Table I. Catalytic Activity of $Fe(NO)_2(thf)_n$ Prepared Electrochemically or Chemically (T (°C), 22; reaction time, 3 h)

	reduction at −1.1 V		reduction by Zn	
diene	conversion^{a,b}	selectivity (%)	conversion^{b,c}	selectivity (%)
nbd	300	exo-trans-exo-dimer (93)^d	310	exo-trans-exo dimer (93)^d
is	750	1,4- (2,4-) dimethyl-4-vinylcyclohexene (94)^e	1000	1,4- (2,4-) dimethyl-4-vinylcyclohexene (94)^e
bd	270	4-vinylcyclohexene (100)	9500^f	4-vinylcyclohexene (100)

[a] Moles of diene dimerized per faraday. [b] Conversion and selectivity determined by GPC on a Chromosorb PAW-10% SE-30 column with internal standards. The products have been identified by ^{1}H and ^{13}C NMR and mass spectrometry. [c] Moles of diene dimerized per mole of catalytic precursor; this system was not optimized. [d] Exo-trans-endo dimer, 7%. [e] 1-Methyl-5- (4-) isopropenylcyclohexene, 6%. [f] Run performed under autogenous butadiene pressure.

the formation of $Fe(NO)_2(thf)_n$. It is noteworthy that the number of moles of $Fe(NO)_2(thf)_n$ appearing after the reduction at ca. −0.7 V is half of that arising at ca. −1.1 V. Moreover the characterization of each of the reduction steps has revealed that electrochemistry is a powerful technique to generate *selectively* unsaturated iron nitrosyl complexes[12] which can be valuable candidates for catalysts. To this respect, our work was first focused on the catalytic behavior of $Fe(NO)_2(thf)_n$.

Catalytic experiments were performed with 20 mL of thf solution of **1** (10^{-2} M) containing $Bu_4N^+PF_6^-$ (0.1 M) as the supporting electrolyte and an excess of dienes (diene/Fe = 500-2000). Electrolysis was achieved either at the level of the B or C wave. After reduction at ca. −0.7 V the conversion is half of that obtained after reduction at ca. −1.1 V, thus confirming the reduction mechanism. Parallelly, chemical reduction of **1** by highly divided Zn powder was performed in the presence of dienes[21] and the catalytic activity checked. The results of typical catalytic runs are reported in Table I.

Table I shows clearly the good agreement between the two types of reduction. Norbornadiene and isoprene conversions are quite similar, whereas the discrepancy observed with butadiene is probably due to the electrochemical cell design.[22] The only products detected are the cyclodimers for every catalytic run, and, whatever the nature of the reactant, one cyclodimer is formed predominantly. The selectivity observed is specific to the iron nitrosyl complexes as stated earlier,[4-9] but in this work the activity is increased[23] 10-100-fold. Moreover, this work reports for the first time the identification and characterization, under the conditions of catalysis of the nitrosyl complex responsible for the cyclodimerization of dienes, i.e., $Fe(NO)_2(thf)_n$, a d^{10} electronic configuration according to ref 2c.

In conclusion, the electrochemical approach described in this paper outlines on one hand the catalytic properties of $Fe(NO_2(thf)_n$ in the cyclodimerization of dienes and on the other hand the possibility of preparing new unsaturated dinitrosyl transition metal complexes. Further work on this second aspect will be published in the near future.

Acknowledgment. The authors thank Dr. I. Tkatchenko for encouragement. This work was supported by the Centre National de la Recherche Scientifique (ATP Utilisation Physiques et Chimique de l'Electricité, Grant No. 3090).

References and Notes

(1) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98,** 2134 (1976).

(2) (a) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Am. Chem. Soc.*, **91,** 5659 (1969); (b) J. P. Collman, P. Farnham, and G. Dolcetti, *ibid.*, **93,** 1788 (1971); (c) R. D. Feltham and J. Enermark, *Coord. Chem. Rev.*, **13,** 339 (1974).

(3) For example, R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974; P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. II, Academic Press, New York, 1975.

(4) J. P. Candlin and W. H. Janes, *J. Chem. Soc. C*, 1856 (1968).

(5) P. L. Maxfield, U.S. Patent 3 377 397 (Oct 22, 1965).

(6) P. L. Maxfield, French Patent 1 535 936 (Sept 2, 1966).

(7) I. Tkatchenko, *J. Organomet. Chem.*, **124,** C39 (1977).

(8) I. Tkatchenko, *J. Mol. Catal.*, **4,** 163 (1978).

(9) D. Ballivet, C. Billard, and I. Tkatchenko, *Inorg. Chim. Acta*, **25,** L58 (1977).

(10) (a) D. M. P. Mingos, *Inorg. Chem.*, **12,** 1209 (1973); (b) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8,** 26 (1975); (c) R. H. Summerwille and R. Hoffman, *J. Am. Chem. Soc.*, **98,** 7240 (1976).

(11) *Chemtech*, 351 (1977).

(12) The other ligands associated with the metal being organic groups (solvent molecules) readily displaced by substrate.

(13) (a) R. E. Dessy, R. Kornmann, C. Smith, and R. Haytor, *J. Am. CHEM/ Soc.*, **90,** 2001 (1968); (b) G. Piazza and G. Paliani, *Z. Phys. Chem. Neue Folge*, **71,** 91 (1970); (c) G. Paliani, S. M. Murgia, and G. Cardaci, *J. Organomet. Chem.*, **30,** 221 (1971); (d) R. E. Dessy, J. C. Charkoudian, and A. N. Rheingold, *J. Am. Chem. Soc.*, **94,** 738 (1972); (e) W. L. Bowden, P. Bonnar, D. B. Brown, and W. E. Geiger, Jr., *Inorg. Chem.*, **16,** 41 (1977).

(14) H. Lehmkuhl, *Synthesis*, **7**, 377 (1973).

(15) D. Ballivet-Tkatchenko, C. Billard, and I. Tkatchenko, unpublished results.

(16) All $E_{1/2}$ are given relative to the aqueous saturated calomel electrode.

(17) The morphology of the wave B depends on **1** concentration, the total height being equal to 1. For a 10^{-2} M concentration the wave is split into two waves at −0.22 and −0.52 V, for a 0.5×10^{-2} M concentration the wave is ill-defined at −0.29 V, and for a 0.5×10^{-3} M concentration the wave is well defined at −0.22 V. These results corroborate the ESR ones.

(18) Height comparison, in the same conditions, between the A wave and that of the system

$$Cp_2Co^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Cp_2Co$$

shows that the A wave corresponds to a one-electron transfer. This implies the formation, on the time scale of electrolysis, of an unstable complex which evolves chemically to give a monoelectronic oxidizable species which decomposes according to

$$2Fe(NO)_2ClS_n + 2Hg \xrightarrow{-2e^-} 2Fe(NO)_2S_n{}^+ + Hg_2Cl_2$$

$$Fe(NO)_2S_n{}^+ \xrightarrow[2.\ -e^-]{1.\ \text{chemical evolution}} Fe^{2+} + 2NO$$

(19) $[Fe(NO)_2Cl_2]^-PPN^+$: ν_{NO} 1775, 1700 cm^{-1}; ESR signal with $g = 2.0339$, line width = 15 G, in agreement with data of J. Schmidt, *Transition Met. Trans. Chem.*, **1,** 252 (1976), and N. G. Connelly and C. Gardner, *J. Chem. Soc., Dalton Trans.*, 1525 (1976).

(20) The reduction wave of PPN$^+$ hinders the waves D and E of Figure 1.

(21) The polarogram of this solution exhibits only the E reduction wave.

(22) An electrochemical cell under pressure will be built in the near future to carry out catalytic experiments with gaseous substrates: R. Ercoli, M. Guainazzi, and G. Silvestri, *Chem. Commun.*, 927 (1967).

(23) Different experimental conditions do not allow direct comparison. In most cases experiments were performed under pressure at high temperature (80 °C).

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Received November 29, 1978

Metal Binding to Four Different Sites in Adenine Ligands. Crystal Structures of 2:1 Methylmercury Complexes with Adenine and 9-Methyladenine

Sir:

Many complexes with purine and pyrimidine bases, nucleosides, and nucleotides have been investigated as model compounds for metal-nucleic acid interactions. It is generally admitted that metal ions usually bind to N-7 in N-9-substituted adenine ligands.[1] Sometimes, N-1 protonation or metalation occurs as well.[1,2] Metal coordination to N-1 exclusively has

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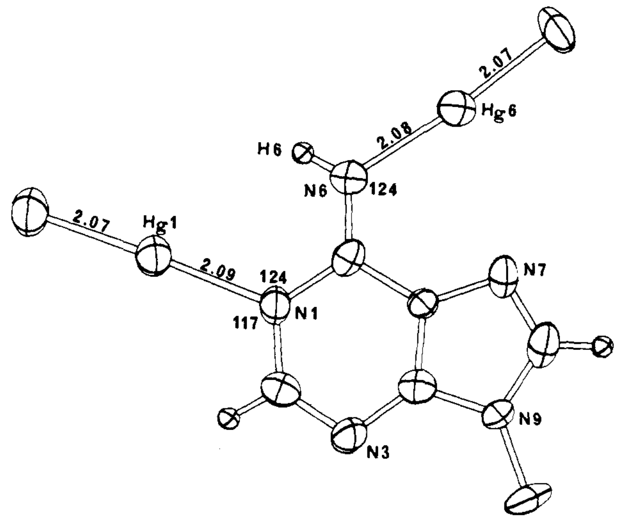

Figure 1. Structure of the $[(CH_3Hg)_2(9\text{-methyladenine})]^+$ ion in the perchlorate salt. Standard deviations are 0.01 Å and 1°.

been reported for only one crystal structure,[3] but there is evidence that CH_3Hg^+ ions bind to N-1 in aqueous solutions of adenosine.[4,5] Reactions with the amino group have been proposed in early reports, but this is now known to be quite uncommon. Some years ago, Ag^+ and Hg^{2+} were reported to displace an amino proton from adenosine.[6] However, it was not clear whether metal coordination elsewhere on the ring enhanced the acidity of the amino group or the metal actually coordinated to a deprotonated amino group. The latter type of interaction, originally proposed by Simpson,[4] was preferred by Tobias and co-workers[7] on the basis of Raman difference spectroscopy. Clarke[8] recently provided evidence for metal binding to the amino group in ruthenium complexes. One of the structures reported in this paper appears to be the first crystallographic evidence for metal-adenine interactions involving the amino group.

A 2:1 complex of formula $[(CH_3Hg)_2C_6H_6N_5]ClO_4$ was obtained from an aqueous mixture of 9-methyladenine, CH_3HgClO_4 (1 M solution), and NaOH (1 M solution) in a 1:2:1 ratio. A similar 2:1 compound of adenine, $[(CH_3Hg)_2C_5H_4N_5]NO_3\cdot 2H_2O$, was obtained by reacting adenine and CH_3HgNO_3 (1 M solution) in a 1:1 ratio. One half of adenine reacts with methylmercury, while the rest acts as an acceptor for the proton displaced in the reaction.

Both compounds are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units per cell. The cell parameters are as follows: $a = 10.903$ (5), $b = 12.68$ (1), $c = 11.479$ (7) Å and $\beta = 115.32$ (6)° (9-methyladenine compound); $a = 9.365$ (2), $b = 20.774$ (5), $c = 7.661$ (2) Å and $\beta = 94.79$ (2)° (adenine compound). Intensity data were collected with a Nonius CAD-4 diffractometer using graphite monochromatized Mo $K\bar{\alpha}$ radiation and the $\omega/2\theta$ scan technique. The data were corrected for absorption. The structures were solved by the heavy-atom method, and anisotropic refinement was carried out for all nonhydrogen atoms. The final R factors are 0.036 (1494 independent observed reflections) for the 9-methyladenine compound and 0.048 (1687 reflections) for the adenine complex.

CH_3Hg^+ ions are bound to N-1 and to the deprotonated amino group of 9-methyladenine (Figure 1). The Hg-6-N-7 contact (2.85 Å) is probably too long to indicate any appreciable bonding. Since the amino lone pair is involved in the ring π system, preventing free rotation about C-6-N-6, the amino-bonded CH_3Hg group must lie in the molecular plane. A scale drawing using the normal geometry of adenine[9] shows that substitution of H-6 by mercury would have introduced severe steric hindrance with Hg-1. Instead, with van der Waals radii of 1.20 Å for H and 1.50 Å for Hg,[10] Hg-1 and H-6 are found to be just tangent in the present arrangement. Equal Hg-1-N-1-C-2 and Hg-1-N-1-C-6 angles are also consistent with the lack of significant steric hindrance between H-6 and Hg-1. Nevertheless, on a purely steric ground, a slightly more favorable structure would result if one of the CH_3Hg groups occupied N-7 instead of N-1, whereas H-6 and Hg-6 were interchanged.

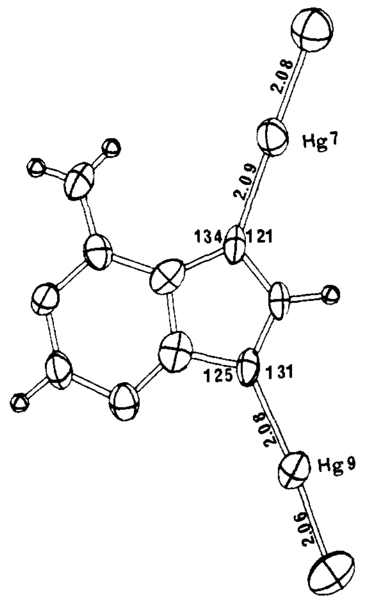

Figure 2. Structure of the $[(CH_3Hg)_2(\text{adenine})]^+$ ion in the nitrate salt. Standard deviations are 0.01 Å and 1°.

With adenine (Figure 2), coordination to N-9 after proton displacement is not surprising. Since this site is blocked in nucleic acids, the complex is of little value as model compound, but it is interesting to note that the second CH_3Hg group binds to N-7 even though N-1 is free. Angles Hg-7-N-7-C-8 and Hg-7-N-7-C-5 differ by 13° (Figure 2); a smaller, but significant, difference is also observed for the angles at N-9. As mentioned above, those differences cannot be ascribed to intramolecular steric hindrance. They are probably due to crystal packing and they do not affect the Hg-N distances, which are equal to those observed in the 9-methyladenine complex.

Methylmercury is a unique Lewis acid: only one site is available for bonding and the linear coordination of Hg removes attractions and repulsions found for other geometries between coordinated ligands. Rejecting the unlikely assumption of a determining influence of crystal packing forces, we have to suppose that the structures observed here depend mainly on which bonds are broken and formed. In both compounds, the most acidic proton has been displaced, that is H-9 for adenine and an amino hydrogen for 9-methyladenine. Replacement of that hydrogen by a more electropositive mercury atom should result in electron density flowing into the ring, enhancing the basicities of other donors. Such inductive effects are presumably short ranged and should not appreciably cross over the C-4-C-5 barrier, so that the relative basicities of N-1 and N-7, which are believed not to differ greatly,[11] may be altered. Hence, hydrogen substitution on one ring would tend to promote further coordination with a free nitrogen atom of the same ring.

References and Notes

(1) D. J. Hodgson, *Progr. Inorg. Chem.*, **23**, 211 (1977); L. G. Marzilli, *ibid.*, **23**, 255 (1977).

(2) C. Gagnon and A. L. Beauchamp, *Acta Crystallogr., Sect. B*, **33**, 1448 (1977); C. J. L. Lock, R. A. Speranzini, G. Turner, and J. Powell, *J. Am. Chem. Soc.*, **98**, 7865 (1976).

(3) M. J. McCall and M. R. Taylor, *Biochim. Biophys. Acta*, **390**, 137 (1975).

(4) R. B. Simpson, *J. Am. Chem. Soc.*, **86**, 2059 (1964).
(5) S. Mansy and R. S. Tobias, *J. Am. Chem. Soc.*, **96**, 6874 (1974); P. W. Schneider, M. Brintzinger, and C. H. Erlenmeyer, *Helv. Chim. Acta*, **47**, 992 (1964).
(6) G. L. Eichhorn, J. J. Butzow, P. Clark, and E. Tarien, *Biopolymers*, **5**, 283 (1967); G. L. Eichhorn and P. Clark, *J. Am. Chem. Soc.*, **85**, 4020 (1963).
(7) S. Mansy, J. P. Frick, and R. S. Tobias, *Biochim. Biophys. Acta*, **378**, 319 (1975).
(8) M. J. Clarke, *J. Am. Chem. Soc.*, **100**, 5068 (1978).
(9) D. Voet and A. Rich, *Prog. Nucleic Acid Res. Mol. Biol.*, **10**, 183 (1970).
(10) D. Grdenic, *Q. Rev., Chem. Soc.*, **19**, 303 (1965).
(11) L. G. Marzilli and T. J. Kistenmacher, *Acc. Chem. Res.*, **10**, 146 (1977).

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Solution pH-Induced Reversal of Stereoselectivity. Deuteration of Malonate Methylenes in Some Bis(malonato)cobalt(III) Complexes[1]

Sir:

The malonate hydrogens of some cobalt(III) compounds are known to exchange with deuterium in D_2O.[2] We have found that the deuteration of some bis(malonato)cobalt(III) complexes takes place stereoselectively in D_2O. The novel feature of this process is the reversal of the stereoselectivity accompanying the pH change.

Figure 1a shows the malonate portion of the ^{1}H NMR spectrum[3] of $\mathrm{K[Co(mal)_2(en)]}$[4] in acidified D_2O (pD 3.23) taken at suitable time intervals after dissolution. Initially, one set of an AB quartet is observed, which is expected because, of the two malonate proton, one proton (H_N) is adjacent to the NH_2 group in any conformation of the malonate-cobalt ring while the other (H_O) is adjacent to the malonate oxygen.[2] The low-field resonance pair could be assigned[5] to H_N and the high-field one to H_O. As time passes, the singlet begins to appear and grows in intensity. This singlet originates from the species CDH_O produced by deuteration of only H_N, because the chemical shift of this singlet is that of H_O.[6] The broad nature of the H_O singlet is due to marginally resolved, small spin-spin coupling (~2.0 Hz) to deuterium ($I = 1$) in CDH_O. The intensity of the singlet eventually diminishes owing to the deuteration of the remaining hydrogen H_O. Therefore, the whole spectral change with time can be understood in terms of the process

$$CH_NH_O \rightarrow CDH_O \rightarrow CDD$$

The above scheme implies that the deuteration takes place stereoselectively; the rate of deuteration of H_N is much faster than that of H_O.

Figure 1b illustrates the time variation of the NMR spectrum of the same compound in basic D_2O solution (pD 8.09), which contrasts with Figure 1a in that two singlets can be observed in addition to the AB quartet. Since the two singlets correspond to CH_ND (low-field singlet) and CDH_O (high-field singlet), and since the low-field H_N singlet is larger in intensity than the H_O singlet, the deuteration of H_O is, under this condition, faster than that of H_N; the apparent stereoselectivity is now greater for H_O. Similar reversal of stereoselectivity could be found in the deuteration of *cis*-$\mathrm{K[Co(mal)_2(NH_3)_2]}$.

Natural logarithms of NMR intensities of the AB quartet and of the H_N or H_O singlet were plotted against time and from these plots pseudo-first-order rate constants k_{AB} and k_{HN} or k_{HO} were obtained on the assumption that $k_{AB} = k_{HN} + k_{HO}$.[7] Figure 2 indicates that the deuteration process is acid catalyzed at pD <4.5, while it is base catalyzed at pD 4.5~7.0. Up to pD ~7.0, the H_N exchanges faster with deuterium. At around pD ~7.0, the k_{HN} value begins to decrease with pD but the k_{HO} value does not, and eventually the high field H_O hydrogen becomes fast exchanging at pD ~7.5, which corresponds to the crossover point in Figure 2. At higher pD values, it is H_O and

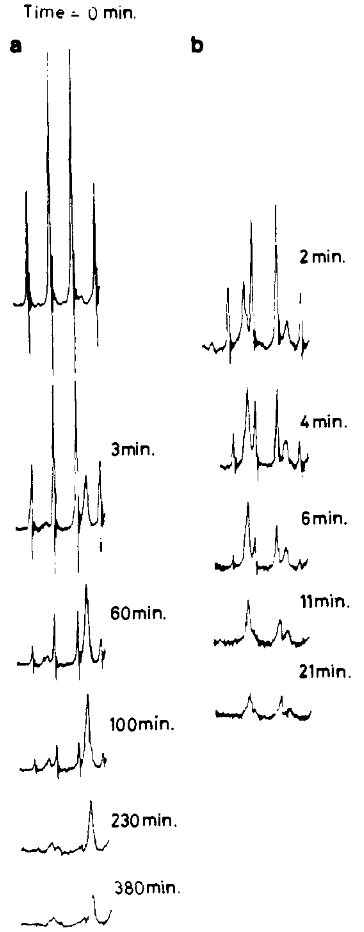

Figure 1. The malonate portion of the ^{1}H NMR spectra of $\mathrm{K[Co(mal)_2(en)]}$ in (a) (left) acidified D_2O (pD 3.23, HCl) and (b) (right) basic D_2O (pD 8.09, Na_2CO_3), taken at suitable time intervals after dissolution.

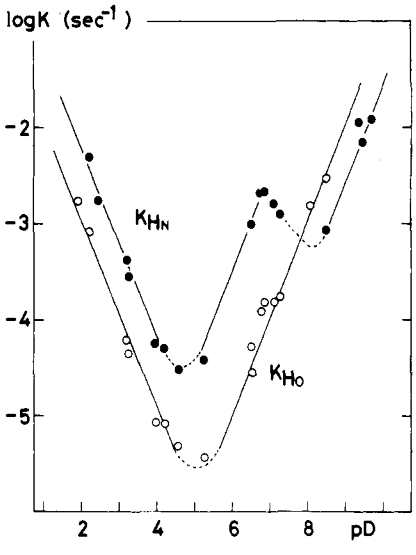

Figure 2. The log (k_{HN}) and log (k_{HO}) vs. pD plots for the deuteration of malonate hydrogens in $\mathrm{K[Co(mal)_2(en)]}$ in D_2O. Solid line was drawn by assuming a slope of +1 or −1.

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