

THE MECHANISM OF GENERATION OF HYDROGEN FROM WATER WITH THE AID OF TRANSITION METAL DITHIOLENES

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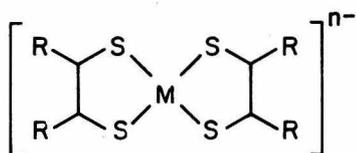
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SUMMARY.—This paper presents a theoretical analysis of the generation of H_2 with the aid of transition metal bisdithiolenes, a reaction reported by Kisch and coworkers, and by Viček and Viček. After a general discussion of the electronic structure of metal bisdithiolenes, a correlation diagram is constructed for the concerted elimination of H_2 from a diprotonated dithiolenic complex. This is found to be a thermally forbidden reaction. An alternative reaction cycle incorporating sequential promotion, radical formation and heterolytic elimination of H_2 is suggested by the calculations.

RESUMEN.—En este artículo se presenta un análisis teórico de la generación de H_2 catalizada por bisditiolenos de metales de transición, una reacción estudiada por Kisch y colaboradores y por Viček y Viček. Después de una descripción general de la estructura electrónica de bisditiolenos metálicos, se construye un diagrama de correlación para la eliminación concertada de H_2 a partir del ditioleno-complejo diprotonado. Tal reacción resulta ser prohibida térmicamente. Los cálculos sugieren un ciclo de reacciones alternativo, incluyendo protonación secuencial, formación radical y eliminación heterolítica de H_2 .

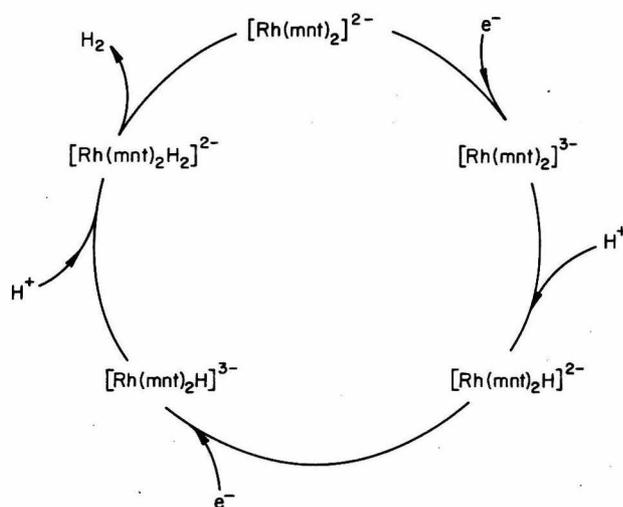
Transition metal bisdithiolenes of type 1 have contributed much to contemporary inorganic chemistry¹. They obviously can act as sources and sinks of electrons, and as such initiate or participate in many reactions. One such reaction is the subject of this paper.



1

Two reports have been made in the last years of generation of hydrogen with the aid of metal dithiolenes: Kisch² photochemically obtained hydrogen from water using $[Ni(Ph_2C_2S_2)_2]^-$ or $[Zn(mnt)_2]^{2-}$ (mnt = maleonitriledithiolate). On the other hand, Viček³ and Viček³ obtained hydrogen by electrochemically reducing $[M(mnt)_2]^{2-}$ (M = Co, Rh) in the presence of a weak organic acid, apparently through the steps represented in Scheme 1.

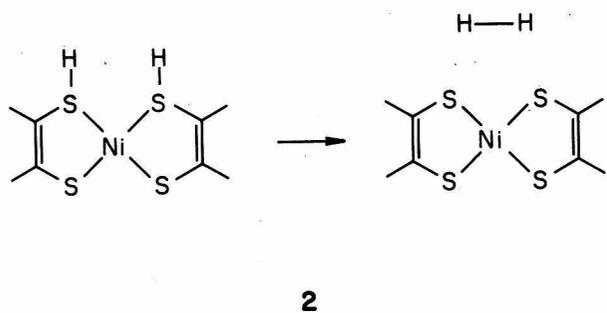
As the sulfur atoms are known to undergo electrophilic attack by alkyl halides,⁴ it is reasonable to assume that



Scheme 1

the protons attack the sulfur atoms in the same way and subsequently form a H-H bond, while the S-H bonds are broken in a concerted fashion. This crucial elimination step is shown in 2.

It should be possible to say something about the orbital symmetry constraints on this reaction. But before we



can do that we must know something about the electronic structure of the dithiolenes. There are a number of MO calculations of these molecules,⁵ yet it is useful to analyze here another simple one, an extended Hückel calculation with parameters specified in the Appendix.

The MO diagram for $\text{Ni}(\text{edt})_2$ (edt = ethylenedithiolato, 1, R = H), shown in Figure 1, presents the usual pattern for square planar transition metal complexes with

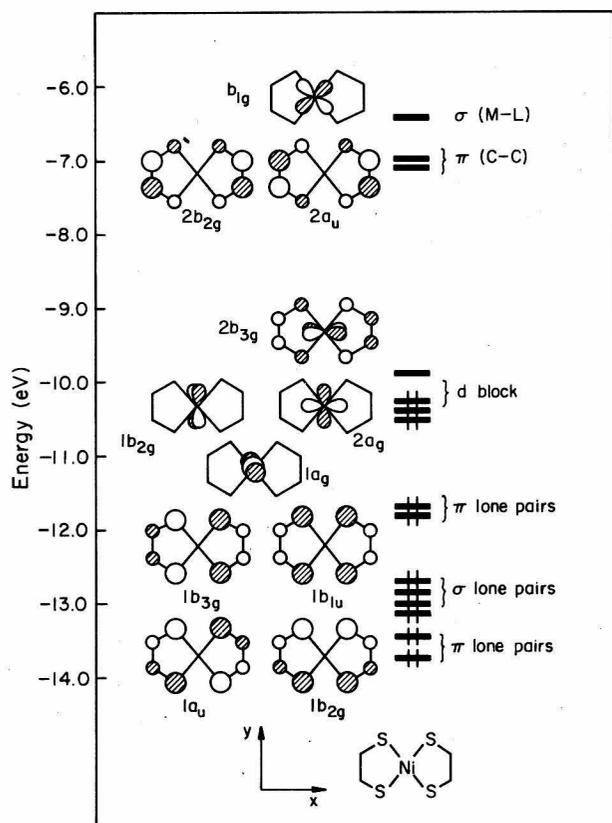


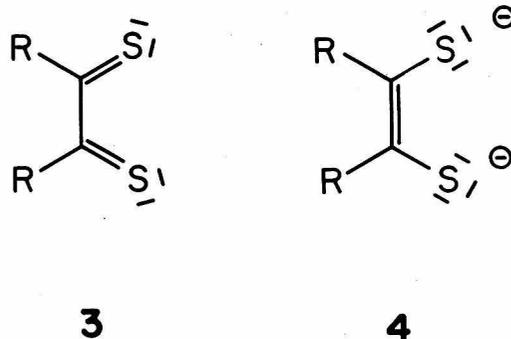
Figure 1

Molecular Orbital Diagram for $[\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2]$.

one (b_{1g}) above four d-orbitals. One of them (d_{x^2}) interacts with the $b_{3g}(\pi)$ orbital of the π -donor ligands, thus opening a gap, a small one, but large enough to account for the diamagnetism and low-energy absorption band of $\text{Ni}(\text{edt})_2$ ^{5a} and related d^6 compounds¹ⁿ, and in agreement with the ${}^2B_{3g}$ ground state found in the ESR of d^7 compounds $\text{M}(\text{mnt})_2$ (1, R = CN; M = Ni, Pd, Pt).^{6,7} Below the d block is a group of four orbitals of π symmetry interspersed with a block of four lone pairs primarily localized on S. Two further π orbitals are at still lower energy, and are not shown in Figure 1.

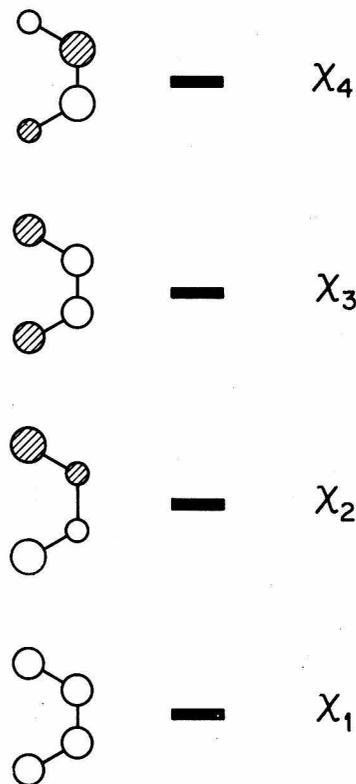
We specified a d electron count above, d^7 in $\text{Ni}(\text{mnt})_2$. This is a dangerous step in any discussion of transition metal dithiolenes, and we had better face up immediately to the ambiguities of electron counting and oxidation state in this field.

Dithiolenes are non-innocent ligands. They could be viewed as neutral 3 or dianionic 4. The two extremes differ in the number of π electrons: the neutral form has 4



π electrons and the dianionic 6. Either extreme has four sulfur σ lone pairs. If one adopts the neutral formalism $\text{Ni}(\text{mnt})_2^-$ would be $\text{Ni}(-I)$, " d^{11} ", while with the dithiolene dianionic we would reach $\text{Ni}(\text{III})$, d^7 .

Let us look into the metal-bis(dithiolene) electronic structure in detail to see what it tells us. Making no judgment as to electron count, the dithiolene unit bears 4 π orbitals, butadienoid in character. These are shown in 5. For two dithiolene units these are doubled, as symmetric and antisymmetric combinations, $\chi_{nA} \pm \chi_{nB}$, where A is one dithiolene, and B the other one.



We can find these in Figure 1. The lowest combinations are not in the figure. But the next π orbitals $1a_u + 1b_{2g}$ are $\chi_{2A} - \chi_{2B}$ and $\chi_{2A} + \chi_{2B}$ respectively. And above them are $1b_{3g}$ and $1b_{1u}$, $\chi_{3A} - \chi_{3B}$ and $\chi_{3A} + \chi_{3B}$, respectively. $\chi_{4A} \pm \chi_{4B}$ are unfilled, near the top of the Figure. Clearly the electronic structure of the metal-bis(dithiolene) is telling us that there are three mainly dithiolene-based π orbitals filled per dithiolene. This is consistent with a dianionic dithiolene resonance structure, 4.

Another approach to specifying the electron count is to actually extract from a fragment MO analysis the population of the fragment dithiolene π orbitals in the complex. The numbers we obtain are χ_1 1.98, χ_2 2.00, χ_3 1.72, χ_4 0.02.

While these observations favor the dianionic dithiolene formulation, we should keep in mind the essential ambiguity of any oxidation state formalism. Furthermore, there may be substantial variation in the role of the various resonance forms, as the metal and total molecular charge vary.

We discuss elsewhere⁵ the substantial experimental evidence for this level scheme. The only ambiguity, important for d^9 compounds, is the relative ordering of the b_{1g} (σ^* M-L) and $2b_{2g}$, $2a_u$ (π^* C-C) orbitals. Let us proceed to use this level scheme for the analysis of the hydrogen elimination.

The correlation diagram for the concerted process 2 is shown in Figure 2 where the orbital filling represented corresponds to a d^8 compound Ni^{II} to Ni^{IV} , losing two electrons from its d_{xz} (antisymmetric) orbital to the H_2 σ (symmetric) orbital.

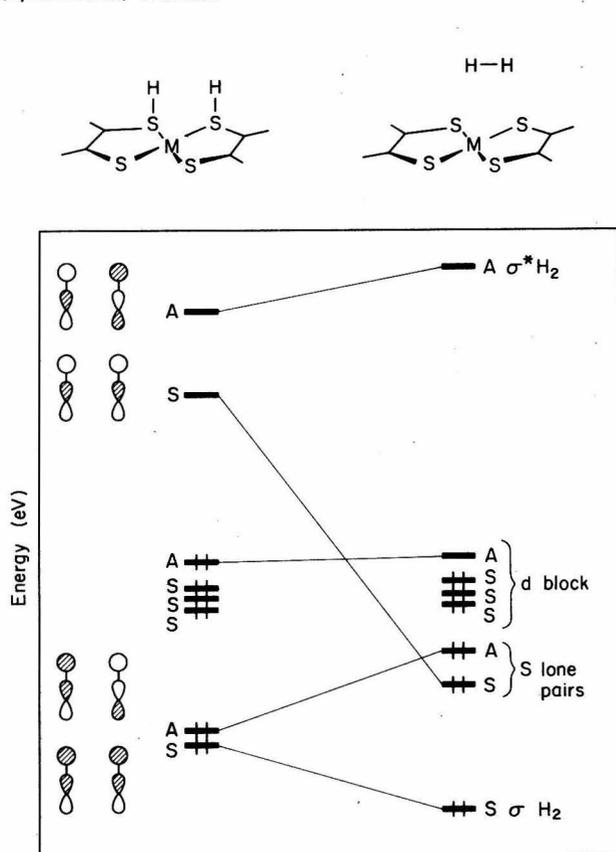


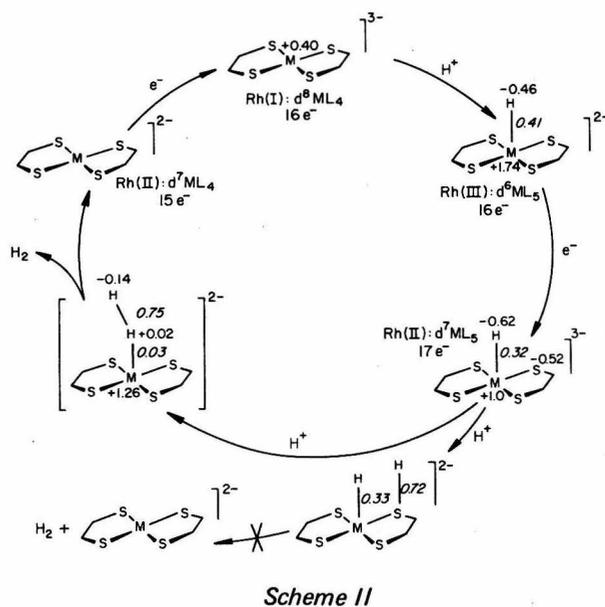
Figure 2

Correlation diagram for the evolution of hydrogen from the adduct $[Ni(HS_2C_2H_2)_2]$.

The concerted process is thus symmetry forbidden for d^8 compounds but is feasible for an excited state, as found for $Ni(II)$.² The fact that the rate of hydrogen evolution is not sensitive to changes in the oxidation state of the metal (for 8 or less d electrons^{2d}) would arise from the fact that the d orbitals are not crucial in this reaction (Figure 2). Although it has been demonstrated that for the zinc bisdithiolene dianion in THF/ H_2O the reaction involves a dehydrodimerization of the THF and decomposition of the complex,^{2d} we feel that the proposed mechanism is a reasonable one for metals with lower electron counts and further studies on them are worthwhile, especially if solvent interference could be avoided.

For the rhodium case (Scheme I), it is experimentally found that the hydrogen production takes place after two successive one-electron reductions of the $Rh(II)$ compound, leading to a 17 electron species. If the additional electron is placed in Figure 2, the concerted process is expected to be thermodynamically favoured. We cannot, however, rule out other mechanisms, such as those based on an initial attack to the metal atom as proposed by Vlček and Vlček.³

Following the sequence in Scheme I after the first reduction the proton could attach itself to the top of the metal atom, the d_{z^2} orbital donating two electrons to the hydrogen atom which formally becomes a hydrido ligand while the rhodium is formally oxidized back to $Rh(III)$. This information is summarized in Scheme II, an electron accounting version of Scheme I, where some overlap populations and atomic charges from model calculations on



Scheme II

the isoelectronic nickel compounds are shown to illustrate the discussion. Now the addition of one electron takes the rhodium to $Rh(II)$, a 17 electron compound, which can undergo electrophilic attack by another proton either at the hydrido ligand or at a sulfur atom or even at the metal atom. Let us first assume that it goes to the apical hydride. This is a likely event, due to the fact that the hydride occupied orbital covers a wide conical angle (Figure 3). Then the incoming proton interacts with the bonding and antibonding combinations of the d_{z^2} and $1s(H)$ orbitals as in 6. The d_{z^2} orbital becomes a non-bonding one, the metal-hydrogen bond is largely weakened, a hydrogen-hy-

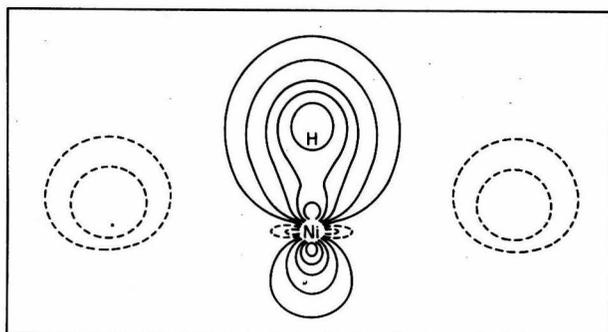


Figure 3

Electron density contours of the hydrido orbital in $[\text{NiH}(\text{S}_2\text{C}_2\text{H}_2)_2]^-$.

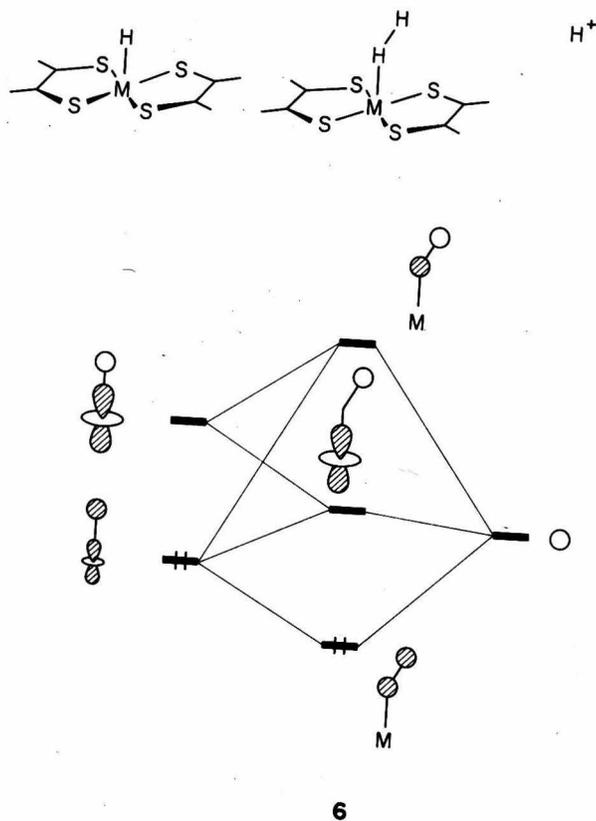
drogen bond is formed, and the H_2 molecule can easily dissociate.

We can look at this step in other ways: as soon as the second proton approaches the hydrido ligand, a hydrogen molecule is formed, $\text{H}^- + \text{H}^+ \rightarrow \text{H}_2$, and the coordinated H_2 molecule is known to be extremely labile in the only H_2 complex isolated so far.⁹ The Rh(II) complex is then regenerated after this Lewis base dissociation step.

If the second proton were to go to a sulfur atom, no weakening of the M-H bond would be produced since both hydrogens interact with different MO's. We think formation of the H-H bond would require substantial activation—one would need to go a long way toward cleaving strong M-H and S-H bonds to allow both hydrogens to approach each other.

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APPENDIX

In our calculations the edt ligand was chosen to have the following geometry: all angles 120° ; C-C = 1.34, C-S = 1.70 Å. The ligand-metal distance Ni-S was 2.22 Å.

Extended Hückel calculations¹⁰ with weighted H_{ij} 's¹¹ were carried out on the model molecules. The parameters used for those calculations⁸ are shown in the Table.

TABLE I
Extended Hückel Parameters

Atom	Orbital	H_{ij} (eV)	$\zeta_i(c_i)$
H	1s	-13.60	1.30
C	2s	-21.40	1.625
	2p	-11.40	1.625
S	3s	-20.00	1.82
	3p	-13.30	1.82
Ni	3d	-10.58	5.75 (0.5681)
	4s	-7.34	2.10
	4p	-3.74	2.10

Note added in proof. Recently, D. Katakis and coworkers have reported the generation of hydrogen from water and the methylviologen radical ion using a monoanionic nickel bisdithiolene com-

plex as catalyst¹². A related process in which a proton is attached to a transition metal atom and subsequently produces H_2 has been observed in ferrocenophanes¹³.

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