complexes.[19] With this in mind it is immediately obvious from Table I that imidazole does indeed *enhance* the affinity of Cu(II) for O donors compared to N donors, thus leading to discriminating properties of $Cu(im)^{2+}$ and $Cu(im)_2^{2+}$: the $\Delta \log K_M$ values for the 6-membered chelates of malonate or 5-sulfosalicylate are larger than those of histamine; similarily, the 5-membered chelate of glycinate is preferably formed compared to 2,2′-bipyridyl.[20,22,23]

To summarize: the results of Table I do then indeed *support*, and *not* contradict, the conclusion shortly indicated at the end of the introductory paragraph. They are in line with the π accepting properties of the imidazole group, which are less pronounced than those of the pyridyl moiety, as is confirmed by the stability data given in Table II for several amine/Cu^{2+}/pyrocatecholate and AMP systems.[24] Moreover, the stability increasing effect *and* the discriminating qualities of the imidazole moiety in ternary complexes do not hold only for Cu^{2+} but also for the other metal ions of the second half of the 3d series.[4,13] This is confirmed by the results (Table III) obtained recently for ternary complexes containing histidinate or histamine[25] and is in agreement with the stability of $M(nitrilotriacetate)(imidazole)^-$ complexes (Table IV).[12d,26a–c] The coordination tendency of imidazole to $M(nta)^-$ is comparable with that to $M(aq)^{2+}$, i.e., the $\Delta \log K_M$ values are around zero, and the increased stability becomes clearly unequivocal if the data are compared with the statistical (st) value,[27] $\Delta \log K_{st} = -0.5$. This contrasts with the coordination tendency of ammonia toward $Cu(nta)^-$ which is much lower than the one toward $Cu(aq)^{2+}$; i.e., $\Delta \log K_{Cu}$ is now strongly negative:[28] $\Delta \log K_{Cu} = \log K^{Cu(nta)}_{Cu(nta)(NH_3)} - \log K^{Cu}_{Cu(NH_3)} = 2.55$ (cf. ref 29) − 4.19 (cf. ref 30) = −1.64. The observation[31] that adenosine forms through the coordination of N(7) a complex with $Ni(hydrogen\ triphosphate)^{2-}$ which is 11 times more stable than the one with $Ni(aq)^{2+}$ must also be noted in this connection, especially as the 3d ions may coordinate to N(7) of the imidazole part of the purine moiety of nucleotides.[31a] Hence, we may still conclude,[4] but now with even a more profound legitimation: "One starts to understand why mixed-ligand complexes are so widely used in nature, and one is tempted to predict that in many (more)[16c] naturally occurring mixed-ligand complexes an imidazole group together with a ligand having O donors is involved".[32]

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[19] (a) Sigel, H.; Huber, P. R.; Pasternack, R. F. *Inorg. Chem.* **1971**, *10*, 2226. (b) Sigel, H.; Caraco, R.; Prijs, B. *Inorg. Chem.* **1974**, *13*, 462.

[20] The data of the ternary aspartate complexes must be neglected in this comparison because aspartate may function as a tridentate ligand.[21]

[21] (a) Evans, C. A.; Guevremont, R.; Rabenstein, D. L. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York and Basel, 1979; Vol. 9, p 41. (b) Martin, R. B. *Ibid.*, p 1.

[22] In additon Abbott et al.[18] state: "The contrasting behavior of bpy and imidazole is demonstrated by the species distribution plots for the bpy/Cu(II)/mal and the im/Cu(II)/mal systems. In the former system the concentration of the ternary complex reaches a maximum of ca. 92% while in the latter system the ternary complexes are at a concentration of less than 50% over the pH range 2–8". This conclusion is misleading, to say the least, because bpy is a bidentate ligand and imidazole a monodentate one; the given different concentrations for the two ternary systems demonstrate mainly the well-known chelate effect. Even if for the Cu^{2+}/im/mal system $\Delta \log K_{Cu}$ would be +1.0 log unit (for Cu^{2+}/bpy/mal, $\Delta \log K_{Cu} = +0.3$),[10,18] the concentration of the ternary imidazole complexes would still be much lower than that of Cu(bpy)(mal) because $\log K^{Cu(mal)}_{Cu(mal)(bpy)} = 8.4$ (ref 18), a value which is still by a factor of 1000 larger than $\log K^{Cu(mal)}_{Cu(mal)(im)} = 4.28$ (ref 18) + 1.0 = 5.3—and there can be no doubt a $\Delta \log K_{Cu}$ value of +1.0 log unit for the Cu^{2+}/im/mal system would have been celebrated as a tremendous stability increase. It may be added that the overall stability constants[18] $\beta^{Cu}_{Cu(mal)(bpy)} = 10^{13.2}$ and $\beta^{Cu}_{Cu(mal)(im)_2} = 10^{11.15}$ cannot be compared because their dimensions are different.

[23] Part of the observed discrimination may possibly arise from steric effects, but the results listed in Tables III and IV (cf. also the last paragraph of the text) should in this context also be viewed (positive values for $\Delta \log K_M$ can never originate from steric hindrance).[28]

[24] (a) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945. (b) Huber, P. R.; Sigel, H. *Z. Naturforsch. B* **1972**, *27*, 1319.

[25] (a) Sővágő, I.; Kiss, T.; Gergely, A. *J. Chem. Soc. Dalton Trans.* **1978**, 964. (b) Brookes, G.; Pettit, L. D. *J. Chem. Soc. Dalton Trans.* **1977**, 1918. (c) Gergely, A.; Sővágő, I. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4355.

[26] (a) Sillén, L. G.; Martell, A. E. "Stability Constants of Metal-Ion Complexes"; *Chem. Soc. Spec. Publ.* **1964,** *No. 17*; **1971**, *No. 25*. (b) Perrin, D. D. "Stability Constants of Metal-Ion Complexes"; Pergamon Press: Oxford, 1979; Part B. (c) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York and London, 1975; Vol. 2. (d) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York and London, 1976; Vol. 4.

[27] At a regular octahedral (oh) coordination sphere six edges are available for the entering imidazole, while only two possibilities remain if four positions are occupied by nta^{3-}; as the probability of dissociation is the same for the binary and ternary complexes, i.e., 1, the statistical value is $^2/_6 = 0.333$, i.e., $\Delta \log K_{st/oh} = -0.5$. For the square-planar (or distorted octahedral)[5] coordination sphere of Cu^{2+} the value is $^1/_4$ (or $^1/_6$) = 0.25 (0.167), i.e., $\Delta \log K_{st/sp(do)} = -0.6$ (−0.8).

[28] The steric restrictions within the coordination sphere of Cu^{2+} are rather somewhat smaller for NH_3, than for imidazole, as is evident from a comparison of the differences between the successive stability constants of the corresponding binary complexes (for NH_3 see ref 26d; for imidazole see ref 18). Hence, the observed differences *cannot* be explained by steric effects.

[29] 25 °C; $I = 0.1$, $NaNO_3$. Still, E. *Anal. Chim. Acta* **1979**, *107*, 105.

[30] 25 °C; $I = 0$–2. The value is the average of the constants listed in ref 26a,d.

[31] (a) Martin, R. B.; Mariam, Y. H. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York and Basel, 1979; Vol. 8, p 57. (b) Mariam, Y. H.; Martin, R. B. *Inorg. Chim. Acta* **1979**, *35*, 23.

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Congruence of Product Stereochemistry and the Site of Metal–Carbonyl Bond Breaking in Substitution Reactions of Octahedral Metal Carbonyl Complexes Proceeding via Fluxional Intermediates[1]

Sir:

It has long been known that, in octahedral metal carbonyl complexes containing stereochemically different carbonyls, randomization of a stereospecifically introduced label (usually ^{13}C) can occur on the time scale of ligand substitution.[2] The development of an understanding of this process for $Mn(CO)_5Br$, in particular, involved the work of several research groups over a decade.[3–10]

Since where scrambling occurs the site of initial metal–carbon bond breaking[11] need not reflect the stereochemistry of the reaction product where CO is replaced by another ligand (L), there has also been considerable interest in the elucidation of the bond-breaking site for a variety of octahedral species.[9,10,12–16] It is the purpose of this correspondence to point

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[1] Part 50 of the series, "Octahedral Metal Carbonyls". For part 49, see ref 26. This work was sponsored by the Robert A. Welch Foundation under Grant No. B-434.

[2] D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Am. Chem. Soc.*, **93**, 2807 (1971).

[3] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

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[5] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

[6] B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, and A. Wojcicki, *J. Chem. Soc. A*, 692 (1968).

[7] T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

[8] P. W. Robinson, M. A. Cohen, and A. Wojcicki, *Inorg. Chem.*, **10**, 2081 (1971).

[9] A. D. Berry and T. L. Brown, *Inorg. Chem.*, **11**, 1165 (1972).

[10] J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 3380 (1975).

[11] There is also evidence for nondissociative scrambling in such systems. See, e.g., D. J. Darensbourg and B. J. Baldwin, *J. Am. Chem. Soc.*, **101**, 6447 (1979), and references cited therein.

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Table I. Data for Ligand-Exchange Reactions of Octahedral Metal Carbonyl Complexes[a]

substrate[b]	site of M–C bond breaking	L (incoming)	product stereochemistry	ref
$Mn(CO)_5Br$	10/1 axial	$P(OMe)_3$	*fac* (trisubstd)	10
	10/1 axial	PPh_3	*cis*	10
cis-$Mn(CO)_4Br(PPh_3)$	axial ≫ equat	PPh_3	*mer*	12
$Re(CO)_5Br$	axial ≫ equat	PPh_3	*fac* (trisubstd)	12
cis-$Re(CO)_5Br(PPh_3)$	axial ≫ equat	PPh_3	*fac*	12
	axial ≫ equat	$P(OPh)_3$	*fac*	12
	axial ≫ equat	py	*fac*	12
$(bpy)Cr(CO)_4$	stereosp axial	any	*fac*	13, 15
$(phen)Cr(CO)_4$	stereosp axial	any	*fac*	13, 15
$(phen)Mo(CO)_4$	stereosp axial	any	*fac*	16
$(phen)W(CO)_4$	stereosp axial	any	*fac*	16
$(diphos)Cr(CO)_4$	stereosp axial	$C_6H_{11}NH_2$	*fac*[c]	14
	stereosp axial	PPh_3	*mer*[c]	14

[a] All intermediates are fluxional. [b] Ligand abbreviations: bpy = 2,2′-bipyridyl; phen = *o*-phenanthroline; diphos = 1,2-bis(diphenylphosphino)ethane. [c] Under thermodynamic control.

Table II. Data for Combination of Five-Coordinate Intermediates with L

intermediate	L	k_3/k_3° [a]	k_3, $M^{-1}\,s^{-1}$	$\Delta G^{\ddagger}_3$,[b] kcal/mol	$\Delta(\Delta G^{\ddagger})$,[c] kcal/mol	ref
$[Cr(CO)_5]$[d]	CH_3CN	22.9	1.60×10^8	2.2	0.0	23
	$(CH_3)_2CO$	18.6	1.30×10^8	2.3	0.1	23
	$C_2H_5OCOC_2H_5$	13.1	9.2×10^7	2.5	0.3	23
	CH_3OH	4.4	3.1×10^7	3.1	0.9	23
	$(C_2H_5)_2O$	1.6	1.1×10^7	3.8	1.6	23
	C_6H_6	1	7.0×10^6	4.0	1.8	23
$[Mo(CO)_5]$[e]	piperidine	1.35			0.0	24
	$(C_6H_5)_3As$	1.35			0.0	24
	$(C_6H_5)_3P$	1.15			0.1	24
	$P(OCH_3)_3$	1			0.2	24
$[Mo(CO)_4P(C_6H_5)_3]$[e]	CO	7.71			0.0	25
	$(C_6H_5)_3As$	5.07			0.2	25
	$(C_4H_9)_3P$	3.50			0.5	25
	py	2.38			0.7	25
	piperidine	2.22			0.7	25
	$(C_6H_5)_3Sb$	2.19			0.7	25
	$(C_6H_5)_3P$	1.62			0.9	25
	$P(OCH_2)_3CC_2H_5$	1			1.2	25
$[(diphos)Mo(CO)_3]$[f]	py		$2.60\ (10) \times 10^6$	4.6		26
$[(H_2PC_2H_4PH_2)W(CO)_3]$[f]	py		$9.47\ (6) \times 10^6$	3.8		26

[a] Ratio of rate constant k_3 for L vs. rate constant k_3° for reaction exhibiting slowest rate. [b] Determined from values of k_3 and the diffusion-controlled rate: J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1966, p 627. [c] Determined from values of k_3/k_3°. [d] Cyclohexane solvent. [e] Hexane solvent. [f] Cyclohexane solvent; room temperature.

out, however, that sufficient evidence is now available to lead to a general conclusion for a ligand-substitution reaction under kinetic control: except in certain usually predictable circumstances, *the stereochemistry of the reaction product will mirror the site of initial M–CO bond breaking, whether or not scrambling of carbonyls occurs on the time scale of ligand substitution.*

Consider substitution in $Mn(CO)_5Br$, for example

$$Mn(CO)_5Br + L \rightarrow cis\text{-}Mn(CO)_4Br(L) + CO \quad (1)$$

Isotopic enrichment (replacement of CO by ^{13}CO) or ligand substitution (replacement of CO by L) proceeds via initial fission of a Mn–CO bond trans to another CO (axial loss).[10,17] The five-coordinate intermediate thus produced is probably square pyramidal.[18] Eventual scrambling of the stereospecifically introduced label also is observed, but upon replacement of CO by another ligand (L), only the product in which X and L are mutually cis is produced.[3] Scheme I depicts the mechanism for this overall process, and it identifies the scrambling process which takes place upon substitution by accounting for the positions of the (identical) carbonyls during the steps of the substitution process.

It is clear that the randomization of a "label" cannot occur *during* but can occur only *after* its introduction.[12] For the introduction of the stereospecific label in $Mn(CO)_5Br$, the principle of microscopic reversibility dictates that only a or the equivalent a′ (Scheme I) can afford an isotopically enriched species (via the path governed by k_3), since the low-energy path which leads to dissociation of CO must also be the favored path of recombination.[7] Thus, randomization of the carbonyls in an isotopically labeled species cannot involve the path governed by k_4, k_5.

In systems in which CO is replaced by L (eq 1), the principle of microscopic reversibility no longer holds rigorously. However, to the extent that the difference between the free energies of activation for combination of CO and L with a or a′ ($|\Delta G^{\ddagger}_{CO} - \Delta G^{\ddagger}_{L}| = \Delta(\Delta G^{\ddagger})$) approaches zero, the principle of microscopic reversibility will be operative. In this event, the stereochemistries of reaction products produced under kinetic control will reflect the site of initial M–CO bond breaking. This is observed for $Mn(CO)_5Br$.

Consider data in Table I. The observation that axial loss is strongly favored for substrates containing a variety of metal

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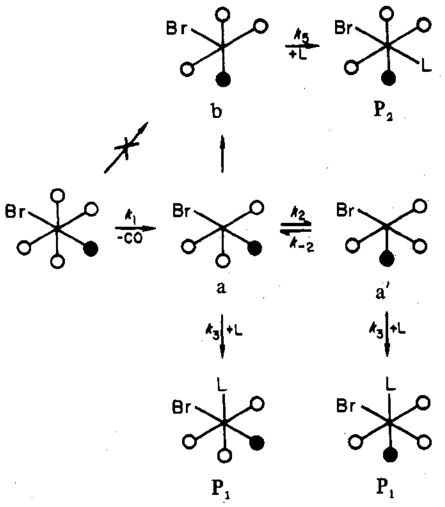
(12) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3155 (1976).
(13) M. A. Cohen and T. L. Brown, *Inorg. Chem.*, **15**, 1417 (1976).
(14) G. R. Dobson, K. J. Asali, J. L. Marshall, and C. R. McDaniel, Jr., *J. Am. Chem. Soc.*, **99**, 8100 (1977).
(15) G. R. Dobson and K. J. Asali, *J. Am. Chem. Soc.*, **101**, 5433 (1979).
(16) G. R. Dobson and K. J. Asali, manuscript in preparation.
(17) So that ambiguities in delineating the stereochemistry of dissociation for complexes exhibiting differing degrees of substitution are avoided, *axial* refers to a configuration in which a carbonyl is trans to another carbonyl. Thus *axial* dissociation is a dissociation of a carbonyl trans to CO.
(18) See citations in ref 8 of D. J. Darensbourg, G. R. Dobson, and A. Moradi-Araghi, *J. Organomet. Chem.*, **116**, C17 (1976).

Scheme I[a]



[a] Key: ○, CO originally trans to CO; ●, CO originally trans to Br; L, Lewis base or ^{13}CO.

atoms and substituents and exhibiting differing degrees of substitution is consistent with both ground-state[19,20] and transition-state[21] bonding arguments and is indicative of very significant differences in the free energies of activation for axial vs. equatorial dissociation of carbonyls.[22]

Also note values of $\Delta G^{\ddagger}$ and $\Delta(\Delta G^{\ddagger})$ for combination of nucleophiles with various five-coordinate species (Table II). The values of the latter for a given combination are in the range $0 < \Delta(\Delta G^{\ddagger}) < 2$ kcal/mol, too small to redirect the stereochemical path of the reaction to that governed by k_4, k_5.[27]

Thus in these systems "quasi microscopic reversibility" dictates that, where there is initial M–CO bond breaking trans to CO, a product containing L trans to another L cannot be produced under kinetic control regardless of possible fluxionality of the five-coordinate species. As has been pointed out by Atwood and Brown,[12] however, exceptions may arise where steric crowding at an octahedral face or edge could significantly increase the free energy of combination via k_3 in Scheme I.

These conclusions are consistent with data in Table I. Products in which the incoming nucleophile is trans to CO, expected on the basis of the preferential fission of a M–CO bond trans to CO (axial) rather than to L, are observed in all cases save those in which there are obvious steric impediments to the path dictated by quasi microscopic reversibility, e.g., for *cis*-Mn(CO)$_4$Br(PPh$_3$) in its reaction with triisopropyl phosphite, for which there would be severe congestion at an octahedral face.[12,28]

It is not appropriate to give a detailed analysis of the stereochemical consequences of the results here. In the most favorable cases, however,[22] where L is electron releasing relative to CO and poses minimal steric demands, it is highly improbable that an octahedral complex containing more than the minimal number of trans pairs of carbonyls can be prepared under kinetic control. For amines and related ligands, no such complexes are known.

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(19) L. H. Jones in "Advances in the Chemistry of the Coordination Compounds", S. Kirschner, Ed., Macmillan, New York, 1961, pp 398–411.

(20) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970); G. R. Dobson, *Ann. N.Y. Acad. Sci.*, **239**, 237 (1974).

(21) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976).

(22) In the method for determination of the site of initial M–CO bond fission employed by Brown and coworkers, "the calculated (infrared) spectra are essentially insensitive to an increase in the ratio (k_{ax}/k_{eq}) beyond about 10. This ratio might in fact be (and indeed we believe it is) much larger than this".[13]

(23) J. M. Kelly, D. V. Bent, H. Hermann, D. Schulte-Frohlinde, and E. Koerner von Gustorf, *J. Organomet. Chem.*, **69**, 259 (1974).

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(25) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973).

(26) G. R. Dobson and J. C. Rousche, *J. Organomet. Chem.*, **179**, C42 (1979).

(27) Darensbourg and Graves, for related systems, have pointed out that process a → P$_2$ (see Scheme I) need not involve the formation of discrete b intermediates and may, in fact, be concerted (D. J. Darensbourg and A. H. Graves, *Inorg. Chem.*, **18**, 1257 (1979)). Such a concerted process would involve a high degree of reorganization and, by Hammond's postulate, would be expected to be energetically unfavorable relative to that governed by k_3.

(28) It is reasonable to presume that, where there is crowding at an octahedral edge or face, a trans or *mer* product would be thermodynamically more stable than a cis or *fac* product, as well as being kinetically accessible. Thus, (diphos)Mo(CO)$_4$ reacts with triphenylphosphine to afford *mer*-(diphos)Mo(CO)$_3$(PPh$_3$) under thermodynamic control. See also, e.g., E. P. Ross, R. T. Jernigan, and G. R. Dobson, *J. Inorg. Nucl. Chem.*, **33**, 3375 (1971).

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Examples of Possible Polymeric Borane Structures

Sir:

No structural characterization has been made of the intractable polymeric products of pyrolysis of diborane or other boron hydrides. Their approximate composition[1] is $(BH)_x$ where x is a large integer. These polymers can reasonably be expected to bridge the region between small borane molecules and polymeric borides and therefore are probably mainly based upon presently known structural features which I now describe.

At least 10 modes of bonding between polyhedral species, or their fragments, can be listed, followed by only one or two examples of each mode: (1) a single bond in[2] B$_{10}$H$_{16}$, which is a dimer of B$_5$H$_8$; (2) a single three-center BHB bond in[3] B$_{20}$H$_{19}^{3-}$; (3) two BHB bridges, in[3,4] *photo*-B$_{20}$H$_{18}^{2-}$; (4) one three-center BBB bond, probably in[5] B$_{15}$H$_{23}$ and in[6,7] μ-Fe(CO)$_4$B$_7$H$_{12}^-$; (5) two three-center BBB bonds, in[8,9] B$_{20}$H$_{18}^{2-}$; (6) one shared atom, known for a metal atom but not boron, in[10] (η^5-C$_5$H$_5$)CoC$_2$B$_8$H$_{10}$CoC$_2$B$_8$H$_{10}^-$; (7) two shared boron atoms, cis in[11] B$_{14}$H$_{20}$ and trans in[12] *n*-B$_{18}$H$_{22}$; (8) three shared

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(1) A Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N.Y., 1933.

(2) R. N. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **47**, 996 (1961).

(3) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **88**, 3873 (1966).

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