These air-stable red crystals have mp 109-110 °C; IR ($CHCl_3$) 1996 (s), 1926 (m) cm^{-1} (CO); mass spectral parent molecular ion at *m/e* 322 for $C_5H_5As^{98}Mo(CO)_3$.

The upfield shift of the NMR proton and carbon signals of **4c** relative to **1c** are similar to those observed in arene-metal complexes,[10] thus clearly demonstrating π complexation.[11] The three different ring protons of the π complex vary only slightly in their chemical shift values. In contrast, the corresponding protons of free arsabenzene are quite distinct with the α-proton signals nearly 2 ppm downfield from the β- and γ-proton signals. This effect has been attributed to the influence of the large arsenic atom anisotropy directed perpendicular to the ring plane.[12] It is thus particularly interesting that this effect is completely eliminated by π complexation perpendicular to the ring but unaffected by σ complexation in the ring plane.

We have not succeeded in preparing σ complexes of stibabenzene (**1d**) by methods used to prepare **3b** and **3c.** However, the π complex **4d** may be easily obtained by boron trifluoride etherate catalyzed ligand displacement from tris(pyridine)-molybdenum tricarbonyl. These air-stable red-brown crystals have mp 106-108 °C; IR ($CHCl_3$) 1990 (s), 1919 (m) cm^{-1} (CO); mass spectral parent peak ion at *m/e* 370 for $C_5H_5{}^{123}Sb^{98}Mo(CO)_3$. The ^1H and ^{13}C NMR spectra of **4d** are nearly identical with those of **4c.** Stibabenzenemolybdenum tricarbonyl is considerably more stable than free stibabenzene. This suggests that, much like cyclobutadieneiron tricarbonyl,[13] the high energy π electrons of the ligand are stabilized by donation to the metal. Since the π-ionization potential of bismabenzene (**1e**) is even lower,[14] we anticipate that it should be even a stronger π base. As yet our efforts to produce **4e** have been frustrated by the extreme lability of bismabenzene.[7]

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Arthur J. Ashe, III,* Joel C. Colburn

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

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Site of Bond Breaking in Ligand-Exchange Reactions of 1,2-Bis(diphenylphosphino)ethanetetracarbonylmolybdenum(0)[1]

Sir:

There is mounting evidence that the five-coordinate intermediates arising from metal-carbon bond breaking taking place during ligand-exchange reactions of octahedral metal carbonyls and derivatives, e.g.,

$$L_xM(CO)_{6-x} + L' \rightarrow L_xL'M(CO)_{5-x} + CO \qquad (1)$$

may be fluxional on the time scale of the substitution process. Thus, where the substrate possesses chemically nonequivalent carbonyls, it is not possible to infer the site of initial metal-carbon bond breaking from the stereochemistry of the reaction products, where $L' \neq {}^*CO$.[2] However, a knowledge of that site is crucial to the development of bonding-reactivity relationships for such systems.[3]

An early, much-studied example is that which has been observed for the carbon monoxide exchange in manganese pentacarbonyl bromide.[2,4] The work of Brown and coworkers,[5] in which infrared spectroscopy was employed to determine the rates of substrate decay and of appearance and disappearance of the eleven possible ^{13}CO enrichment products, revealed that Mn-C bond breaking occurs exclusively at the equatorial positions (Br is axial), and that the resulting $Mn(CO)_4Br$ intermediate is fluxional. The Brown method has been applied to other systems as well, but in some instances the results have been less than unequivocal.[6]

Herein is presented an alternate procedure for the elucidation of the site of metal-carbonyl bond breaking which involves the study of molecules each containing only a single isotopic label, and the application of that procedure to (diphos)-$Mo(CO)_4$ (diphos = 1,2-bis(diphenylphosphino)ethane) in its reaction with cyclohexylamine. The key to the procedure is the stereospecific introduction of a single ^{13}CO label into the substrate under conditions much milder than those under which metal-carbonyl bond breaking takes place.

(diphos)$Mo(CO)_4$ reacts with Lewis bases (L) with replacement of a carbonyl to afford, depending upon the identity

Scheme I. Reaction Scheme for Determination of the Site of Bond Breaking in (diphos)$Mo(CO)_4$ and the Degree of Fluxionality of the Resulting [(diphos)$Mo(CO)_3$] Intermediate for the Reaction of (diphos)$Mo(CO)_4$ with Cyclohexylamine. The Conversions **1a** → **1c** **1c** → **1e** Are Wholly Analogous.

$$(\text{diphos})\text{Mo}(\text{CO}[1.1])_4$$

1a

$$\xrightarrow[125\ ^\circ\text{C},\ -\text{CO}]{+C_6H_{11}NH_2,\ \text{neat}} \textit{fac}\text{-}(\text{diphos})(C_6H_{11}NH_2)\text{Mo}(\text{CO}[1.1])_3$$

1b

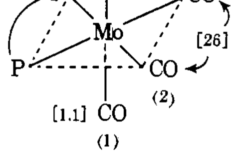
$$\xrightarrow[+^{13}\text{CO}[90]]{-C_6H_{11}NH_2,\ 30\ ^\circ\text{C}} \textit{fac}\text{-}(\text{diphos})(^{13}\text{CO}[90])\text{Mo}(\text{CO}[1.1])_3$$

1c

$$\xrightarrow[125\ ^\circ\text{C},\ -\text{CO}]{+C_6H_{11}NH_2,\ \text{neat}} \textit{fac}\text{-}(\text{diphos})(C_6H_{11}NH_2)\text{Mo}(^*\text{CO})_3$$

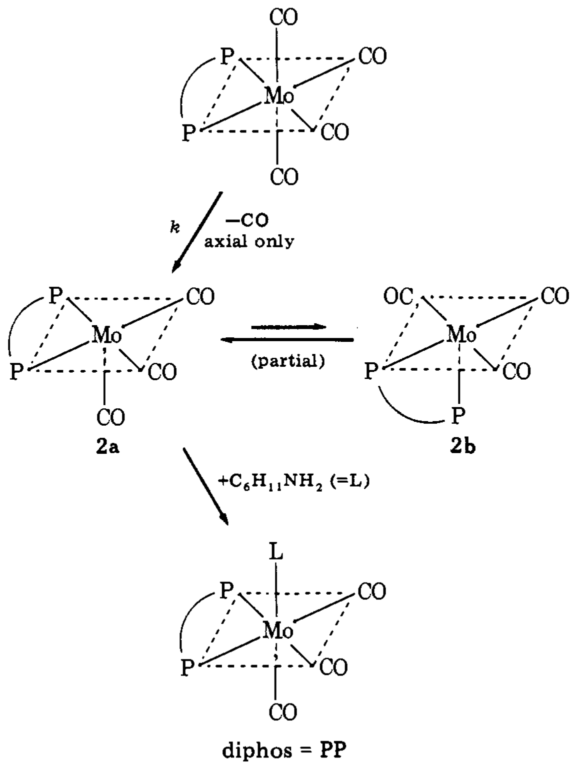
1d

$$\xrightarrow[+\text{CO}[1.1]]{-C_6H_{11}NH_2,\ 30\ ^\circ\text{C}}$$



1e

Scheme II. Mechanism of Reaction of (diphos)Mo(CO)$_4$ with Cyclohexylamine. For Reaction of the Substrate with Triphenylphosphine under the Same Conditions, *mer*-(diphos)(PPh$_3$)Mo(CO)$_3$ is obtained via Intermediate **2b.**



of L, *fac*- or *mer*-(diphos)(L)Mo(CO)$_3$ products.[7] Rate data are consistent with a mechanism involving rate-determining fission of a Mo–C bond.[8]

The elucidation of the site of bond breaking (either axial (1) or equatorial (2), **1e,** Scheme I) was effected through ^{13}C Fourier transform NMR spectroscopy (CDCl$_3$ solvent, 0.07 M Cr(acac)$_3$ "shiftless relaxation reagent",[9] JEOLCO Model JNM PFT-100 spectrometer) on complexes **1a, 1c,** and **1e** prepared via Scheme I. Reactions were carried out employing an apparatus described by Dobson and Smith,[10] modified so that introduction of the solid substrate could take place after saturation of the solvent with ^{13}CO; enrichment was effected in a closed system.

The natural isotopic abundance ^{13}C NMR spectrum for (diphos)Mo(CO)$_4$ (**1a**) is that reported by Braterman and coworkers;[11] it exhibits a doublet of doublets centered at 217.4 ppm (downfield from TMS) assignable to the equatorial carbonyls, and split by two magnetically nonequivalent ^{31}P nuclei, and a triplet centered at 208.3 ppm attributable to the axial carbonyls, and split by two magnetically equivalent ^{31}P nuclei. An ~6:1 intensity ratio for the 24 phenyl carbons (complex multiplet centered at ~157.6 ppm) vs. the four carbonyl carbons is that expected in the absence of a nuclear Overhauser effect. The relative intensities of the phenyl vs. carbonyl carbons were observed not to change employing a 100-s pulse interval vs. the 5-s pulse interval employed in data acquisition. Thus 5 s > 5 T_1. The spectrum of **1c** shows only the carbonyl triplet, with intensity relative to that of the "internal standard" phenyl carbon multiplet of ~3.2:1, demonstrating stereospecific incorporation of >90% of the 90 mol % label at the axial position. The spectrum of **1e** exhibits both the carbonyl quartet and triplet with relative intensities of ~1.3:1; the relative intensities of the carbonyl carbons vs. the phenyl carbons were found to be ~1.6:1. These results are explicable only for the approximate per cent enrichments in **1c** and **1e** shown in brackets in Scheme I, and dictate the mechanism for the exchange process illustrated in Scheme II, in which initial Mo–C bond breaking occurs exclusively at the axial position, and the resulting five-coordinate intermediate, probably square pyramidal,[12] is partially (~85% of the stereospecific label in **1c** randomizes) fluxional at 125 °C. Studies of the relative intensities, corrected for differences in molar absorptivity, of the high-energy A$_1$ mode (symmetrical stretch of axial ^{12}COs) in **1a** and the corresponding A′ mode (one ^{13}CO label) in **1c** and **1e** (Perkin-Elmer Model 621 grating spectrophotometer, linear absorbance mode, C$_2$H$_4$Cl$_2$ solvent) are also consistent with these results.

It is also to be noted that reaction of *fac*-(diphos)(C$_6$H$_{11}$NH$_2$)Mo(CO)$_3$ with triphenylphosphine at 30 °C affords exclusively the *fac*-(diphos)(PPh$_3$)Mo(CO)$_3$ isomer (identified by IR spectrum (C$_2$H$_4$Cl$_2$ solvent) ν(CO) 1940 (A$_1$, strong) and 1845 (E, strong, broad) cm^{-1}) and elemental analysis, while direct reaction of (diphos)Mo(CO)$_4$ with PPh$_3$ at 125 °C affords exclusively the known[7] *mer*-(diphos)(PPh$_3$)(diphos)Mo(CO)$_3$ product. These results are explicable only when [(diphos)Mo(CO)$_3$], if formed via dissociation of C$_6$H$_{11}$NH$_2$ at 30 °C, as in conversion of **1b** to **1c** and of **1d** to **1e**, is nonfluxional,[13] but, if it formed via axial loss of CO at 125 °C, as in conversion of **1a** to **1b** and of **1c** to **1d,** is fluxional. A study of the conversion of *fac*-(diphos)(PPh$_3$)Mo(CO)$_3$ to *mer*-(diphos)(PPh$_3$)Mo(CO)$_3$ is in progress in this laboratory.

In contrast to the behavior of (diphos)(PPh$_3$)Mo(CO)$_3$, only *fac*-(diphos)(C$_6$H$_{11}$NH$_2$)Mo(CO)$_3$ is observed as a product of the reaction of (diphos)Mo(CO)$_4$ and C$_6$H$_{11}$NH$_2$ despite the fluxionality of the intermediate (diphos)Mo(CO)$_3$ under the required reaction conditions. Thus it may be inferred that intermediate **2a** of Scheme II is the predominant fluxional species, since, on steric grounds, reaction of C$_6$H$_{11}$NH$_2$ with **2b** should be more facile. The inferred greater thermodynamic stability of **2a** is consistent with the "site preference" model for reactivity in these systems,[14] with partial ^{13}CO-labeling results for (diphos)Mo(CO)$_4$[6] and with data for [Ph$_3$PW(CO)$_4$].[15]

The method is being applied to other systems, and preliminary results for (dipy)Cr(CO)$_4$ (dipy = 2,2′-dipyridyl) and (*o*-phen)Cr(CO)$_4$ (*o*-phen = *o*-phenanthroline), via *fac*-(dipy)(PPh$_3$)Cr(CO)$_3$ and *fac*-(*o*-phen)(PPh$_3$)Cr(CO)$_3$,[10] suggest these molecules to be fluxional, and to undergo exclusively axial carbonyl loss, in substantial agreement with previous work.[6]

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Gerard R. Dobson,* Khalil J. Asali
James L. Marshall, Cato R. McDaniel, Jr.
Department of Chemistry
North Texas State University, Denton, Texas 76203
Received August 1, 1977

Polymerization of $NiBr_2[P(CH_2CH_2CN)_3]_2$: a "Triply-Specific" Solid-State Reaction

Sir:

The reactivity of coordination complexes in the solid state has been little explored.[1] Because of the rather stringent directional requirements, the most interesting solid-state reactions of coordination complexes are undoubtedly polymerization processes.[2] Studies of the potentially topochemical polyreactions of monomeric coordination complexes, by analogy with other inorganic and organic systems,[3] can thus lead to an understanding of synthetic, dimensional, and symmetry-based criteria for the solid-state preparation of crystalline coordination polymers. Square-planar, red monomeric complexes of the type NiX_2CEP_2 (X = Cl, Br; CEP = $P(CH_2CH_2CN)_3$) are obtained as kinetic products at room temperature, and have been shown to undergo polymerization reactions in solution or in the solid state[4] to yield highly crystalline, blue, octahedral coordination polymers, insoluble in organic solvents and decomposed slowly by water. For $NiBr_2CEP_2$,[4a] we have examined the polymerization in acetone solution and in single crystals (Scheme I). Further, we find that the reaction is characterized by (a) product specificity, (b) stereospecificity, leading to formation of linear polymer, (c) "crystallographic specificity", and (d) highly anisotropic "front motion" through individual single crystals.

When either an acetone solution of monomer or individual single crystals of monomer moist with acetone are allowed to polymerize at various temperatures, the blue polymeric product is *always* contaminated with a green powder (~5%), which has defied characterization.[5] However, when dry individual single crystals are allowed to polymerize at temperatures below ~130 °C, only the blue polymeric product is formed. Thus, this reaction is readily product specific *only* in the solid state. While the rate of polymerization is slower ($\sim\frac{1}{6}$) in the solid state at room temperature and below, the rates are about equal at 80 °C, and the solid-state transformation is increasingly faster above the latter temperature.

To determine the probable geometrical course of the reaction, we have carried out complete three-dimensional x-ray structure analyses on single crystals of monomer and polymer grown from solutions of monomer:

monomer, orthorhombic,	→	polymer, monoclinic,
Pbca		$B2_1/c$[6]
$a = 13.169, b = 22.004,$		$a = 13.907, b = 21.055,$
$c = 8.487$ Å		$c = 8.496$ Å
$V = 2459.3$ Å^3		$\beta = 97.46°, V = 2466.7$ Å^3
R (all 1721 data) = 0.075		R (2127 data; $I > 2\sigma(I)$) = 0.031

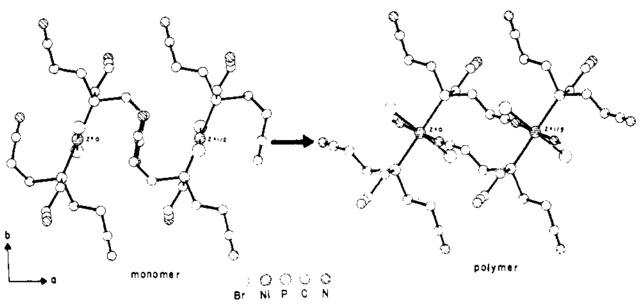
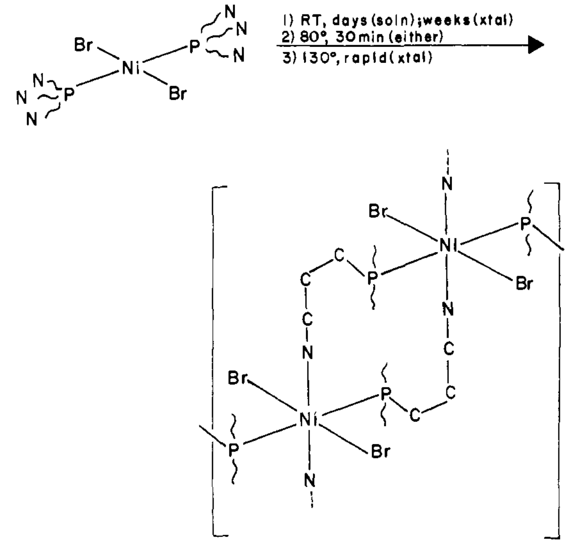


Figure 1. Pairs of square-planar reactant and octahedral product molecules viewed normal to the *ab* plane of the respective unit cells. Polymerization occurs in *ac* planes perpendicular to this view. No intermolecular bonds are present in the pure reactant phase.

Scheme I



In both the monomer and polymer phases, Ni atoms occupy the centers of symmetry (0,0,0), $(\frac{1}{2},0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$. The crystal structure of the product phase shows that only Ni complexes at (0,0,0) and $(\frac{1}{2},0,\frac{1}{2})$ have reacted to form part of a repeating polymer chain, while Ni complexes at $(\frac{1}{2},\frac{1}{2},0)$ and $(1,\frac{1}{2},\frac{1}{2})$ have reacted to form a second polymer chain. This is a significant observation: since it can be shown that the solid-state reaction pathway is identical with that suggested by this structural study of reactant and solution-grown product (vide infra), we conclude that polymerization occurs only in specific *ac* planes in the crystal. Such a "layer-by-layer" reaction precludes cross-linking of polymer chains and may be expected to lead to the formation of rigorously linear polymer, as well as highly oriented crystalline product.

At temperatures >20 °C the crystals do not show well-defined front motion as the reaction proceeds; hence we have confined our initial studies of reacting crystals to temperatures near −5 °C. Crystals of the monomer are well-defined, wine-red, nearly opaque prisms, elongated along [001], with well-defined $\{010\}$, $\{100\}$, (111), $(\bar{1}11)$, $(\bar{1}1\bar{1})$, and $(11\bar{1})$ faces. Reaction *always* begins on a single (100) face or on a pair of (100) faces; the reaction proceeds (over a 6-month period), with the first significant observation being a thin blue coloration of the entire (100) face. A very distinct blue reaction front then moves across the crystal, virtually parallel to the (100) face. X-ray diffraction studies of partially reacted crystals (5–60% complete) show that the reaction is topotactic,[7] and, further, that ($a^*_{reactant}$, $a^*_{product}$) and ($b^*_{reactant}$, $b^*_{product}$) are aligned. The c^* axis in the monoclinic product lies ~7.5° away from the c^* axis of the reactant phase (note that in the transformation from orthorhombic to monoclinic, β changes from