(2) H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).
(3) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(4) (a) S. G. Shore, *Pure Appl. Chem.*, **49**, 717 (1977); (b) S. G. Shore in "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, 1975, Chapter 3.
(5) (a) K. Wade, *Chem. Br.*, **11**, 177 (1975); (b) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).
(6) R. J. Remmel, H. D. Johnson, II, I. S. Jaworiwsky, and S. G. Shore, *J. Am. Chem. Soc.*, **97**, 5395 (1975).
(7) (a) P. C. Ford, R. G. Rinker, C. Ungerman, R. M. Laine, V. Landis, and S. A. Maya, *J. Am. Chem. Soc.*, **100**, 4595 (1978); (b) R. M. Laine, R. G. Rinker, and P. C. Ford, *ibid.*, **99**, 252 (1977); (c) R. M. Laine, *ibid.*, **100**, 6451 (1978).
(8) K. E. Inkrott and S. G. Shore, *J. Am. Chem. Soc.*, **100**, 3954 (1978).
(9) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(10) P. F. Jackson, B. F. G. Johnson, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 920 (1978).
(11) (a) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976); (b) P. Chini and B. J. Heaton, *Top. Curr. Chem.*, **71**, 1 (1977).
(12) (a) R. D. Johnston, *Adv. Inorg. Chem. Radiochem.*, **13**, 471 (1970); (b) R. B. King, *Prog. Inorg. Chem.*, **15**, 235 (1972).
(13) J. E. Ellis and E. A. Flom, *J. Organomet. Chem.*, **99**, 265 (1975).
(14) J. E. Ellis, R. A. Faltynek, and S. G. Hentges, *J. Organomet. Chem.*, **120**, 389 (1976).
(15) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976).
(16) M. Darensbourg, H. Barros, and C. Borman, *J. Am. Chem. Soc.*, **99**, 1647 (1977).
(17) (a) A. Forster, B. F. G. Johnston, J. Lewis, and T. W. Matheson, *J. Organomet. Chem.*, **104**, 225 (1976); (b) S. Aime, L. Milone, D Osella, M. Valle, and E. W. Randall, *Inorg. Chim. Acta*, **20**, 217 (1976); (c) G. L. Geoffroy and W. L. Gladfelter, *J. Am. Chem. Soc.*, **99**, 6775 (1975).
(18) (a) G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 7 (1977); (b) G. L. Geoffroy and W. L. Gladfelter, *ibid.*, **99**, 6775 (1977); (c) F. A. Cotton, B. E. Hanson, and J. D. Jamerson, *ibid.*, **99**, 6588 (1977); (d) E. Band and E. L. Muetterties, *Chem. Rev.*, **78**, 639 (1978); (e) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *ibid.*, **79**, 91 (1979).
(19) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).
(20) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974).
(21) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.
(22) K. Inkrott, R. Goetze, and S. G. Shore, *J. Organomet. Chem.*, **154**, 337 (1978).
(23) M. Yamuchi, D. J. Saturnino, and S. G. Shore, *Inorg. Synth.*, **19**, 243 (1979).
(24) R. J. Remmel, Ph.D. Dissertation, The Ohio State University, 1975, p 57.
(25) S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
(26) We have recently discovered that when a large excess of KOH is present in aqueous alcoholic solution, $H_2Ru_4(CO)_{12}^{2-}$ is formed rather than $H_3Ru_4(CO)_{12}^{-}$.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Intramolecular Hydrogen-Bonding Implications on the Lability of the Molybdenum–Piperidine Bond. Kinetic and Mechanistic Studies of the Reaction of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ with Carbon Monoxide

DONALD J. DARENSBOURG

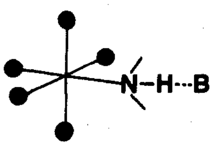
Received March 9, 1979

^{13}C NMR and infrared spectral properties in the CO region are provided for the *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivative. The effects of intramolecular hydrogen-bonding interactions between the –P–O···H–N– groupings in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ on the solution dynamics of this species toward amine-displacement reactions are reported. This hydrogen-bonding interaction results in an enhanced stabilization of the piperidine ligand toward dissociative loss as compared with the analogous process in the $Mo(CO)_5NHC_5H_{10}$ derivative, ΔH^* for NHC_5H_{10} dissociation being 3.5 kcal mol^{-1} higher for the former process. The reaction of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ with ^{13}CO was found to afford stereospecifically the equatorially ^{13}CO-substituted derivative $Mo(CO)_4(^{13}CO)P(OMe)_3$. Additionally, *fac*-$Mo(CO)_3(^{13}CO)[P(OMe)_3]NHC_5H_{10}$ was synthesized and observed to react with ^{13}CO to yield exclusively the equatorially ^{13}CO substituted $Mo(CO)_3(^{13}CO)_2P(OMe)_3$ species.

Introduction

Intermolecular hydrogen bonding between a metal-bound amine ligand containing a N–H grouping and added base has been demonstrated to accelerate greatly the rate of amine displacement in substituted metal–carbonyl–amine derivatives.[1] This type of interaction as well explains many of the solvent effects on reaction rates noted in these ligand-substitution processes.[1,2] The reaction can be described in a general manner by eq 1, where B may be either an incoming ligand or the solvent. Diffusion of MA and B to form the hydrogen-bonding intermediate trapped in a solvent cage has been observed to occur in a fast step with the chemical conversion step being rate determining.

$$MA + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MA{:}B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MB{:}A \xrightarrow{k_3} MB + A \quad (1)$$

MA:B =


Previously, solid-state structural data have been presented to support the existence of a weak intramolecular N–H···O hydrogen bond in the derivative *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$.[3] In this paper we report kinetic measurements for the dissociative loss of amine (eq 2) in this species in order to assess the role that this interaction plays in the amine-dissociation process. The stereochemical position occupied by the incoming carbon monoxide ligand in eq 2 in addition to scrambling processes in the $[Mo(CO)_4P(OMe)_3]$ intermediate has been investigated with the aid of ^{13}CO.

$$cis\text{-}Mo(CO)_4[P(OMe)_3]NHC_5H_{10} + CO \rightarrow Mo(CO)_5L + NHC_5H_{10} \quad (2)$$

Experimental Section

Materials. Reagent grade hexane was distilled from $CaSO_4$ under a nitrogen atmosphere. Molybdenum hexacarbonyl was the generous gift of Climax Molybdenum Corp. ^{12}C carbon monoxide was supplied by Matheson, whereas ^{13}CO gas enriched to >90% was obtained from Prochem, B.O.C. Ltd., London. The *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivative was prepared from *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$ and $P(OMe)_3$ as previously described.[4]

Kinetic Measurements. Piperidine substitution reactions of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivatives were carried out in Schlenk storage tubes (25-mL capacity) under a static atmosphere of carbon monoxide in heptane solvent at a variety of temperatures. The tubes were fitted with septum caps secured by copper wire. The reaction

0020-1669/79/1318-2821$01.00/0

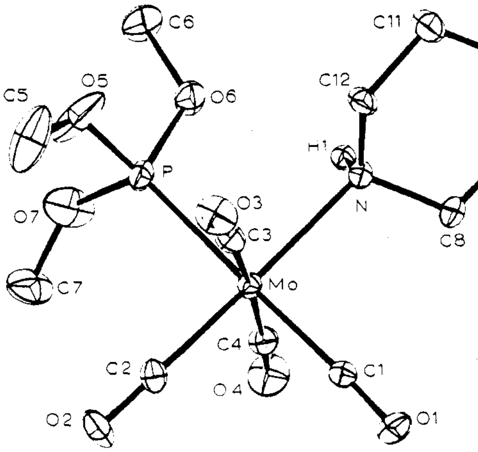


Figure 1. Molecular structure of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ with the atoms represented as their 40% probability ellipsoids for thermal motion.

flasks were placed in a constant-temperature bath (regulated to ±0.05 °C) and samples were withdrawn at regular time intervals with a hypodermic syringe for infrared spectral analysis. The rates of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10} \rightarrow Mo(CO)_5P(OMe)_3$ were followed by observing the decrease in the lowest frequency ν(CO) absorption, the B_2 mode, with time. Rate constants were calculated by using a linear least-squares computer program for the first-order rate plots of ln $(A_t - A_\infty)$ vs. time, where A_t is the absorbance at time t and A_∞ is the absorbance at infinity.

Synthesis of ^{13}C-Enriched *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$. Because of the solution instability of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ in $CDCl_3$ over prolonged periods of time, it was necessary to synthesize the ^{13}CO-enriched derivative in order to obtain good-quality ^{13}C NMR spectra. A randomly ^{13}CO-enriched *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$ sample was prepared from $Mo(CO)_6$ (^{13}C-enriched photochemically in heptane) and piperidine in refluxing heptane. The bis(piperidine) derivative was then reacted with an excess of $P(OMe)_3$ in refluxing dichloromethane for ~5 min. Upon partial removal of solvent followed by the addition of methanol the yellow product was obtained as the precipitant. Alternatively, a stereospecifically labeled derivative was prepared from *fac*-$Mo(CO)_3(^{13}CO)[NHC_5H_{10}]_2$ (synthesized from $Mo(CO)_3(^{13}CO)$(triene) and excess $C_5H_{10}NH$ in chloroform at room temperature) and excess $P(OMe)_3$ as described above. That the product was *fac*-$Mo(CO)_3(^{13}CO)[P(OMe)_3]NHC_5H_{10}$ was discernible by ^{13}C NMR and infrared spectroscopy in the ν(CO) region (vide infra).

Reaction of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ with ^{13}CO. Reaction of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ with ^{13}CO in purified hexane (olefins removed by sulfuric acid treatment followed by distillation from lithium aluminum hydride) at 40 °C for 18 h afforded $Mo(CO)_4(^{13}CO)P(OMe)_3$. This species was demonstrated to be stereospecifically enriched in ^{13}CO in an equatorial site as evidenced by only a strong ^{13}C resonance at 204.8 ppm (J_{P-C} = 13.7 Hz). Similarly, the stereospecifically enriched *fac*-$Mo(CO)_3(^{13}CO)[P(OMe)_3]NHC_5H_{10}$ was subjected to reaction with ^{13}CO to provide only equatorially ^{13}CO-labeled $Mo(CO)_5P(OMe)_3$.

Carbon-13 Nuclear Magnetic Resonance Measurements. ^{13}C resonances were measured on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent in 10-mm tubes. Chemical shifts are expressed in parts per million relative to $(CH_3)_4Si$, with positive δ(C) values being at lower field than $\delta((CH_3)_4Si)$. Typically, spectra resulted from the accumulation of 1000–6000 transients with an acquisition time of 1.02 s, a pulse repetition rate of 5.0 s, and a flip angle of 30°.

Infrared Measurements. The infrared spectra were recorded on either a Perkin-Elmer 521 or 283 spectrophotometer, both equipped with a linear-absorbance potentiometer. The spectra were calibrated against a water vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. Matched sodium chloride cells (1.0 mm) were used in the measurements.

Results and Discussion

The molecular structure of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ is portrayed in Figure 1. The Mo–C distances determined were Mo–C2 = 1.971 (8) Å, Mo–C1 = 2.006 (6) Å, Mo–C3 = 2.045 (6) Å, and Mo–C4 = 2.022 (6) Å. That is, the Mo–C distances increase as the π-acceptor ability of the ligand trans to the bond in question increases ($NHC_5H_{10} < P(OMe)_3 < CO$). For the series of complexes $M(CO)_5L$ (M = Cr, Mo, W), where L is a group 5a ligand of lesser π-acceptor ability than carbon monoxide, it has been demonstrated that carbonyl carbons trans to the substituent L are deshielded relative to carbonyl carbons cis to L.[5-7] Further, it was suggested that within a series of closely related derivatives the carbonyl carbon chemical shifts are a linear function of the extent of metal → CO π back-donation; thus, as metal → CO π back-donation increases, the ^{13}C chemical shift is deshielded. This proposal was supported as well by X-ray crystallographic data for $LCr(CO)_5$ and $L_2Cr(CO)_4$ derivatives where the Cr–C bond length decreases as the δ(C) is deshielded.[8]

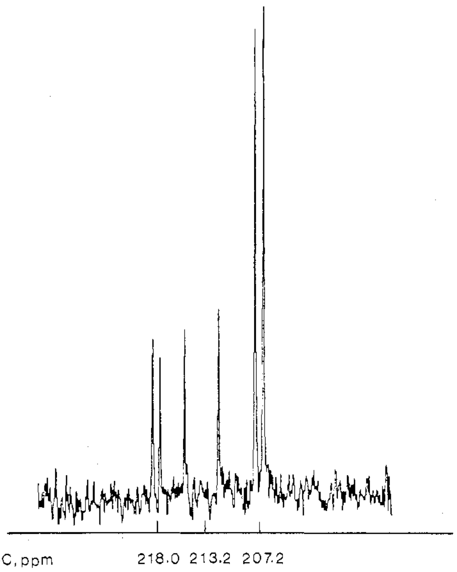


Figure 2. ^{13}C NMR spectrum of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ in the CO region in $CDCl_3$ at −45 °C.

It was therefore of interest to determine the ^{13}C chemical shifts of the carbonyl ligands in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$, where the Mo–C distances are very accurately known with the carbonyl carbons being trans to ligands of diverse π-acceptor strengths (NHC_5H_{10}, $P(OMe)_3$, CO) within one molecular framework. The ^{13}C NMR spectrum in the carbonyl carbon region is displayed in Figure 2, with chemical shifts at ambient temperature (−45 °C values given in parentheses) assigned[9] to C2, C1, and C3 and C4 occurring at 217.9 (218.0), 213.2 (213.4), and 207.7 (207.2) ppm, respectively. The generally observed trend in ^{31}P–^{13}C coupling constants in phosphorus-substituted derivatives of molybdenum hexacarbonyl is also illustrated in Figure 2 where J_{P-C} for the trans arrangement is considerably greater (53.7 Hz) than that for the cis J_{P-C} geometry (11.7 and 13.7 Hz).[10] Thus these results advance the proposal of a relationship between ^{13}C chemical shifts, M–C bond lengths, and M–C π back-bonding.[11]

Infrared spectral results in the ν(CO) region of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ are also indicative of a nonequivalency in the two equatorial (trans to $P(OMe)_3$ and NHC_5H_{10}) CO groups. The four-band pattern anticipated and observed (Figure 3) for the $Mo(CO)_4$ framework of C_s symmetry (3 A′ + A″) was found to be related to the corresponding ν(CO) pattern in stereospecifically axially ^{13}CO-labeled *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ of C_1 symmetry (4 A) as illustrated in Figure 4. The observed ν(CO) frequencies for the all-^{12}CO- and mono-^{13}C-substituted de-

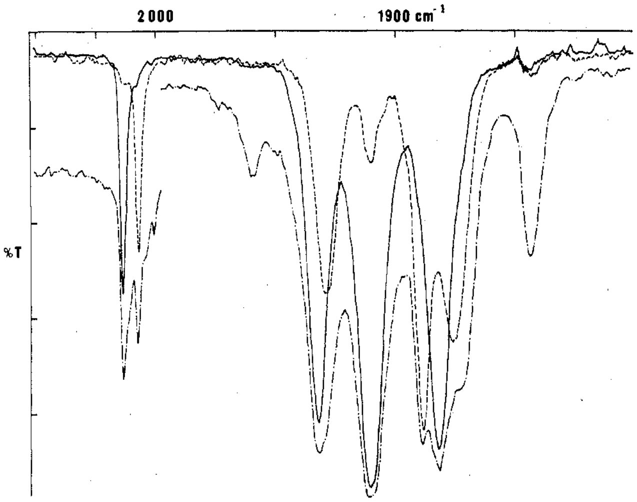


Figure 3. Infrared spectra in the ν(CO) region in hexane solution: (—) *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$; (---) mono-$^{13}CO$, axially labeled *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$; (-•-) *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ partially ^{13}CO enriched randomly.

Table I. Infrared Spectra in the ν(CO) Region of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ and Its ^{13}CO Analogues[a]

all-^{12}CO molecule		mono-^{13}CO, ax		mono-^{13}CO, eq	
ν(CO)	sym	ν(CO)	sym	ν(CO)	sym
2024.0	A′	2011.0	A	2018.0	A′
1927.2	A′	1924.2	A		A′
1905.2	A″	1883.8	A	1905.2	A″
1876.8	A′	1871.0	A	1838.2	A′

[a] Spectra determined in saturated hydrocarbon solvent; ν(CO) in cm^{-1}.

Table II. Rate Constants for the Dissociation of Piperidine in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ Derivatives[a]

T, °C	10^4k,[b] s^{-1}	T, °C	10^4k,[b] s^{-1}
42.7	0.852 ± 0.02	55.1	5.19 ± 0.25
46.9	1.62 ± 0.02	58.5	8.45 ± 0.31
50.7	2.79 ± 0.06		

[a] Reactions carried out in CO-saturated heptane. [b] Error limits represent 95% confidence levels.

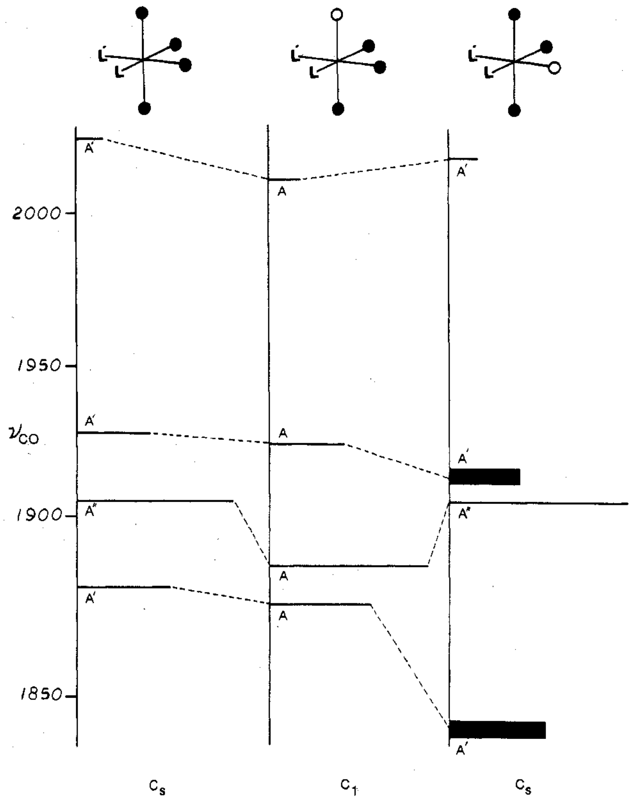


Figure 4. Diagram illustrating how the CO stretching spectra of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ transform, with peak positions, in proceeding from the all-^{12}CO molecule to the mono-^{13}CO axially and equatorially labeled species.

Table III. Comparative Rate and Activation Parameters for Piperidine Displacement in *cis*-$Mo(CO)_4[L]NHC_5H_{10}$ Derivatives[a]

L	10^5k_1,[b] s^{-1}	E_{act}, kcal	ΔH^*, kcal	ΔS^*, eu
CO[c]	2.77 (1.00)	26.4 ± 1.4	25.8 ± 3.7	+2.8 ± 11.6
$P(OMe)_3$	5.65 (2.04)	30.0 ± 0.4	29.4 ± 0.4	+13.8 ± 1.3
PPh_3[d]	465 (168)	26.1 ± 3.7	25.5 ± 3.7	+10.1 ± 12.4

[a] Error limits represent 95% confidence levels. [b] All reactions carried out in saturated hydrocarbon solvent and comparative rates are at 39.7 °C with relative rates given in parentheses. [c] Data taken from ref 2. [d] Data taken from ref 14. Error analysis recomputed to be consistent with the rest of the data.

rivatives are given in Table I. As noted in Figure 4 and Table I, all four ν(CO) bands shift to lower frequency upon axial ^{13}CO substitution, whereas in cis-disubstituted derivatives containing two equivalent L groups (and hence two equivalent equatorial CO groups), the lowest frequency A′ vibrational mode remains unshifted.[12] On the other hand, substitution of a ^{13}CO ligand in an equatorial site affords a *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ species of C_s symmetry with the A″ ν(CO) vibrational mode being unshifted from that in the all-^{12}CO molecule (see Figure 4).

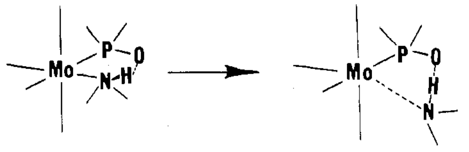
The rate of substitution of the piperidine ligand in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ (eq 2) has been demonstrated to follow the first-order rate law (3) in CO-saturated heptane

$$\text{rate} = k_1[\textit{cis}\text{-}Mo(CO)_4[P(OMe)_3]NHC_5H_{10}] \qquad (3)$$

solution. The reaction was observed to be clean with $Mo(CO)_5P(OMe)_3$ being the only product. Further reaction of the $Mo(CO)_5P(OMe)_3$ derivative with carbon monoxide to afford $Mo(CO)_6$ or to exchange CO groups requires more rigorous conditions. Temperature-dependent rate data are given in Table II, whereas comparative values of the rate constants k_1 at 39.7 °C for the process described in eq 2 and related processes are provided in Table III along with the corresponding activation parameters.

Reaction 2 therefore proceeds by a dissociative process with the coordinatively deficient species $[Mo(CO)_4P(OMe)_3]$ being trapped by the large excess of carbon monoxide present in solution. However, in excess piperidine the reaction is greatly retarded as a consequence of competitive reactions of NHC_5H_{10} and CO with the unsaturated intermediate $[Mo(CO)_4P(OMe)_3]$. In addition, piperidine can participate in the dissociative –P–O···H– hydrogen process described in eq 1, where under these conditions $k_{-1}/k_2 \gg 1 + k_{-1}k_2/k_2k_3$ such that the forward rate constant reduces to $(k_1/k_{-1})k_2$.

The activation parameters cited in Table III demonstrate that the enhanced stability of the trimethyl phosphite derivative over that of its triphenylphosphine analogue is due to a greater enthalpy of activation for piperidine dissociation in the former case.[13,14] Indeed, this is further illustrated upon comparing ΔH^* for piperidine dissociation in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ vs. $Mo(CO)_5NHC_5H_{10}$. Thus, as the solid-state structural data would suggest, –P–O···H–N– hydrogen bonding in the ground state and/or transition state is important in the solution reactivity of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$. It is highly probable in the transition state, where the metal–nitrogen bond is essentially severed, that hydrogen-bonding interaction between the amine and the bound phosphite ligand is intensified (eq 4). This argument is based on geometrical considerations alone (i.e., a linear



(4)

N–H···O arrangement being possible); however, on electronic grounds the uncoordinated amine group should be less susceptible to hydrogen-bonding interactions.

Experiments designed to intimately probe the nature of the substitution reaction described in eq 2 were carried out. These involved trapping experiments of the coordinatively unsaturated [$Mo(CO)_4P(OMe)_3$] species, which in saturated hydrocarbon solvent may be considered to have a coordination site which is "readily available" as opposed to being completely "free",[15] with ^{13}C-labeled carbon monoxide. Reaction 2, employing 93% ^{13}CO, affords the $Mo(CO)_4(^{13}CO)P(OMe)_3$ derivative which is exclusively labeled in an equatorial position as indicated by a single carbon resonance at 204.8 ppm (J_{P-C} = 13.7 Hz); see Figure 5B. This observation indicates that the intermediate resulting from loss of a piperidine in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ closely resembles the transition state, or, in other words, the transition state requires little reorganization about the metal center in going to the intermediate. It was further demonstrated from the reaction of axially labeled *cis*-$Mo(CO)_3(^{13}CO)[P(OMe)_3]NHC_5H_{10}$ (**1**) with ^{13}CO that the square-pyramidal intermediate [$Mo(CO)_4P(OMe)_3$] is nonfluxional during its solution lifetime.[16-18] When the [$Mo(CO)_3(^{13}CO)P(OMe)_3$] transient was trapped with ^{13}CO, the resulting $Mo(CO)_3(^{13}CO)_2P(OMe)_3$ derivative was shown by ^{13}C NMR (Figure 5C) to contain *only* equatorially labeled carbon monoxide groups. Scheme I summarizes these observations.

Substitution reactions of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ with the phosphorus donor ligands L (where L = PPh_3, P-*n*-Bu_3, or PCy_3) afford the corresponding *cis*-$Mo(CO)_4[P(OMe)_3]L$ derivatives.[19] However, when L = $P(OMe)_3$, a mixture of *cis*- and *trans*-$Mo(CO)_4[P(OMe)_3]_2$ is produced, dominant in the trans isomeric form. In an analogous manner the reaction of $Mo(CO)_4$(diene) derivatives with $P(OMe)_3$ has been found to yield a comparable mixture of *cis*- and *trans*-$Mo(CO)_4[P(OMe)_3]_2$.[12] We have recently shown that the pure *trans*-$Mo(CO)_4[P(OMe)_3]_2$ species isomerizes to a cis/trans equilibrium mixture (trans isomer predominant) by means of an *intramolecular, nondissociative process*.[19,20] Although the kinetic parameters for the *cis*-$Mo(CO)_4[P(OMe)_3]_2 \rightarrow$ *trans*-$Mo(CO)_4[P(OMe)_3]_2$ isomerization are currently unavailable, it appears qualitatively that this process occurs too slowly to account for the observed cis/trans distribution, particularly in the diene substitution reaction.[12] In other words, the propensity for the bis(trimethyl phosphite) derivative of molybdenum tetracarbonyl derivative to exist as the trans isomer appears to be, at least in part, kinetically controlled. A clear understanding of reaction 2 where $P(OMe)_3$ is the incoming ligand will have to await further experimental measurements.

In summary, our studies of substitutional reactions of primary and secondary amine ligands in transition-metal derivatives reveal that these processes can be greatly enhanced by *intermolecular* hydrogen bonding between the amine and the incoming ligand or the solvent.[1,21] This hydrogen-bonding phenomenon which involves a rapid preequilibrium (see eq 1) leads to steric repulsion in the outer-sphere complex, thus activating the dissociative amine-substitution process. Additionally, this rapid reversible associative preequilibrium process serves to increase the activity of the incoming ligand at the reaction center, thereby acting as an "entropy trap".[21] On the other hand, the current investigation has demonstrated that when the opportunity for *intramolecular* hydrogen bonding exists in the substrate molecule, a stabilizing effect is noted; i.e., the 3.5 kcal mol^{-1} (14.6 kJ mol^{-1}) increase in ΔH^* for dissociation of piperidine in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ as compared with that in $Mo(CO)_5NHC_5H_{10}$ is attributed to intramolecular hydrogen bonding in the ground state and/or transition state. The solid-state structure of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ is indeed supportive of this proposal. In the absence of specific hydrogen-bonding interactions, substitution of $P(OMe)_3$ for carbon monoxide would be expected to lead to an enhanced labilization of NHC_5H_{10}, since this results in an increase in electron density at the metal center, in turn lowering its affinity for binding to an amine. The considerations presented above should hold in general for substitutional processes of amine ligands containing N–H groupings at transition-metal centers, and efforts to expand these studies are currently underway in our laboratory.[22]

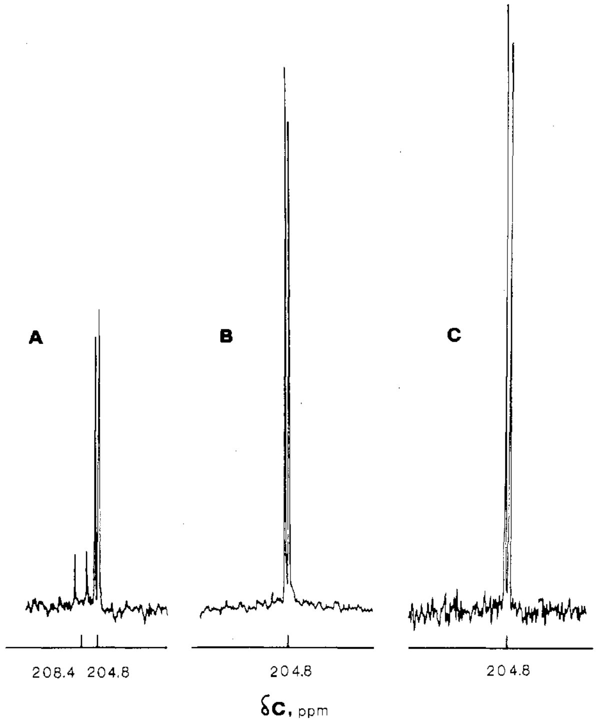
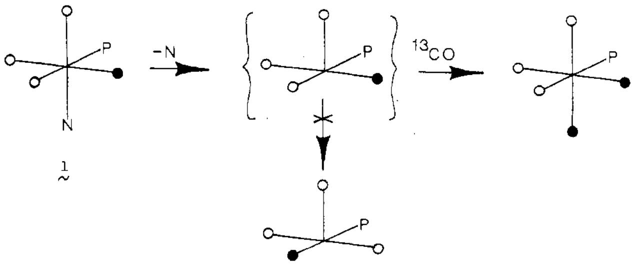


Figure 5. ^{13}C NMR spectra of $Mo(CO)_5P(OMe)_3$ in $CDCl_3$: (A) Natural-abundance spectrum of $Mo(CO)_5P(OMe)_3$, $\delta(C_{trans})$ 208.4 (J_{P-C} = 40.0 Hz) and $\delta(C_{cis})$ 204.8 (J_{P-C} = 13.7 Hz). (B) $Mo(CO)_5P(OMe)_3$ from the reaction of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ and ^{13}CO at 40 °C. (C) $Mo(CO)_5P(OMe)_3$ from the reaction of *fac*-$Mo(CO)_3(^{13}CO)[P(OMe)_3]NHC_5H_{10}$ and ^{13}CO at 40 °C.

Scheme I



Acknowledgment. The financial support of the National Science Foundation through Grant CHE 78-01758 is greatly appreciated.

Registry No. *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$, 63105-41-9.

References and Notes

(1) Ewen, J.; Darensbourg, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 6874.
(2) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.

(3) Atwood, J. L.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 2314.
(4) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.
(5) Gansow, O. A.; Kimura, B. Y.; Dobson, G. R.; Brown, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 5922.
(6) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027.
(7) Bodner, G. M.; Kahl, S. B.; Bork, K.; Storhoff, B. N.; Wuller, J. E.; Todd, L. J. *Inorg. Chem.* **1973**, *12*, 1071.
(8) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335.
(9) Assignments are based on intensity ratios, relative magnitudes of P–C coupling constants, and spectral measurements on a stereospecifically labeled derivative.
(10) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.
(11) There is some attenuation of these correlations for tungsten derivatives.
(12) Darensbourg, D. J.; Salzer, A. *J. Am. Chem. Soc.* **1978**, *100*, 4119.
(13) On the basis of kinetic evidence, these amine-displacement reactions proceed with essentially complete amine–molybdenum bond breaking.[2,14]
(14) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286.
(15) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259.
(16) The related 16-electron group 6b metal derivative [Cr(CO)$_5$] has an average characteristic inverse lifetime in CO-saturated cyclohexane solution of $\sim 3 \times 10^4$ s^{-1}.[17,18]
(17) Kelly, J. M.; Hermann, H.; Koerner von Gustorf, E. *J. Chem. Soc., Chem. Commun.* **1973**, 105.
(18) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.
(19) Darensbourg, D. J.; Baldwin, B. J., unpublished results.
(20) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14.
(21) Ewen, J.; Darensbourg, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 4317.
(22) Darensbourg, D. J.; Alejandro, L., unpublished results.

Contribution from the Istituto di Chimica Generale e Inorganica, Università di Milano, Milano, Italy, and the Central Research Institute for Chemistry of the Hungarian Academy of Science, Budapest, Hungary

Complexes with Diastereoisomeric Ligands. 1. Copper(II) Complexes with the Tridentate Schiff Bases of (1*R*)-3-(Hydroxymethylene)camphor or (1*R*)-2-(Hydroxymethylene)menthone and (*S*)- or (*R*)-Amino Acids

LUIGI CASELLA,[1a] MICHELE GULLOTTI,[1a] ALESSANDRO PASINI,*[1a] and ANTAL ROCKENBAUER[1b]

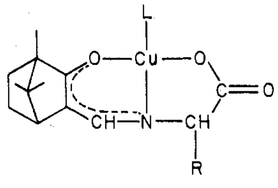
Received October 13, 1978

Copper(II) complexes with tridentate Schiff bases derived by the condensation of (+)-(hydroxymethylene)camphor or (+)-(hydroxymethylene)menthone with a series of (*S*)- and (*R*)-amino acids have been synthesized. Little interaction between the various chiral centers has been found and the conformation of the chelate rings depends mainly on the configuration of the α-carbon atom of the amino acid. ESR and electronic spectra results indicate that a competitive mechanism between the σ and π bondings, as well as between the different kinds of σ bondings of the complex, is operative. The variations of the *K* Fermi term are interpreted by considering an exchange polarization of the partially filled 4s orbital.

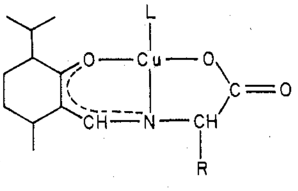
Introduction

The problem of stereoselectivity in the formation of complexes of amino acids with metal ions is still an open question and its understanding is still poor, although relevant effects have often been reported.[2] For instance ternary complexes of the type Cu(*S*-aa′)(*R*,*S*-aa″)[3] have been used to separate aa″ in its optical isomers[4] and some ligand reactions within the coordination sphere have been reported to proceed with a high chiral recognition. Some examples are decarboxylation of 2-amino-2-methylmalonic acid,[5] racemization of amino acids,[6] hydrolysis of amino acid esters,[7] and stereoselective formation of threonine vs. allothreonine.[8] In particular, metal complexes of amino acid Schiff bases have received little attention from the stereochemical[9] standpoint, though their importance as model systems of pyridoxal-dependent enzymes is well-known.[10]

We have therefore synthesized a series of copper(II) complexes with the Schiff bases formed between (1*R*)-3-(hydroxymethylene)camphor or (1*R*)-2-(hydroxymethylene)menthone and a series of (*R*)- or (*S*)-amino acids and studied their conformational properties with the hope of elucidating the behavior of a chiral amino acid in Schiff base chiral environment. The general formulas of the complexes are shown in structures I and II.



I



II

A detailed study of the electronic properties of this new class of compounds has also been carried out to have a deeper knowledge of the coordination and bonding properties of copper(II) complexes with tridentate amino acid Schiff bases. Until now only scattered reports have appeared on this subject.[11,12]

Some preliminary results on the conformational aspects have already appeared[13] and more recently the structure of a member of this class of compounds, namely, [*N*-[(+)-(hydroxymethylidene)camphorato]-(*S*)-phenylalaninato]copper(II), has been resolved.[14] This investigation has shown that the Schiff base has formed through the condensation of the formyl rather than the ketone group of (hydroxymethylene)camphor as was expected on the grounds of previous studies on the Schiff bases formed between the same β-diketone and optically active diamines.[15]

Experimental Section

Analyses (Table I) were from the microanalytical laboratory, the University of Milan. Molecular weights (in chloroform and pyridine) were determined at the Franz Pascher Microanalytisches Laboratorium, Bonn, West Germany. Magnetic moments were measured at 97 and 294 K with the Faraday method; the diamagnetic contribution was calculated with Pascal's constant. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer, electronic spectra were recorded on a Beckman DK-2A instrument equipped with a reflectance attachment, and a Varian NV 14 was used to record ^{1}H NMR spectra with Me$_4$Si as internal reference. CD spectra were recorded on a Jobin-Yvonne Mark III instrument; solid-state spectra were obtained on potassium bromide pellets of known concentration (weight of product/total weight) and of constant thickness (0.2 mm). ESR spectra were recorded in the atmosphere on a JEOL JES-ME-3X spectrometer with freshly prepared solutions and calibrated with Mn–MgO. Computer simulations of the spectra were carried out on

0020-1669/79/1318-2825$01.00/0