Notes

MO Explanation of the Structures of Azo−Transition Metal Complexes

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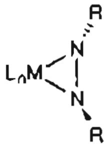
The bonding of dinitrogen and dinitrogen compounds to transition metal complexes is of fundamental interest in chemistry because of its relation to the activation and reduction of the dinitrogen molecule by enzymes.[1] A variety of transition metal complexes containing the dinitrogen molecule, or dinitrogen system, having single- or double bond character between the nitrogen atoms, have been prepared and characterized.[2]

Azo compounds, R−N=N−R (R might be a hydrogen atom or an organic substituent), have the possibility of a rich variety of binding modes to a transition metal.[2] One of these binding modes is an η^2-coordination of the two nitrogen atoms to the metal, **1**.



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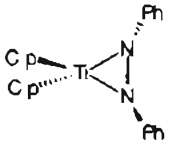
Several transition metal complexes with an η^2-coordinated azobenzene have been prepared, and it has been found that azobenzene binds quite well to both early, as well as, late transition metals.[2-4] An example of an η^2-coordinated azobenzene bound to an early transition metal complex is *e.g.* $Cp_2Ti(PhNNPh)$, **2**,[3a] while $((CH_3)_3CNC)_2Ni(PhNNPh)$, **3**,[3e] is an example of azobenzene bound to a late transition metal.



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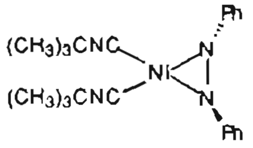

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The structure of the η^2-coordinated azobenzene to transition metals shows a remarkable change when moving from the early- to the late metals as the dihedral angle, φ, defined in **4**, changes from ≈90° for the titanium complex, **2**,[3a] to 153.2° for the nickel complex, **3**.[3e]

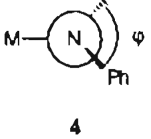

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Table 1. The Change in Dihedral Angle, φ, between the Phenyl Substituents for the η^2-Coordinated Azobenzene−Transition Metal Complexes and *trans*-Azobenzene with N−N Bond Lengths Also Given

entry	complex	dihedral angle/φ	N−N bond length/Å
1	$Cp_2Ti(PhNNPh)$[3a]	≈90°	1.34
2	(2,6-*i*-Pr-Ar-O)$_2$Ti(PhNNPh)[3b]	95.5°	1.42
3	$Cp_2Zr(PhNNPh)(C_5H_5N)$[3c]	91.3°	1.43
4	$Cp(CO)_2Re(PhNNPh)$[3d]	137.0°	1.42
5	$((CH_3)_3CNC)_2Ni(PhNNPh)$[3e]	153.2°	1.39
6	$(Tos_3P)_2Ni(PhNNPh)$[3f]	156.5°	1.37
7	*trans*-azobenzene[5]	180.0°	1.25

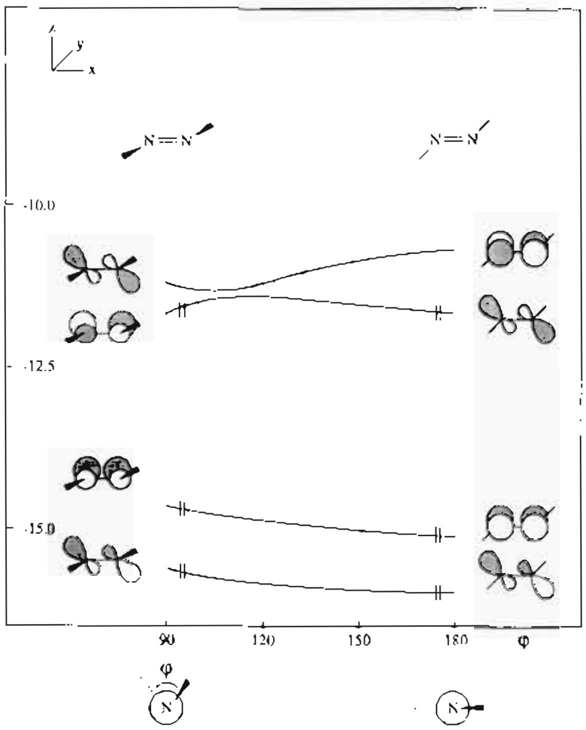

Figure 1. Walsh diagram for change in dihedral angle, φ, in azobenzene.

Table 1 gives the dihedral angle, φ, for the η^2-coordinated azobenzene−transition metal complexes characterized, as well as for *trans*-azobenzene.

It appears from the variation in dihedral angle, φ, for the η^2-coordinated azobenzene-transition metal complexes that a remarkable increase in φ is found when moving from the early to the late transition metals, whereas no significant trends in N−N bond length are observed. It is notable that the N−N bond in **2** is about 0.1 Å shorter than the other N−N bonds in

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(1) See *e.g.*: (a) *Molybdenym Enzymes*, Spiro, T. G., Ed.; John Wiley: New York, 1985. (b) *Biology and Biochemistry of Nitrogen Fixation*, Dilworth, M. J., Glenn, A. R., Eds.; Elsevier: New York, 1991.

(2) For an excellent review about organometallic diazo compounds: Sutton, D. *Chem Rev.* **1993**, *93*, 995 and references therein.

(3) Ti: (a) Fochi, G.; Florine, C; Bart, J. C. J.; Giunchi, J. *J. Chem. Soc., Dalton Trans* **1983**, 1515. (b) Durfee, L. E.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. Zr: (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Organomet. Chem.* **1993**, *428*, 13. Re: (d) Einstein, F. W. B.; Sutton, D.; Tyers, K. G. *Inorg. Chem.* **1987**, *26*, 111. Ni: (e) Dickson, R. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2988. (f) Ittel, S. D.; Ibers, J. A. *J. Organomet. Chem.* **1973**, *57*, 389.

(4) It should also be noted that two samarium complexes also have been charaterized: (a) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Dodens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983. (b) Takats, J.; Zhang, X. W. *Organometallics* **1993**, *12*, 4286.

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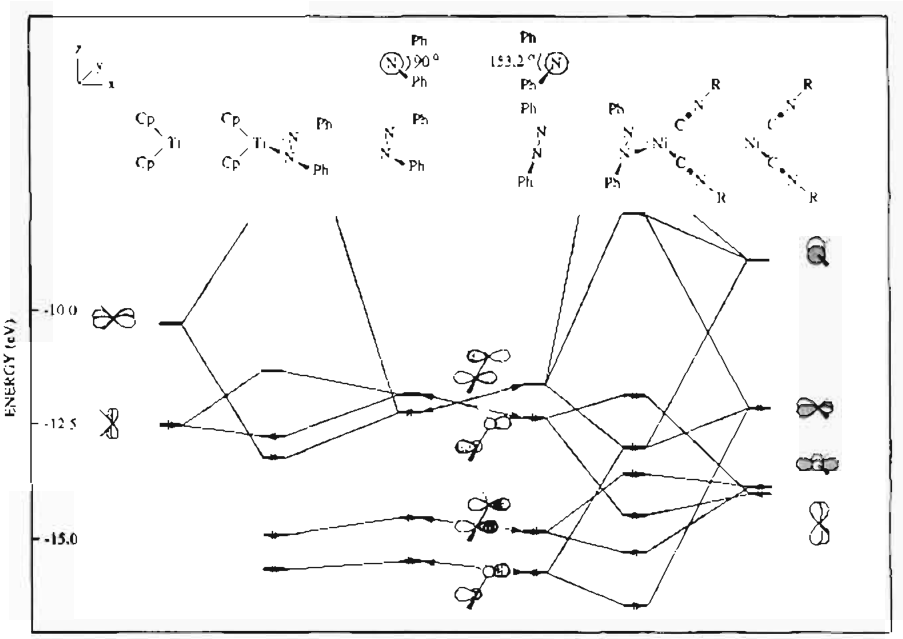

Figure 2. Interaction diagram for $Cp_2Ti(PhNNPh)$, **2**,[3a] and $((CH_3)_3CNC)_2Ni(PhNNPh)$, **3**.[3c] To the left is the interaction for Cp_2Ti with PhNNPh, and to the right is the interaction of PhNNPh with $(CH_3)_3CNC)_2Ni$.

η^2-coordinated azobenzene early transition metal complexes. One might wonder if this variation in φ is due to (*i*) a change in the bonding picture between the metal and the η^2-coordinated azobenzene and/or (*ii*) the bonding capacity of azobenzene changes as φ changes.

This note will try to explain this variation in the structure for transition metal complexes having an η^2-coordinated azobenzene, and for this purpose extended Hückel calculations[6] have been performed. Although the extended Hückel method belongs to the "old-fashioned" calculational types, it can still provide chemists with important insights into the electronic structure of transition metal complexes thus allowing one a better understanding of the geometrical structure of these systems.

As a starting point the variation in frontier orbitals of *trans*-azobenzene as a function of the dihedral angle, φ, between the phenyl substituents will be investigated. Figure 1 shows a Walsh diagram for the change in frontier orbital energy as a function of the dihedral angle, φ.

To the right in Figure 1 is the frontier orbitals of the trans configuration of the azo compound; the LUMO of the system is $\pi^*_{N=N}$, located at −10.72 eV. The HOMO, at −11.65 eV, is a combination of the s, p_x and p_z orbitals at the nitrogen atoms, and antibonding between the nitrogen atoms. The second highest occupied MO is the $\pi_{N=N}$, located at −15.15 eV, and at −15.99 eV the bonding combination of the HOMO is located. Decreasing the dihedral angle, φ, leads to changes in the frontier orbitals of the system as shown when moving from right to left in Figure 1. The HOMO and LUMO of the azo compound crosses at about 110°, leading to a system where the LUMO now is located at −11.21 eV, while the HOMO is at −11.68 eV for a dihedral angle, φ, of 90°. By the decrease of φ from 180° to 90° the two remaining orbitals increases in energy by about 0.5 eV. The composition of the HOMO and LUMO of the azo compound does only change slightly by the variation of φ in the range 180° to 90°. The LUMO and the second HOMO (φ = 180°) mix in some p_x orbital character by decreasing φ to 90°. But, the HOMO and the second HOMO of the azo compound with φ = 90° are still mainly of p_y character at the nitrogen atoms. The change in HOMO and LUMO of the azo compound by decreasing φ from 180° to 90°, will thus change the interaction pattern of the system depending on the dihedral angle: azobenzene with φ of about 90° will primarily act as a π-donor, while azobenzene with φ of about 155° will primarily act as a π acceptor.

The electronic structure of $Cp_2Ti(PhNNPh)$, **2**, and $((CH_3)_3CNC)_2Ni(PhNNPh)$, **3**, has also been investigated. Figure 2 shows an interaction diagram for the interaction of Cp_2Ti with PhNNPh to the left, and to the right is a similar diagram for the interaction of $((CH_3)_3CNC)_2Ni$ with PhNNPh outlined. In the middle are the frontier orbitals of azobenzene with the dihedral angles, φ, for the respective complexes found. The energy of these orbitals are slightly changed relative to those given in Figure 1 because of a longer N−N bond length in **2** and **3**, compared with *trans*-azobenzene. The change in HOMO and LUMO of azobenzene when moving from a dihedral angle, φ, of 90° to 153.2° is indicated with the connection lines in the middle of Figure 2. To simplify the orbital drawing for the azobenzene fragment, the shapes of the orbitals are slightly changed relative to those shown in Figure 1. In order to make this comparison between the early, and the late azobenzene transition metal complexes, the interaction diagrams outlined in Figure 2 have been performed for neutral fragments, although we are aware of that azobenzene in **2** is probably better described as a (2−)-ligand, while in **3** azobenzene is probably more neutral charged. The latter charge consideration is nicely found for the calculated complexes as the azobenzene fragment in **2** has a charge of −2.04, while the charge of the azobenzene fragment in **3** is −0.70. Only the frontier orbitals of the metal fragments involved in the interaction with azobenzene are outlined in Figure 2.

To the far left in Figure 2 are the frontier orbitals of the Cp_2Ti fragment involved in the interaction with azobenzene. The lowest unoccupied MO shown is at −10.17 eV and has d_{xy} character, while the occupied MO shown is of d_{yz} orbital character and is calculated to be −12.51 eV. It should be noted that the latter orbital is distributed over several MOs, and that the one with the largest amplitude is located at −8.9 eV. The LUMO and HOMO of azobenzene are, with a dihedral angle,

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(5) *trans*-Azobenzene structure: Brown, C. J. *Acta Cryst.* **1966**, *21*, 146.

(6) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R and Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; *J. Chem. Phys.* **1962**, *37*, 2872.

φ, of 90° nicely set up for interaction with the HOMO and LUMO, respectively, of the Cp_2Ti fragment shown. These interactions are found to be responsible for the binding of azobenzene to the titanium fragment.

To the far right in Figure 2 are some of the frontier orbitals of $((CH_3)_3CNC)_2Ni$. The p and d orbitals of the nickel fragment is generally located lower in energy, compared with the same orbitals of titanium fragment—a well-known phenomenon when moving from the left to the right in the transition metal series.[7] The LUMO of $((CH_3)_3CNC)_2Ni$ is a degenerated set of a p_y orbital, and the combination of s and p_x orbitals, at −8.84 eV, of which only the p_y orbital is shown. The HOMO, at −12.09 eV is a d_{xy} orbital mixed in with some p_x orbital character. Then follows two nearly degenerated orbitals located at about −14 eV; these orbitals are: $d_{x^2-y^2}$ and d_{yz}. The interactions between $((CH_3)_3CNC)_2Ni$ and azobenzene are more complicated than those leading to **2**. The following interactions of the $((CH_3)_3CNC)_2Ni$ fragment with azobenzene account for the structure of **3**: The LUMO of the azobenzene fragment (corresponding to the HOMO of the azobenzene fragment in **2**) interacts with the nickel $d_{xy}-p_x$ orbital—occupied with two electrons; in this interaction is, also to a minor extent, the p_y orbital at the nickel atom involved. Furthermore, is also the third highest occupied MO of the azobenzene fragment involved. Both the HOMO and the second highest occupied MO of the azobenzene fragment interact in a two orbital—four electron repulsive interaction with the nickel $d_{x^2-y^2}$ and d_{yz} orbitals. The orbital interaction picture for $((CH_3)_3CNC)_2Ni(PhNNPh)$, **3**, could indicate that the azobenzene fragment is more weakly bound to the metal compared with $Cp_2Ti(PhNNPh)$, **2**, as more repulsive interactions between the azobenzene fragment and the nickel fragment are present in the former complex compared with the latter.

The change in dihedral angle, φ, for **2** and **3** has also been investigated; increasing this angle in **2** from 90° to 120° causes an increase in energy by 8 kcal/mol, while a decrease of this angle in **3** from 153.2° to 135° leads to an increase in energy by 12 kcal/mol. Calculation of the lowest energy for **2** and **3** by variation of φ gives energy minima for φ as 94° for **2** and 148° for **3**. These considerations indicate that the structure of **2** and **3** also represents the most stable structures from an electronic point of view.

Table 2. Atomic Parameters

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	c_1[a]	c_2[a]
Ti	4s	−8.97	1.075			
	4p	−5.44	0.675			
	3d	−10.01	4.55	1.40	0.42061	0.78391
Ni	4s	−10.95	2.10			
	4p	−6.27	2.10			
	3d	−14.20	5.75	2.00	0.5683	0.6292
N	2s	−26.00	1.95			
	2p	−13.40	1.95			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
H	1s	−13.60	1.300			

[a] Coefficients used in a double-zeta expansion of the metal d orbitals.

The electronic structure of $Cp(CO)_2Re(PhNNPh)$ has also been investigated and the orbital picture discussed above accounts also for the structure of the azobenzene fragment in this system.

The variation in structure of η^2-coordinated azobenzene—transition metal complexes when changing the metal from an early to a late transition metal is due to the ability of azobenzene to change its electronic properties by variation of the dihedral angle between the phenyl substituents. The orbital interaction picture of the azobenzene fragment is totally reversed when moving from an early transition metal complex, as the titanium complex, **2**, to a late transition metal complex, as the nickel complex, **3**. In the first case azobenzene acts as a π donor, while in the latter case it is a π acceptor; *i.e.* an η^2-coordinated azobenzene ligand has dual binding properties depending on the dihedral angle between the substituents in the azo fragment and on the electronic properties of metal it is bound to.

Acknowledgment. Thanks are expressed to the reviewers to fruitful comments about one of the structures.

Appendix

The extended Hückel[6] calculations have been performed using the structures published for **2**[3a] and **3**.[3e] The parameters are given in Table 2.

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(7) See *e.g.*: (a) Andersen, O. K. In *The Electronic Structure of Complex Systems*, Phasiseau, P.; Temmerman, W. M., Eds.; Plenum Press: New York, 1984. (b) Varma, C. M.; Wilson, A. J. *Phys. Rev.* **1980**, *B22*, 3795.