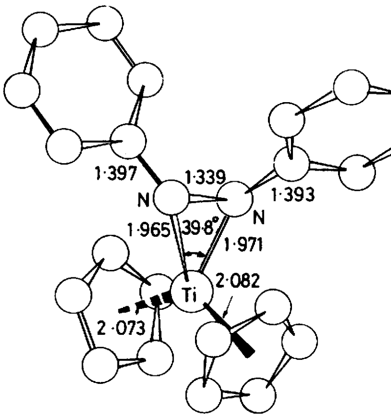
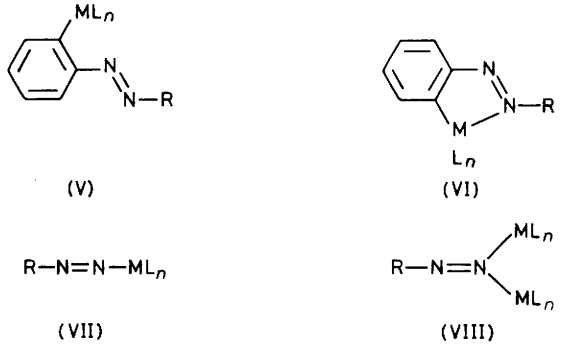


Figure 1. Perspective view of *cis*-azobenzenebis(η^5-cyclopentadienyl)titanium

systems where diazo-molecules act as π-acids, in electron-poor metal systems they prefer to function as σ-donors through a nitrogen atom lone pair. For an edge-on donor to form a σ-bond to the metal, it is necessary that a low-lying empty σ-orbital is available on the metal atom in the proper region of space. The considerable configurational differences between the azobenzene ligands in $[Ti(cp)_2(PhN{=}NPh)]$, $[Ni(CNBu^t)(PhN{=}NPh)]$,[20] and $[Ni(C_6H_4Me\text{-}p)_2(PhN{=}NPh)]$ [21] could mean that the stable lone-pair orbitals of the nitrogen atoms do not interact effectively with the metal orbitals. Substantial deviations from sp^2 geometry at N indicate that the lone pairs occupy orbitals directed away from the metal. Forward donation from a filled N–N π_{xy} orbital to a vacant dp^2 metal hybrid orbital $(d_{xy} + p_x + p_y)$ with back-donation from a filled $d_{x^2-y^2}$ metal orbital to an unoccupied π^*_{xy} antibonding orbital of the azo-function is in accordance with lengthening of the unsaturated bond and bending of the substituents away from the metal.

Whereas the molecular geometry of $[Ti(cp)_2(PhN{=}NPh)]$ is almost C_2 (Figure 1), the metal co-ordination (cp ring centroids and the nitrogen atoms) is pseudotetrahedral (C_{2v}). Essentially planar metal co-ordination is found for the π-bonded nickel complexes $[Ni(CNBu^t)(PhN{=}NPh)]$,[20] $[Ni\{P(C_6H_4Me\text{-}p)_3\}(PhN{=}NPh)]$,[21] and $[Ni(CNBu^t)(daf)]$ (daf = diazofluorene),[22] where the metal acts as a strong electron donor. In $[Ti(cp)_2(PhN{=}NPh)]$ lowering of the Ti p_z orbital probably increases its involvement in bonding favouring a dihedral angle of 90°. If we consider a unidentate azo-ligand, the titanium co-ordination (centres of gravity of the cp's and midpoint of N–N) is planar. However, steric crowding is more like that of tetrahedral $Ti(cp)_2$ complexes as the cp–Ti–cp angle (133.0°) is within the common 129—139° range of such complexes and differs considerably from the 145.7(3)° bending in a trigonal $Ti(cp)_2$ compound.[2]

The N–N distances in the *trans*-azobenzene complexes $[Ni(CNBu^t)(PhN{=}NPh)]$ [20] and $[Ni\{P(C_6H_4Me\text{-}p)_3\}(PhN{=}NPh)]$ [21] [1.385(5) and 1.371(6) Å, respectively] exceed those in $[Ti(cp)_2(PhN{=}NPh)]$ [1.339(8) Å] and are all significantly longer than the double bond in $HN{=}NH$,[23] $CH_3N{=}NCH_3$,[24] and $PhN{=}NPh$ [25] [1.238(7), 1.254(3) and 1.253(3) Å, respectively], thus suggesting σ-donor and π-acceptor properties for the ligand, which reduce the N–N bond order. In no reported structure of azobenzene complexes is the N–N distance indicative of a double bond. The N–N bond length in $[Ti(cp)_2(PhN{=}NPh)]$ may be compared to the 1.438(12) Å single bond distance in a hydrazine chelate, $[\{Cu(bh)_2\}Cu_3Cl_5]$ (bh = *N*-benzoylhydrazine).[26]



Scheme 2. *Ortho*-metallated azo-complexes and diazoalkane co-ordination modes

Table 2. Average bond lengths in metal co-ordinated dinitrogen ligands

	Bond lengths (Å)	
Bonding mode [a]	N=N	N–C
(I)	1.242	1.500
(II)	1.26	1.459
	1.363 [b]	1.344 [b]
(III)	1.390	1.462
(IV)	1.366	1.415
(V)	1.235	1.472
(VI)	1.283	1.392
(VII)	1.202	1.420
	1.126 [c]	
(VIII)	1.233	1.446

[a] See Schemes 1 and 2. [b] In pyrazole derivatives [*cf.* N–N and N–C bond lengths of 1.342(2) and 1.31—1.35 Å, respectively, in unco-ordinated pyrazole [27]]. [c] In N=N derivatives (*cf.* bond length of 1.0976 Å in free N_2 [34]).

To evaluate properly the N–N bond length in complex (1) it is useful to notice the modest changes in the azo-linkage on co-ordination according to the σ-bonding modes (I), (II), (V), (VII), and (VIII) (see Scheme 2 and Table 2). In fact, for *trans*-azo-compounds (unco-ordinated N–N, 1.250; N–C, 1.430 Å) and pyrazole and pyrazolyl derivatives (unco-ordinated pyrazole: N–N, 1.342(2); N–C, 1.31—1.35 Å),[27] co-ordination *via* nitrogen lone pairs with concomitant $M(d_{\pi^*})$–$N(p_{\pi^*})$ back-bonding [(I) and (II)] does not greatly affect the geometry (and conformation) of the ligand with respect to the free state (Table 2). In the *ortho*-metallated complexes (V) and (VI) with a σ M–C bond, the double bond character of the azo-group is essentially preserved with a slight electron delocalization in the chelate ring in the case of (VI) with a more complex bonding scheme. End-on co-ordination of the phenylazo-ligand with co-linearity of M–N–N atoms in (VII) results in a considerable $L_n\overset{-}{M}{=}\overset{+}{N}{=}\ddot{N}\diagdown_{R}$ contribution, as in $[Mo(CO)_2\{HB(pz)_3\}(N_2Ph)]$ (pz = pyrazolyl) [28] and $[ReCl_2(PMe_2Ph)_3(N_2Ph)]$.[29] The N–N bond length in the phenylazo-ligand is close to that in free azobenzene. Similar findings hold for $L_nM{-}N{\equiv}N$ and $L_nM{-}N{\equiv}N{-}ML_n$ complexes. In (VIII) the phenyldiazo-ligand acts as a three-electron donor by bridging two metal atoms.

The major bond length effects in the azo-group are then observed for complexes with bonding modes (III) and (IV). In the former, in addition to the four lone-pair electrons, the diazene donates two π-electrons to the metal causing N–N bond stretching from 1.24 to 1.38 Å. In π-bonded diazoalkane-metal complexes the N–N bond is stretched by *ca.* 0.12 Å [22,30,31] to a double bond value. The considerable N–N bond lengthening in the edge-on azobenzene complexes is to be compared to the bis-co-ordinated compounds [{Ni[P(C_6H_{11})$_3$]$_2$}N$_2$],[32] [{Ti(η^5-C_5Me_5)$_2$}$_2$N$_2$][2] and [(NH_3)$_5$RuN$_2$Ru(NH_3)$_5$][BF_4]$_4$·2H_2O[33] with end-on co-ordination and a linear M–N≡N–M system. In these cases, the low-lying empty π-orbitals of Ti effect only a slight increase in N–N bond length (up to 1.16 Å; *cf.* free dinitrogen, 1.0976 Å).[34] It thus appears that the N–N distances in edge-on dinitrogen or π-bonded azo-complexes differentiate sharply from those in an end-on fashion (VII). It is to be stressed, however, that a sizeable reduction in N–N bond order does not necessarily imply N_2 activation.

Lengthening of the N–N bond is accompanied by shortening of the C–N bonds (to 1.395 Å on average), even though these bonds in [Ti(cp)$_2$(PhN=NPh)] are surprisingly shorter than in the two complexed *trans*-azobenzene molecules [av. 1.424(7) Å].[20,21] On the basis of Lofthus' bond order–bond length relationships,[35] the N–N and C–N bond orders in [Ti(cp)$_2$(PhN=NPh)] are 1.55 and 1.36 v.u., respectively.

The best appraisal of the titanium–nitrogen bonding in complex (1) is that the symmetrically disposed and equidistant Ti–N bonds of 1.968 Å are among the shortest observed (1.69—2.46 Å),[18] shorter than those [1.980(5) and 2.219(7) Å] in [Ti(cp)$_2$(dedm)] (dedm = diethyl diazomalonate)[30] though slightly longer than the pure single Ti^{IV}–N bond length of 1.905 Å. Comparison of the Ti–N bond in (1) with the M–N bond length in other dinitrogen and azo-complexes is quite instructive. Metal dinitrogen geometries are influenced by the nature of the metal atom, the azo-ligand and the remaining ligand atoms. Structural data for compounds with bonding modes (I)—(IV) and (VI)—(VIII) (not reported) containing mono- and di-substituted diazenes, aryldiazo, pyrazole, and pyrazolylborate ligands show various interesting trends. The M–N bond distances decrease in the order (I), (II), (III), (IV), (VI), and (VII). In the end-on complexes (VII) this is understandable in view of contributions of limiting formulae of the type $L_n\overset{-}{M}=\overset{+}{N}=\ddot{N}\diagdown_{R}$. Yet, even here, the M–N bond is usually not as short as a formal double bond. In complexes with bonding mode (VI), the M–N bonds are only slightly shorter than single bonds, suggesting a small degree of metal–ligand multiple bonding. In the binuclear bonding mode (III) each N is formally a three-electron rather than a one-electron donor as in (IV). The structural data for (III) have previously been interpreted in terms of (tetravalent) N–N and M–N σ bonds of formal unit order. However, comparison of Fe–N bonds in type (III) complexes [Fe$_2$(CO)$_6$(MeN=NMe)] (1.878 Å) and [Fe$_2$(CO)$_6$(PhN=NPh)] (1.914 Å) with the complex [Fe(CO)$_2$(COCH$_3$){HB(pz)$_3$}] (2.042 Å) shows bond shortening in type (III) compounds.[36] It is suggested that bonding in (III) is best described by (IIIb) with some residual π-bonding.

Structural evidence for edge-on co-ordination [as in (IV)] has first been provided by Dickson and Ibers[20] in [Ni(CNBu^t)(PhN=NPh)] with a bonding situation analogous to metal–olefin complexes (IVa). This geometry has also been viewed as a σ-bonded rigid three-membered ring (IVb), as formulated for [IrCl(CO)(PPh$_3$)$_2${(NCOOEt)$_2$}],[37] [Pt(PPh$_3$)$_2${(NCOOEt)$_2$}],[38] [Mo(cp)$_2$(PhN=NPh)],[39] and [Ni(PPh$_3$)$_2$(PhN=NPh)].[40] Structural data of the nitrogen bridged mono- and binuclear metal complexes (IV) and (III) indicate fairly small N–N bond length differences (Table 2). The acute N–M–N bond angles in the (III) and (IV) complexes are fairly similar, namely 42.7(2), 42.9(2), 42.8(2), 41.6(2), and 39.8(5)° in [Fe$_2$(CO)$_6$(MeN=NMe)],[40] [Fe(CO)$_6$(PhN=NPh)],[36] [Ni(CNBu^t)(PhN=NPh)],[20] [Ni{P(C_6H_4Me-*p*)$_3$}(PhN=NPh)],[21] and [Ti(cp)$_2$(PhN=NPh)], respectively. A smaller angle of 33.0(2)° is observed in [Ti(cp)$_2$(dedm)].[30]

Table 3. Geometrical parameters assumed for molecular orbital calculations

Molecule or fragment	Geometry (distances, Å; angles, °)
TiCl$_2$	Ti–Cl, 2.26;[a] Cl–Ti–Cl, 128
Ti(cp)$_2$	Ti–cp, 2.078; C–C, 1.409; C–H, 1.080, cp–Ti–cp, 133 (eclipsed conformation of cp$_2$)
MeN=NMe	N–N, 1.24; N–C, 1.47; C–N–N, 110 (*trans*)
[TiCl$_2$(MeN=NMe)]	TiCl$_2$, as above; Ti–N, 1.970;[b] N–N, 1.34;[b] N–C, 1.42; C–N–N, 118; the torsion angle C–N–N–C has been varied from 0 to 60°
[TiCl$_2$(C_2H_4)]	TiCl$_2$, as above; Ti–C, 2.35;[c] C–C, 1.40;[c] C_2H_4 plane assumed parallel to the Cl · · · Cl direction, with C · · · C vector perpendicular to Cl · · · Cl vector
[TiCl$_2$(σ-N$_2$)]	TiCl$_2$, as above; Ti–N(1), 2.0; Ti–N(2), 3.2[d]
[TiCl$_2$(η^2–N$_2$)]	TiCl$_2$, as above; Ti–N(1), Ti–N(2), 1.97; N(1)–N(2), 1.35[e]

[a] *cf.* Ti–Cl mean distance in I. W. Bassi, M. Calcaterra, and R. Intrito, *J. Organomet. Chem.*, 1977, **127**, 305. [b] *cf.* crystallographic data for [Ti(cp)$_2$(PhN=NPh)].[18] [c] G. Allegra, *Makromol. Chem.*, 1971, **145**, 235; L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 499. [d] Ref. 2. [e] *cf.* Ref. 1 for MN$_2$ edge-on arrangement.

Taking into account the observed N–N bond distance, it follows that complexation in (IV) leads to more severe perturbation in metal co-ordination and bonding of the ligand than in most other bonding modes of Schemes 1 and 2.

Electronic Structure of some Titanium–Dinitrogen and Related Complexes.—The weakening of the N–N bond and eventually some multiple bond character for Ti–N in [Ti(cp)$_2$(PhN=NPh)] conform to the usual picture of π-bonding of the olefins to transition metals. Although it is a matter of dispute whether the nitrogen lone pairs in edge-on dinitrogen complexes participate in bonding,[41,42] if we accept that some degree of N (σ) ⟶ M bonding is present even in an apparent π-bonding situation, then a bidentate linkage as in (IVc) is a realistic description of the metal–dinitrogen interaction.

In order to investigate the differences from bonding in a classical π-bonded system (IVa), we have computed the electronic structures of the TiCl$_2$ and Ti(cp)$_2$ moieties, of *cis*-azomethane and of the model compounds [TiCl$_2$(MeN=NMe)], [TiCl$_2$(C_2H_4)], [TiCl$_2$(σ-N$_2$)] (end-on), and [TiCl$_2$(η^2-N$_2$)] (edge-on). The modifications induced by titanium complexation on the electronic structure of the dinitrogen compounds are examined through analysis of the electron populations.

Molecular geometries were taken as indicated in Table 3; in particular, the geometrical parameters of the model compound [TiCl(MeN=NMe)] have been assumed similar to those derived for [Ti(cp)$_2$(PhN=NPh)] (Figure 1). Observed differences in charge distribution, namely a higher antibonding effect between the nitrogen atoms for the extended basis set, suggest the need to make reference to the same basis set calculations for the purpose of comparison. Consequently, the results of the electron population analysis reported here must be taken on a relative scale.

Analysis of the atomic orbital contributions to the highest occupied molecular orbital (h.o.m.o.) of the TiCl$_2$ moiety reveals a predominant 3*d* contribution of titanium; instead, the lowest unoccupied molecular orbital (l.u.m.o.) of the same complex shows contributions by 4*s*(Ti) and 3*p*(Cl) atomic orbitals. Similarly for Ti(cp)$_2$, h.o.m.o. has a predominantly 3*d*(Ti) character and l.u.m.o. a 4*s*(Ti) orbital

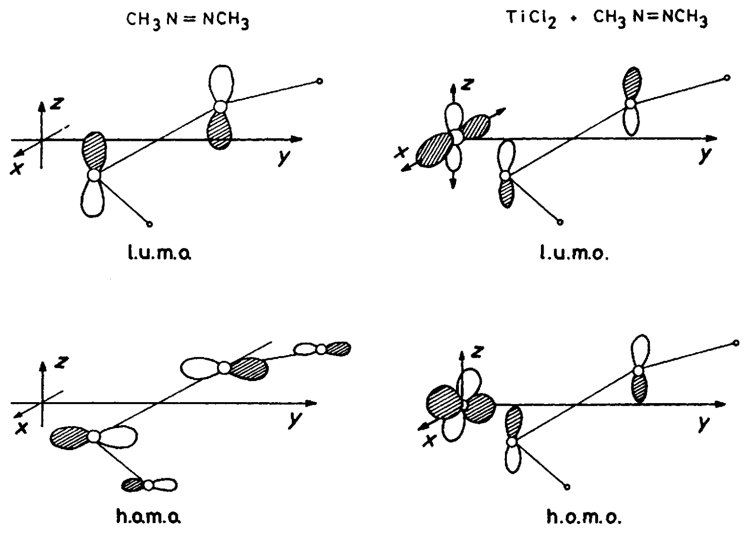


Figure 2. Schematic plot of the atomic orbital contributions to l.u.m.o. and h.o.m.o. of azomethane Me_2N_2 and [$TiCl_2$(MeN=NMe)]. Titanium at origin; dashed lobes indicate the positive phase of the aromatic orbitals

contribution. The ionization potentials, calculated according to Koopman's theorem, amount to −8.0 eV for $TiCl_2$ and −7.6 eV for $Ti(cp)_2$ moieties (rather similar values); on the contrary, the ionization potential calculated for $TiCl_4$ with the same basis set is −11.7 eV.[43] This result, associated with the fact that the calculated 'net atomic charge' of Ti is 20.60, 20.40, and 19.40 e for $TiCl_2$, $Ti(cp)_2$, and $TiCl_4$, respectively, indicates that a similar oxidation state can be invoked for $TiCl_2$ and $Ti(cp)_2$ fragments.

The similarity of the atomic contributions in h.o.m.o. and l.u.m.o. and of the ionization potentials justify the use of $TiCl_2$ instead of $Ti(cp)_2$ in our calculations. The high energy part of the electronic structure of Me_2N_2 (h.o.m.o. and l.u.m.o.), represented in Figure 2, shows orbitals of π^* symmetry; the ionization potential of Me_2N_2 is −10.9 eV (minimal basis set) or −10.3 eV (extended basis set). The h.o.m.o. and l.u.m.o. of the *cis*-[$TiCl_2$(MeN=NMe)] complex are also sketched in Figure 2. Clearly, h.o.m.o. is formed by mixing the 3*d*(Ti) atomic orbital with l.u.m.o. of the free *cis*-azomethane.

In order to gain insight into the occurrence of the distorted *cis* conformation of Ph_2N_2 in [$Ti(cp)_2$(PhN=NPh)], we have subjected the model compound [TCl_2(MeN=NMe)] to calculations of the total energy variations at different geometric conformations of Me_2N_2. Figure 3 shows the obtained total energy values corresponding to rotations of the methyl groups around the N–N bond, up to 30° in opposite directions. The resulting decrease of the total energy in [$TiCl_2$(MeN=NMe)], as opposed to the increase of the energy of the free Me_2N_2, clearly evidentiates the efficiency of the $TiCl_2$ moiety to alter the N–N bond and fits in with the crystallographic data of [$Ti(cp)_2$(PhN=NPh)], where the phenyl groups are rotated with respect to the *cis* conformation.

The choice of Me_2N_2 to describe the interaction between titanium and nitrogen in the complex determined by practical reasons of computing time, can be justified *a posteriori* by examination of the electron population analysis of Me_2N_2. Table 4 reports the electronic net charges and overlap populations of all the studied compounds, according to the Mulliken definitions.[44] It is observed that the methyl groups of Me_2N_2 show only a small change in charge distribution upon formation of the [$TiCl_2$(MeN=NMe)] complex, as opposed to the large variation in the overlap population, which indicates partial loss of bonding character and points to an increase of the titanium oxidation state. In the case of *cis*-Me_2N_2 linked to the $TiCl_2$ moiety (N–N, 1.34 Å), the calculated interaction energy, *i.e.* the difference between the energy of a complex and the sum of the energy of the two component species, is −67 kcal mol^{-1}: high enough to consider the Ti–N linkage a chemical bond. This value should be compared to the interaction energy of the same $TiCl_2$ moiety with C_2H_4 (in planar rather than upright conformation), which is −35 kcal mol^{-1}. The stronger Ti–Me_2N_2 bond, as compared to the Ti–olefin case, is also evidenced by a higher Ti–N than Ti–C overlap population (Table 4).

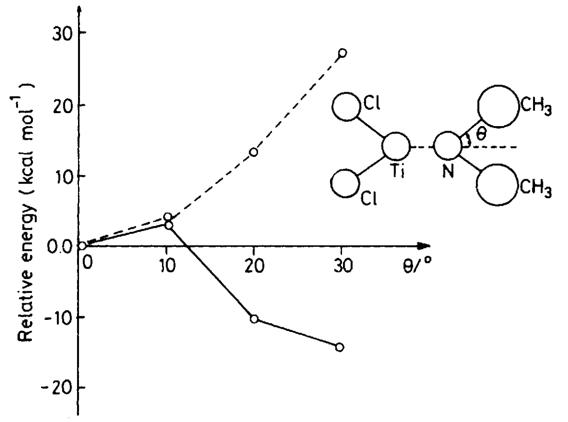


Figure 3. Total energy variation due to rotation of the internal rotation angle in free Me_2N_2 (– – – –) (N–N, 1.24 Å) and in the complex [$TiCl_2$(MeN=NMe)] (——) (*cf.* Table 3 for geometrical parameters); θ represents the half-internal rotation angle of Me_2N_2

As compared to the binding properties of the azo-compound, the N_2 molecule exhibits different behaviour. For this species we have found stable co-ordination to the $TiCl_2$ moiety only in the end-on conformation (N–N, 1.20 Å; Ti–N, 2.0 Å), with an interaction energy of −4.2 kcal mol^{-1}. Preference of the end-on to the edge-on conformation of the $TiCl_2N_2$ model compound is in agreement with the principle of maximum overlap,[45] with the correlation diagram of Hoffmann *et al.*[46,47] and with recent theoretical studies of the bonding nature of

Table 4. Calculated electronic population analysis according to Mulliken

	Net atomic charges						Overlap population						
Compound	N(1)	[N(2)]	C	H	Ti	Cl	N–N	N–C	C–H	Ti–N(1)	Ti–Cl	Ti–C	C–C
$TiCl_2$					20.60	17.60					0.11		
$[Ti(cp)_2]$			5.19 *	0.47 *	20.41				0.86 *			−0.03 *	1.08 *
MeN=NMe ($\theta = 0°$)	6.52		5.04	0.52 *			0.94	0.62	0.76 *				
($\theta = 10°$)	6.52		5.04	0.51 *			0.94	0.62	0.76 *				
($\theta = 20°$)	6.54		5.03	0.51 *			0.91	0.62	0.76 *				
($\theta = 30°$)	6.56		5.02	0.51 *			0.88	0.62	0.76 *				
$[TiCl_2(MeN{=}NMe)]$($\theta = 0°$)	6.88		4.95	0.56 *	19.74	17.57	0.60	0.69	0.77 *	0.12	0.19		
($\theta = 10°$)	7.17		4.98	0.55 *	19.26	17.60	0.49	0.67	0.77 *	0.10	0.19		
($\theta = 20°$)	7.03		4.95	0.55 *	19.38	17.55	0.51	0.69	0.77 *	0.18	0.20		
($\theta = 30°$)	7.05		4.98	0.55 *	19.38	17.57	0.53	0.67	0.77 *	0.17	0.19		
N_2 (N–N = 1.20 Å)	6.34						1.32						
(N–N = 1.34 Å)	6.42						1.16						
$[TiCl_2(\sigma\text{-}N_2)]$ (N–N = 1.20 Å)	6.50	(6.12)			20.56	17.65	1.37			−0.07	0.11		
(N–N = 1.34 Å)	6.54	(6.24)			20.56	17.65	1.22			−0.05	0.11		
$[TiCl_2(\eta^2\text{–}N_2)]$ (N–N = 1.34 Å)	6.48				20.59	17.64	1.09			−0.10	0.14		
C_2H_4			5.01	0.47					0.84				1.23
$[TiCl_2(C_2H_4)]$			5.31	0.50	19.85	17.61			0.84		0.20	0.05	0.98

* Mean value.

transition metal complexes of molecular nitrogen,[48] amongst which is a similar *ab initio* LCAO-MO-SCF calculation for $Ti(cp)_2N_2$ using a more enlarged basis set.[49]

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