12° from coplanarity with the basal plane of the $B_5H_8Fe(CO)_3$ pyramid (Figure 1). This angle is markedly smaller than the analogous angles for other nido pyramids which contain a metal inserted into a basal boron-boron bond: $Cu[P(C_6H_5)_3]_2B_5H_8$ (52°),[9b] $Fe(CO)_4B_7H_{12}^-$ (56°).[10b] The relatively elevated position of copper in $Cu[P(C_6H_5)_3]$-$B_5H_8Fe(CO)_3$ reflects and accommodates Cu-H-B bonding. Supportive evidence is provided by the infrared spectrum. It contains a band at 2292 cm^{-1} which is in the characteristic region for a Cu-H-B stretching mode.[8b,20] This band is absent from the infrared spectrum of $B_5H_8Fe(CO)_3^-$. Additionally, the Cu-H(5) distance, 1.96 (7) Å, falls within the range observed from X-ray studies of compounds which are said to have Cu-H-B bonding and also exhibit the characteristic Cu-H-B absorption in their infared spectra.[20] The Cu-H(4) distance, 2.25 (6) Å, is significantly longer than the longest Cu-H distance, 2.08 (7) Å, observed in Cu-H-B bonds.[20a] It is closer to the shortest Cu-H distance, 2.33 (9) Å, observed in $Cu[P(C_6H_5)_3]_2B_5H_8$,[9a] a compound which is said to possess no Cu-H-B bonding based upon the absence of a band in the infrared spectrum which is characteristic of the Cu-H-B stretching mode. In view of the significant difference in the Cu-B(4) and Cu-B(5) bond lengths, we believe that the difference in the Cu-H(4) and Cu-H(5) distances is real and that the Cu-H(5) distance is a bonding distance.

Copper is considered to possess a 16-electron configuration in $Cu[P(C_6H_5)_3]_2B_5H_8$.[8,9a] In $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ the presence of Cu-H-B bonding allows for an 18-electron configuration. The difference in these two arrangements is probably a function of the basal plane of the pyramid. The exo hydrogens in the pentagonal base might be more accessible than those in the square base. To test this point we are examining copper(I) derivatives of other nido pyramids: $Cu[P(C_6H_5)_3]_2B_4C_2H_7$ and $Cu[P(C_6H_5)_3]_2B_6H_9$.

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Supplementary Material Available: A listing of atom coordinates, bond distances, and bond angles (15 pages). Ordering information is given on any current masthead page.

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(12) This observation is a timely one in view of recent comments concerning certain metallocarborane systems which do not obey electron counting rules in that they adopt "open" or "slipped" structures instead of the expected closo arrangements. Explanations for such behavior range from the suggestion that the systems might contain unrecognized hydrogens which are not taken into account,[13] to possible electronic effects.[14] Although $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ is not related to such systems, in light of our results we suggest that systems which display extreme "slippage" could involve unanticipated interaction between the metal and exo hydrogens on adjacent boron atoms.

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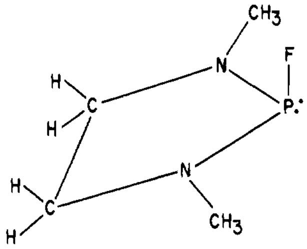
Carbon Monoxide Exchange in 1,2-Dimethyl-1,3,2-diazaphosphenium Tetracarbonyliron Cation

Sir:

In a recent paper[1] it was shown that the cyclic, fluorinated ligand (FL) coordinates to an $Fe(CO)_4$ group to give a trigonal-bipyramidal molecule, $(FL)Fe(CO)_4$, with the fluorinated ligand in the *axial position*. Treatment[2] of this neutral species,



(FL)

in CH_2Cl_2, with PF_5 results in transfer of the fluoride ion of the ligand to PF_5 to give PF_6^- and a cationic complex containing an axially coordinated cyclic phosphenium *cation*, $CH_3\overline{NCH_2CH_2N(CH_3)P}^+$ (L). The process can be represented by the equation

$$(FL)Fe(CO)_4 + PF_5 \xrightarrow[-80\ °C]{CH_2Cl_2} [(L)Fe(CO)_4]^+ + [PF_6]^-$$

The present communication establishes that the CO groups of the cationic $[LFe(CO)_4]^+$ are in labile equilibrium with free CO at temperatures above 0 °C, while the CO groups on neutral $(FL)Fe(CO)_4$ do *not* exchange with external CO at 25 °C. Both ^{13}C NMR and ^{13}C isotope exchange data are presented.

A. Carbon Monoxide Exchange as Indicated by ^{13}C NMR Line Shape. At −20 °C the ^{13}C spectrum of coordinated CO molecules in $[CH_3\overline{NCH_2CH_2N(CH_3)P}F]Fe(CO)_4$ shows a doublet of doublets resulting from $\overline{FPFeC}$ coupling, J_{FC} = 4.0

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Hz, and $\overline{PFeC}$ coupling, $J_{PC} = 24.2$ Hz. All CO groups appear equivalent because of internal rearrangements at −20 °C. When the fluoride is pulled off to generate the cationic ligand, the ^{13}C signal of coordinated CO changes to a *single* doublet at low temperature with a J_{PC} of 8.3 Hz. Methyl and methylene resonances of the ligand cation $(CH_3)\overline{NCH_2CH_2N(CH_3)P}^+$ are also clearly seen as separate doublets with a J_{PC} of ~2 Hz for the phosphorus coupling to the methylene group and a J_{PC} of ~14 Hz for the phosphorus coupling to the methyl groups.

As the temperature of the sample containing the cationic carbonyl complex is raised above −7 °C, the doublet attributable to CO begins to broaden; it finally coalesces into a single peak at 1 °C. *Over this temperature range the methyl and methylene signals remain unchanged while the phosphorus-CO coupling is lost.* We interpret this fact as evidence that the P-Fe linkage remains intact, while the CO molecules bound to the iron undergo exchange. Figure 1 shows the ^{13}CO resonance for $[CH_3\overline{NCH_2CH_2N(CH_3)P}Fe(CO)_4]^+[PF_6]^-$ at several temperatures, along with calculated[3] line shapes corresponding to CO exchange rate constants. Although the small temperature range limits the number of data points for ln (k) vs. $1/T$ and ln (k/T) vs. $1/T$ plots, it can be estimated that $\Delta G^{\ddagger} = 14.4 \pm 1.0$ kcal/mol, $\Delta H^{\ddagger} = 15.7 \pm 1.0$ kcal/mol, $\Delta E^{\ddagger} = 16.2 \pm 1.0$ kcal/mol, and $\Delta S^{\ddagger} = 4.8 \pm 0.5$ kcal/(mol deg).

B. Exchange of Labeled CO Molecules. The NMR result was qualitatively confirmed by use of ^{13}C labeled CO. When $[(L)Fe(CO)_4]^+$ was exposed to an atmosphere containing 90% ^{13}CO-10% ^{12}CO, complete statistical exchange occurred in <0.5 h at 25 °C. By contrast, the neutral species $(FL)Fe(CO)_4$ showed *no* detectable exchange with the 90% ^{13}CO-10% ^{12}CO atmosphere under comparable conditions. Monitoring of exchange was by ^{13}C NMR.

Mechanistic Implications. The extreme lability of CO in $[(L)Fe(CO)_4]^+$ ($\Delta H^{\ddagger} = 15.7$ kcal/mol) is surprising, particularly when it is recalled that $Fe(CO)_5$ has a dissociation half-life of 4 years[4a] and that Seifert and Angelici[5] reported a $\Delta H^{\ddagger}$ of 42.5 kcal/mol for the exchange of CO groups on $(C_6H_5)_3PFe(CO)_4$. Thermal substitution reactions in metal carbonyl reportedly proceed by several pathways, the most common of which involves a preliminary dissociation of CO.[6-8] Because substitution reactions in $(C_6H_5)_3PFe(CO)_4$ are known to be first order in tetracarbonyl and zero order in the substituting ligand, it is assumed that the rate-controlling step is CO dissociation.[5] By analogy it might be *assumed* that loss of CO is the rate-controlling step in the CO exchange process for $[(L)Fe(CO)_4]^+$. If one attempts to correlate CO loss with reduced M-CO bond strength,[4b] increased M-C π bonding should reduce the rate of CO loss. Frequently CO stretching frequencies are used as one probe of M-C π bonding. High stretching frequencies correspond to a lower degree of M-C π bonding. The CO stretching frequencies are in the right order for such a correlation—$[LFe(CO)_4]^+$, 2121 cm^{-1}, fast; $Fe(CO)_5$, 2114 cm^{-1}, slow; $(FL)Fe(CO)_4$, 2061 cm^{-1}, slow—but the numbers are difficult to relate quantitatively to the dramatic exchange result. It is probable that other factors are also important. A bond energy must of necessity involve the components before and after dissociation has occurred; thus factors stabilizing the intermediate would also favor CO dissociation. An attractive possibility is stabilization of the original 16-electron intermediate through chelation of the phosphine ligand using the electron pair on one nitrogen. Because of problems in geometry the intermediate would be of limited stability. Such a hypothesis is in agreement with the known fact[10] that some amines can also bind to $Fe(CO)_4$. Other less attractive possibilities involve CO bridging to phosphorus.

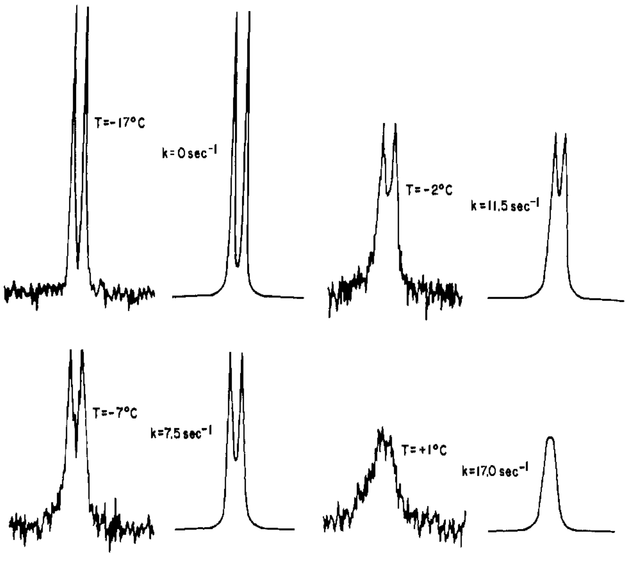
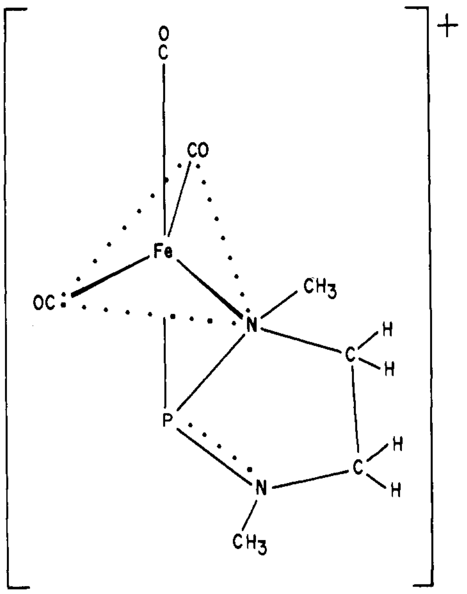


Figure 1. ^{13}C NMR spectra at temperatures shown for the system $CH_3\overline{NCH_2CH_2N(CH_3)P}(F)Fe(CO)_4$ plus PF_5: observed spectra are on the left; spectra calculated for the rate constant given are on the right, original separation at −17 °C is 8.3 Hz. The solvent was CH_2Cl_2.



Two other facts are pertinent. Basolo, Brault, and Pöe[9] noted that $Fe(CO)_5$, $(C_6H_5)_3PFe(CO)_4$, and $[(C_6H_5)_3P]_2Fe(CO)_3$ are inert to substitution in 1,2-dichloroethane but had an exchange half-life of *20 min* when $HOOCCF_3$ or H_2SO_4 was added. A protonated species was assumed to be involved. Further, Cotton and Troup[10] reported that pyridine $Fe(CO)_4$ will pick up ^{13}CO from an atmosphere of ^{13}CO above the solid, but no rate data or conditions were provided. Apparent differences in rates, where known, would suggest probable differences in mechanism from the case considered here, but some similarities to the present study are also noted (i.e., acid catalysis and amine labilization.)

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$$[>P_1 - Fe(CO)_4]^+ \rightleftarrows [>P_1 - Fe(CO)_3]^+ + CO$$

$$CO + [>P_2 - Fe(CO)_3]^+ \rightleftarrows [>P_2 - Fe(CO)_4]^+$$

P_1 and P_2 each have an equal probability of being an α (spin up) or β (spin down) spin state to that, on the average, a given carbonyl exchanges between two equally populated chemical environments.

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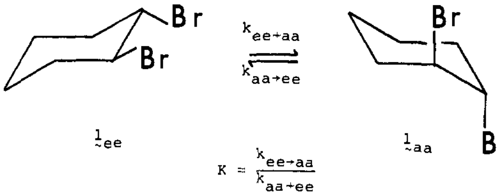
Conformational Analysis of *trans*-1,2-Dibromocyclohexane by Low-Temperature Cyclic Voltammetry

Sir:

Different conformations of a molecule should exhibit different electrochemical behavior. It has been shown that certain cyclic tetraalkylhydrazines give separate oxidation peaks for each of their two principal conformations when studied by cyclic voltammetry (CV) at temperatures sufficiently low to prevent conformational interconversion on the time scale of the experiment.[1] We now report the first example of an electrochemical reduction which shows a separate CV peak for each of two interconverting conformers.

Solutions of *trans*-1,2-dibromocyclohexane (**1**) contain two conformers, axial-axial ($\mathbf{1}_{aa}$) with the bromines anti and equatorial-equatorial ($\mathbf{1}_{ee}$) with the bromines gauche. The



conformational equilibrium is highly solvent dependent with $\mathbf{1}_{aa}$ being favored in nonpolar solvents and roughly equal populations of $\mathbf{1}_{aa}$ and $\mathbf{1}_{ee}$ present in polar solvents suitable for electrochemical studies.[2] An early ^1H NMR study[3] indicated a barrier to ring inversion (see Table I) which is high enough to "freeze out" conformational interconversion on the CV time scale at accessible low temperatures. Also, reference to studies of the electrochemical reduction of rigid cyclic 1,2-dibromides[4] suggests that $\mathbf{1}_{aa}$ should be reduced at a potential several tenths of a volt positive from the reduction of $\mathbf{1}_{ee}$.

At room temperature on Pt or glassy carbon electrodes in dimethylformamide with 0.10 M tetraethylammonium perchlorate or *n*-butyronitrile with 0.10 M tetrabutylammonium perchlorate, a single reduction peak is observed by CV. This peak is due to the totally irreversible, two-electron (confirmed by coulometry) reduction of rapidly interconverting $\mathbf{1}_{aa}$ and $\mathbf{1}_{ee}$ producing bromide ions and cyclohexene. No evidence of reversibility (anodic peak) was found even at scan rates up to 100 V/s, though anodic peaks due to bromide oxidation were always found at positive potentials. Cyclohexene is electroinactive in the potential region studied.

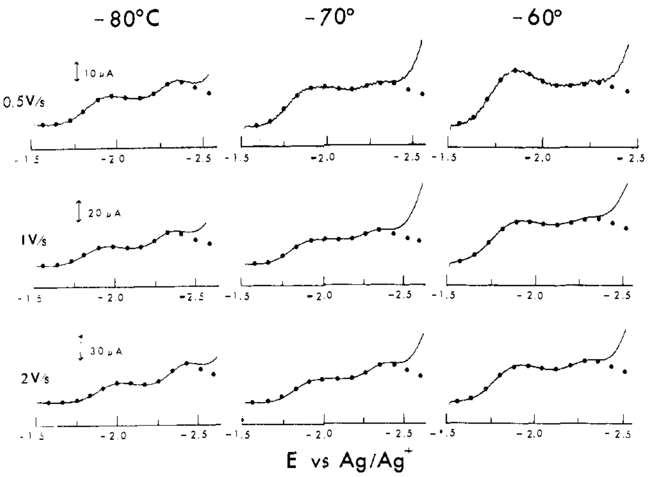


Figure 1. Voltammograms of 1.5 mM *trans*-1,2-dibromocyclohexane: curves, experimental; points, simulations; 0.10 M tetra-*n*-butylammonium perchlorate (TBAP) in *n*-butyronitrile; 0.089-cm^2 planar glassy carbon electrode. Reference electrode uses 0.010 M $AgNO_3$ and 0.10 M TBAP in *n*-butyronitrile. See Table I for simulation parameters.

Table I. Conformational Equilibrium and Kinetic Data for *trans*-1,2-Dibromocyclohexane in *n*-Butyronitrile

temp, °C	K	$k_{ee \to aa}$, s^{-1} [a]	$\Delta G^{\ddagger}$, kcal/mol [b]
−90	0.55	0.53[c]	10.8
−80	(0.55)[d]	2.3	10.8
−70	(0.55)[d]	5.2	11.1
−60	(0.55)[d]	29.0	11.0
−55	0.52[e]		
−84 to −89	1.14[f]		10-12[f]

[a] Average of values used to simulate voltammograms in Figure 1. Average deviation from the three simulations: ±15%. [b] Data for −60, −70, and −80 °C (most reliable) give $\Delta H^{\ddagger} = 9.9$ kcal/mol and $\Delta S^{\ddagger} = -5.1$ eu. [c] Obtained from low scan rate data (<1 V/s). [d] Assumed value. [e] In DMF-d_7.[2] [f] In acetone.[3]

As the temperature is lowered, a second, more negative peak grows in at faster scan rates. This is attributed to the reduction of $\mathbf{1}_{ee}$ which has a longer lifetime at the lower temperature. The heterogeneous rate constant for reduction of $\mathbf{1}_{ee}$ is smaller (hence the overpotential is larger) than for $\mathbf{1}_{aa}$ because the bromine atoms in $\mathbf{1}_{ee}$ are not in the anti configuration advantageous for trans elimination.

Figure 1 shows data obtained at a number of scan rates and temperatures along with digital simulations.[5] The current-potential curves are averages of five scans (background subtracted) obtained with the computer-controlled system described earlier.[6] The electrochemical cell and temperature control system have been described.[1b] Temperatures were maintained constant to within ±0.5 °C. The current increase observed at very negative potentials is associated with solvent breakdown and indicates inadequate background subtraction in this region. The return scans are eliminated for clarity.

At −90 °C the relative heights of the two peaks are independent of scan rate above 1 V/s; i.e., conformational equilibrium is "frozen out" and the peak heights reflect the equilibrium concentrations of $\mathbf{1}_{ee}$ and $\mathbf{1}_{aa}$ and so the equilibrium constant, K, can be derived directly from the simulation. K should be almost constant over the range of temperatures employed;[2] so the value of K obtained at −90 °C was used in the simulations of the higher temperature data.

At −90 °C the height of the first peak is proportional to the

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