(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).

Leonardo Prizant, Marc J. Olivier
Roland Rivest, André L. Beauchamp*
Département de Chimie, Université de Montréal
C.P. 6210, Succ. A, Montreal, Quebec, Canada H3C 3V1

Received November 29, 1978

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 ^1H NMR spectrum[3] of $K[Co(mal)_2(en)]$[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*-$K[Co(mal)_2(NH_3)_2]$.

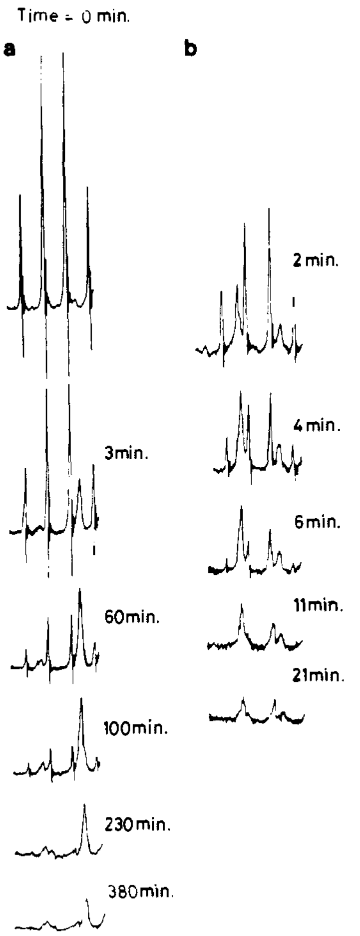


Figure 1. The malonate portion of the ^1H NMR spectra of $K[Co(mal)_2(en)]$ in (a) (left) acidified D_2O (pD 3.23, HCl) and (b) (right) basic D_2O (pD 8.09, Na_2CO_3), taken at suitable time intervals after dissolution.

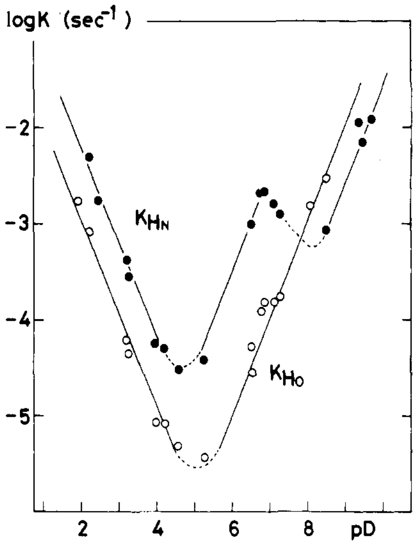


Figure 2. The log (k_{HN}) and log (k_{HO}) vs. pD plots for the deuteration of malonate hydrogens in $K[Co(mal)_2(en)]$ in D_2O. Solid line was drawn by assuming a slope of +1 or −1.

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

0002-7863/79/1501-2767$01.00/0

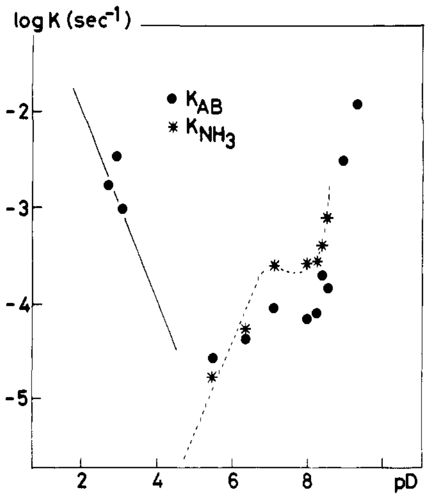


Figure 3. The log (k_{AB}) and log (k_{NH_3}) (deuteration rate of amine group) vs. pD plots for *cis*-K[Co(mal)$_2$(NH$_3$)$_2$].

not H_N that exchanges first with deuterium. Over the whole pD range examined, no change in chemical shift[5] and spin-spin coupling constant[8] was observed.

The origin of the stereoselectivity is not readily apparent.[9] The origin of the reversal of stereoselectivity appears, however, to be explained as follows. It is seen in Figure 2 that the reversal is brought about by an anomalous decrease in k_{HN} and the steady increase in k_{HO} with pD. Next, we note in Figure 3 that, at a pD value of ~7.5, wherein the reversal happens for *cis*-(NH$_3$)$_2$ compound, the deuteration rate of NH$_3$ (k_{NH_3}) exceeds that of CH$_2$ (k_{AB}), but both rates begin to be suppressed. Now, at lower pD values the exchange of amine hydrogens is slower than that of CH$_2$ hydrogens and can not compete with the latter process. If, however, k_{NH_3} increases to a comparable magnitude with k_{AB},[10] amine exchange can interfere with the CH$_2$ change and both amine and CH$_2$ hydrogens scramble for the OD$^-$ catalysis. As a result, both rates will tend to fall together. Even under such circumstances, the deuteration rate of H_O may well be little affected by such competition, because of this proton being situated farthest apart from the amine group. Only the H_N hydrogen, being adjacent to the amine group, pertains to the scrambling for the catalysis, which is consistent with the anomalous decrease of only k_{HN} in Figure 2. Some support to this view seems to be provided by the observation that the reversal did not take place for *N,N'*-dmen, tn, *cis*-py$_2$, and phen compounds. In the first two complexes, exchange rates of amine hydrogens were slower than CH$_2$ exchange and the last two compounds lack exchangeable amine hydrogens.

Acknowledgments. One of the authors (U.S.) acknowledges financial support from The Ministry of Education under Grant No. 446-7054-364214 and The Matsunaga Research Grant.

References and Notes

(1) This work is Proton Magnetic Resonance Spectra of Metal Ammine Complexes. 12.

(2) (a) H. Yoneda and Y. Morimoto, *Inorg. Chim. Acta*, 1, 413 (1967); (b) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967); (c) M. E. Farago and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 2120 (1972).

(3) All the NMR data were collected at 36 °C and 60 MHz. The pD values refer to apparent pH meter readings.

(4) Abbreviation: mal = malonate ion, en = ethylenediamine, *N,N'*-dmen = *N,N'*-dimethylethylenediamine, tn = trimethylenediamine, py = pyridine, and phen = phenanthroline.

(5) The δ values from internal DSS for H_N and H_O are 3.64 and 3.12, 3.60, and 3.08, 3.67 and 3.14, 3.68 and 3.17, 3.90 and 3.13, and 4.06 and 3.39 for en, tn, *N,N'*-dmen, *cis*-(NH$_3$)$_2$, *cis*-py$_2$, and phen complexes, respectively. Since the variation $\delta(H_N)$ is greater and is affected by nitrogen ligands to a greater extent than $\delta(H_O)$, H_N may be closer to coordinating nitrogen.

(6) Apart from small isotope shifts. In the *cis*-py$_2$ compound, a negative isotope shift (downfield shift) was found for H_N, -0.61 and $+1.58$ Hz for H_N and H_O, respectively.

(7) In this equation we assumed no kinetic isotope effect.

(8) The *J* values for all of the complexes examined in this work are almost the same, 18.4 ± 0.4 Hz.

(9) Since the degree of stereoselectivity, defined as the ratio k_{HN}/k_{HO}, is highest for *N,N'*-dmen and en compounds, followed by tn and *cis*-(NH$_3$)$_2$ compounds, and since *cis*-py$_2$ and phen complexes exhibited little or no stereoselectivity, it appears that stereochemically rigid amine group is essential in realizing the stereoselectivity.

(10) The OD$^-$ ion is known to catalyze the amine hydrogen exchange. See, e.g., U. Sakaguchi, K. Maeda, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **49**, 397 (1976), and references cited therein.

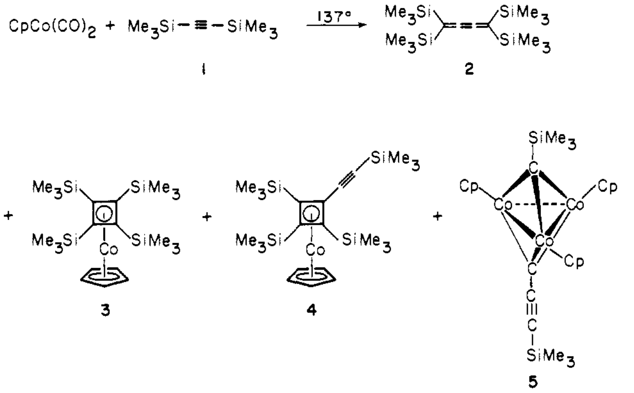
Ushio Sakaguchi, Kaiji Morito, Hayami Yoneda*
Department of Chemistry, Faculty of Science
Hiroshima University, Hiroshima 730 Japan

Received November 28, 1978

Apparent Concurrent Acetylene–Vinylidenecarbene Rearrangements, Silyl–Acetylide Metathesis, and Alkyne Cleavage in the Interaction of Bis(trimethylsilyl)acetylene with (η^5-C$_5$H$_5$)Co(CO)$_2$. Crystal and Molecular Structure of a Novel Biscarbyne Complex: [$\mu_3\eta^1$-CSi(CH$_3$)$_3$][$\mu_3\eta^1$-C$_3$Si(CH$_3$)$_3$][(η^5-C$_5$H$_5$)Co]$_3$

Sir:

We have recently utilized neat bis(trimethyl)silylacetylene (**1**) as a hindered co-oligomerization partner in cobalt-catalyzed reactions with diynes to effect chemospecificity and allow introduction of masked functionality (in the form of the trimethylsilyl group) in synthetic methodology leading to complex molecules.[1] Its use was based on the premise that steric factors would prevent reaction of **1** with itself, thereby allowing it to simply coordinate to the metal and eventually enter the cyclization cycle with added diyne. We now report that, on exposure to larger than catalytic amounts of CpCo(CO)$_2$,[2] compound **1** produces a fascinating array of molecular structures (**2–5**)[3] which point to the concurrent operation of several novel reaction pathways traversed by (sterically hindered) acetylenes in the coordination sphere of cobalt. This communication also contains the first report of a crystallographically characterized trinuclear transition metal cluster capped by two triply bridging carbyne ligands.



Tetrakis(trimethylsilyl)butatriene (**2**) was purified by sublimation and preparative gas chromatography[3] and characterized by its spectral data,[4] particularly the ^{13}C NMR spectrum which shows two nonequivalent carbons at characteristically low chemical shifts.[5] The tetrasilylated cyclobutadiene sandwich complex **3** has been obtained previously in low yield (4.7%) as the sole product from the reaction of **6** with **1**.[6] Spectral investigation[4] of the new sandwich **4**[3] revealed the presence of different trimethylsilyl groups in the ratio 2:1:1 by

0002-7863/79/1501-2768$01.00/0