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Isocyanide Insertion Reactions. 2. Structural and Dynamical Stereochemistry of η^1- and η^2-Iminoacyl Ligands[1]

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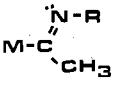
The crystal and molecular structures of the compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (II) and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (III) are reported. II crystallizes in the space group $P2_1/c\text{-}C_{2h}^5$, with a = 7.789 (4) Å, b = 6.810 (3) Å, c = 26.754 (15) Å, β = 91.91 (4)°, and Z = 4. A total of 1875 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ were used in the solution and refinment of the structure. The values of the reliability indices after the final cycle of least-squares refinement were R = 0.039 and R_w = 0.037. The molecule contains a novel η^2-iminoacyl ligand which is bonded to the metal atom through both the carbon and nitrogen atoms of the imino group. Pertinent internuclear distances are Mo—C3 = 2.106 (5) Å, Mo—N = 2.143 (4) Å, and C3═N = 1.233 (6) Å. III is formed by the addition of $P(OCH_3)_3$ to II. III crystallizes in the space group $P\bar{1}\text{-}C_i^1$; a = 8.475 (6) Å, b = 10.571 (8) Å, c = 11.879 (9) Å, α = 89.46 (6)°, β = 74.95 (5)°, γ = 82.60 (5)°, and Z = 2. A total of 2621 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ were used in the structure solution and refinement. The final values of the reliability indices were R = 0.067 and R_w = 0.075. This molecule contains a η^1-iminoacyl ligand. The bonding Mo–C6 distance is 2.272 (10) Å, while the nonbonding Mo···N distance is 3.062 (9) Å. Comparison of the structures and their infrared spectra indicates that the imino C–N bond is stronger in the η^2-iminoacyl ligand than in the monohapto ligand. ^{13}C NMR spectra of the compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (I) and $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (IV) show that these molecules are fluxional. The most likely mechanism for the rearrangement can be described as a rotation of the iminoacyl ligand about an axis defined by the metal atom and the center of the carbon–nitrogen multiple bond. Activation parameters for the rearrangement are the following: for I $\Delta G^{\ddagger}_{298}$ = 15.3 ± 0.6 kcal/mol, $\Delta H^{\ddagger}$ = 14.7 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = −1.7 ± 1.5 eu; for IV $\Delta G^{\ddagger}_{298}$ = 15.3 ± 0.4 kcal/mol, $\Delta H^{\ddagger}$ = 13.8 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = −5.1 ± 0.9 eu.

Introduction

In the preceding paper,[2] we reported the syntheses, physical properties, and reactivity of the complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNCH_3)$ (I) and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNC_6H_5)$ (II) and discussed their importance in the overall scheme of the isocyanide "insertion" reaction. On the basis of their formulas, the two most plausible structural arrangements that may be proposed are **1** and **2**. Structure



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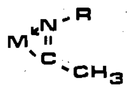

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1 contains a η^1-iminoacyl ligand in which the metal atom has only a 16-electron configuration. Structure **2** contains a η^2-iminoacyl ligand in which the metal atom has an 18-electron configuration. In order to clarify the coordination character of the iminoacyl ligand, we have performed an x-ray crystallographic analysis of II. Since there has only been one previous report of a structural analysis of a complex containing a genuine η^1-dialkyliminoacyl ligand,[3] we have, for comparison, also performed a crystal structure analysis of the compound $(\eta^5\text{-}C_5H_5)Mo(CO)_2P(OCH_3)_3(\eta^1\text{-}CH_3CNC_6H_5)$ (III). This complex was formed from II by the addition of $P(OCH_3)_3$. It undoubtedly contains a metal atom with an 18-electron configuration and would most likely present further clarification of an undistorted η^1-iminoacyl ligand. The crystal and molecular structures of both II and III are reported here.

Due to the widespread occurrence of stereochemical nonrigidity in organometallic compounds,[4] and especially compounds of this general type,[5] we have also investigated the ^{13}C NMR spectra of I, III, and $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_2(CH_3CNCH_3)$ (IV). Compounds I and IV were found to be stereochemically nonrigid and mechanisms for the rearrangement are proposed and discussed.

Experimental Section

The compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (I), $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (II), and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (III) were prepared as previously described.[2] $(\eta^5\text{-}CH_3C_5H_4)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ was prepared similarly to I and II.

^{13}C NMR Studies. High-field ^{13}C NMR spectra were recorded on the Southern New England NMR facility at Yale University, operating at 67.88 MHz. Variable-temperature spectra were recorded on the same instrument using a Bruker Model B-ST 100/700 variable-temperature accessary. Temperatures are expected to be accurate to ±2°C. Samples were prepared under nitrogen using degassed solvents in 10-mm NMR tubes sealed with serum caps. Natural abundance spectra were recorded on samples ranging in concentration from approximately 0.2 to 1.0 M. Tris(acetylacetonato)chromium was added in concentrations of about 0.06 M.[6] Data were collected in the Fourier transform mode using 45° pulse widths with 1500–2500 pulses per spectrum. Line-shape analyses were performed using spectra calculated with the program EXCHSYS by Whitesides.[7] The exchange processes were treated as 1:1 exchanges between uncoupled sites. Rearrangement rates were calculated by the relation $k = 1/2\tau$ where τ is the preexchange lifetime. In compound IV three averaging processes were observed (carbonyls and two sets of cyclopentadienyl resonances (cf. Figure 4)). Each exchange process was analyzed individually. A comparison of the results showed that all had very similar exchange lifetimes. Assuming that all three averaging processes were due to only one molecular transformation, we then averaged all three τ values at a given temperature to obtain the final values from which the simulated spectra and activation parameters were calculated. Comparison of experimental and simulated spectra of the cyclopentadienyl carbons reveals that the right-hand pair does not appear to be sharpening as fast as it should theoretically. Examination of these resonances in the slow-exchange region suggests an explanation, namely, experimentally these two resonances exhibit a slight temperature-dependent chemical shift effect which causes them to separate as the temperature is raised. We did not attempt to incorporate this effect into our calculations. The consequence is that experimentally the averaging process will appear to occur more slowly than if the shift separations had not occurred. This is just as we observe.

Structure Analyses. $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (II). Crystals of II were grown from 1:5 toluene:pentane solutions by cooling to −20 °C. Preliminary precession photographs permitted space group identification. Accurate cell parameters were obtained by a least-squares fit of 12 high-angle (2θ = 24–35°) diffractometer-centered reflections. Crystal data are listed in Table I. Crystals of II exhibited substantial decomposition over a period of several days when maintained at room temperature. As a result, data collection was done at −22 ± 2 °C. A crystal of approximate dimensions 0.08 × 0.20 × 0.35 mm bounded by the faces {100}, {010}, and {001} was

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Table I. Experimental X-Ray Diffraction Data

	$(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{-}(\eta^2\text{-}CH_3CNC_6H_5)$	$(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{-}(P(OC_6H_5)_3)(\eta^1\text{-}CH_3CNC_6H_5)$
(A) Crystal Data		
Space group	$P2_1/c$ $[C_{2h}^5]$, No. 14	$P\bar{1}$ $[C_i^1]$, No. 2
Temp, °C	−22	−5
Cell parameters	$a = 7.789$ (4) Å $b = 6.810$ (3) Å $c = 26.754$ (15) Å $\beta = 91.91$ (4)° $V = 1418.3$ Å^3 $\rho_{calcd} = 1.57$ g/cm^3 $\mu = 9.07$ $Z = 4$	$a = 8.475$ (6) Å $b = 10.571$ (8) Å $c = 11.879$ (9) Å $\alpha = 89.46$ (5)° $\beta = 74.95$ (5)° $\gamma = 82.60$ (5)° $V = 1013$ Å^3 $\rho_{calcd} = 1.50$ g/cm^3 $\mu = 7.4$ $Z = 2$
(B) Intensity Measurement Data		
Radiation	Mo Kα	Mo Kα
Monochromator	Graphite	Graphite
Detector aperture	4 × 4 mm	4 × 4 mm
Reflections measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
Max 2θ	55°	55°
Scan type	Coupled θ(crystal)–2θ(counter)	Coupled θ(crystal)–2θ(counter)
Scan speed	2.0°/min	2.0°/min
Scan range	Kα_1 peak − 0.8° to Kα_2 peak + 0.8°	Kα_1 peak − 0.9° to Kα_2 + 0.9°
Backgrounds	Stationary counter–stationary crystal; 4.0 s at each end of scan	Stationary counter–stationary crystal; 4.0 s at each end of scan

mounted in a random orientation and placed on a goniometer head equipped with an Air Products Model AC-1-101A cryo-tip. A surrounding evacuated chamber was enclosed by a thin-walled beryllium shroud. Intensity data were collected on a Picker FACS-1 automatic diffractometer using monochromatized radiation. Data collection statistics are listed in Table I. Three standard reflections, monitored intermittently showed only random ±3% fluctuations. A total of 3632 reflections were collected. Intensities, I, and backgrounds, B, were converted from decacounts to counts by the relations, $I_{counts} = 10I_{decacounts} + 4.5$, and $B_{counts} = 10B_{decacounts} + 4.5$. The raw intensities were corrected for backgrounds according to the relation, $I_{cor} = I_{counts} - (R/2c)(B_1 + B_2)$, where R = scan time, c = background counting time, and B_1 and B_2 were the background counts. $\sigma(I)$ was determined from counting statistics employing a p-factor value of 0.04.[8] After Lorentz and polarization corrections,[9] 1875 reflections were found to have $F^2 > 3\sigma(F^2)$. These reflections were used in the structure solution and refinement. The linear absorption coefficient for Mo Kα radiation is 9.07 and no absorption correction was made.

Solution and Refinement of the Structure of II. The structure was solved by heavy-atom methods. A three-dimensional Patterson synthesis revealed the position of the molybdenum atom. Two cycles of least-squares refinement with an isotropic temperature factor produced the residuals

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$R_w = [\sum_i w_i(|F_o| - |F_c|)^2 / \sum_i w_i F_o^2]^{1/2}$$

of 0.25 and 0.36, respectively. The weights, w_i, were based on the relation $4F_o^2/\sigma^2(F_o^2)$, and the function minimized in the refinement was $\sum w_i(|F_o| - |F_c|)^2$. Neutral atom scattering factors were calculated from the analytical expressions of Cromer and Waber.[10] Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were made for the molybdenum atom.[11] A difference Fourier synthesis next revealed the positions of all remaining nonhydrogen atoms. Two cycles of refinement with an anisotropic temperature factor for the molybdenum atom and isotropic temperature factors for all remaining nonhydrogen atoms produced the residuals $R = 0.058$ and $R_w = 0.069$. Two further cycles of refinement with anisotropic temperature factors for all nonhydrogen atoms yielded the indices $R = 0.048$ and $R_w = 0.056$. A difference Fourier synthesis next revealed the locations of all hydrogen atoms in reasonable positions. Subsequent refinement with anisotropic temperature factors for all nonhydrogen atoms and coordinate refinement on the hydrogen atoms (arbitrarily assigned isotropic temperature factors of 5.0) produced the residuals $R = 0.040$ and $R_w = 0.039$. The final cycles of least squares were done using our newly acquired Enraf-Nonius structure determination program (SDP) library and led to the final discrepancy indices $R = 0.039$ and $R_w = 0.037$.[12] The goodness fit, error in an observation of unit weight, was 1.163. The largest shift vs. error of any parameter, including those of the hydrogen atoms, in the final cycle of refinement was 0.35. A final difference Fourier synthesis showed no significant features. The largest peaks were 0.50, 0.45, and 0.44 e/Å^3 (approximately the size of the hydrogen atoms) and were in the immediate vicinity of the molybdenum atom. The positional and thermal parameters as well as errors (obtained from the elements of the inverse matrix from the final cycle of least squares) are listed in Tables II and III, respectively. A table of final observed and calculated structure factor amplitudes and a packing diagram are available.[13]

$(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (III). Crystals of III suitable for diffraction studies were grown from pentane solutions by cooling to −20 °C. A combination of precession and Weissenberg photography indicated triclinic symmetry. The space group $P\bar{1}$ was chosen and confirmed by the successful solution and refinement. Accurate cell parameters were obtained by a least-squares fit of 12 high-angle (2θ = 20–28°) diffractometer-centered reflections. Crystal data are listed in Table I. Preliminary studies showed that crystals of III were also thermally unstable. A crystal of dimensions 0.125 × 0.175 × 0.20 mm bounded by the planes {100}, {010}, and {001}, was finally selected and mounted on our low-temperature device (vide supra). At −5 °C, data collection was performed. Additional information concerning data collection is listed in Table I. Three standard reflections, monitored intermittently, showed only random fluctuation through the entire course of data collection. A unique

Table II. Atomic Coordinates for Crystalline $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Mo	0.18173 (5)	0.20897 (7)	0.08880 (2)	H1	0.353 (5)	0.371 (7)	0.008 (2)
O1	0.2401 (6)	0.6112 (6)	0.1413 (2)	H2	0.544 (5)	0.247 (6)	0.072 (2)
O2	−0.1457 (5)	0.4487 (6)	0.0632 (2)	H3	0.455 (6)	−0.096 (7)	0.093 (2)
N	0.1507 (5)	0.0593 (5)	0.1584 (1)	H4	0.201 (6)	−0.176 (7)	0.038 (2)
C1	0.2221 (6)	0.4601 (8)	0.1228 (2)	H5	0.144 (5)	0.120 (7)	−0.013 (2)
C2	−0.0232 (6)	0.3571 (8)	0.0724 (2)	H12	0.408 (6)	0.188 (7)	0.202 (2)
C3	0.0234 (6)	0.0264 (7)	0.1310 (2)	H13	0.520 (6)	0.171 (7)	0.283 (2)
C4	−0.1403 (7)	−0.0787 (9)	0.1371 (2)	H14	0.360 (6)	−0.003 (7)	0.340 (2)
CP1	0.3429 (7)	0.2508 (9)	0.0189 (2)	H15	0.115 (6)	−0.143 (7)	0.310 (2)
CP2	0.4563 (6)	0.1778 (9)	0.0569 (2)	H16	0.025 (6)	−0.136 (7)	0.234 (2)
CP3	0.4066 (6)	−0.0120 (9)	0.0680 (2)	H6	−0.118 (6)	−0.208 (7)	0.141 (2)
CP4	0.2627 (7)	−0.0591 (9)	0.0382 (2)	H7	−0.183 (5)	−0.052 (7)	0.171 (2)
CP5	0.2249 (7)	0.1027 (10)	0.0079 (2)	H8	−0.217 (6)	−0.027 (7)	0.116 (2)
C11	0.2039 (6)	0.0355 (7)	0.2087 (2)				
C12	0.3540 (7)	0.1240 (8)	0.2243 (2)				
C13	0.4146 (7)	0.1074 (9)	0.2729 (2)				
C14	0.3242 (8)	0.0026 (8)	0.3065 (2)				
C15	0.1764 (8)	−0.0854 (9)	0.2913 (2)				
C16	0.1136 (7)	−0.0706 (8)	0.2430 (2)				

Table III. Thermal Parameters for Crystalline $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$[c]

Atom	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.1128 (6)	0.1758 (8)	0.0107 (0)	0.0020 (20)	0.0064 (3)	0.0013 (6)
O1	0.340 (10)	0.190 (10)	0.029 (1)	−0.040 (20)	−0.049 (5)	−0.018 (6)
O2	0.194 (7)	0.370 (10)	0.026 (1)	0.210 (20)	−0.020 (4)	0.020 (6)
N	0.123 (7)	0.150 (10)	0.013 (1)	−0.020 (10)	0.005 (4)	−0.002 (4)
C1	0.174 (10)	0.220 (10)	0.013 (1)	−0.040 (20)	−0.026 (5)	0.022 (6)
C2	0.155 (9)	0.240 (10)	0.013 (1)	−0.020 (20)	0.000 (5)	0.006 (6)
C3	0.127 (8)	0.140 (10)	0.016 (1)	0.020 (20)	0.015 (5)	−0.005 (6)
C4	0.190 (11)	0.330 (20)	0.023 (1)	−0.130 (20)	−0.008 (6)	0.038 (8)
CP1	0.193 (10)	0.370 (20)	0.016 (1)	0.060 (20)	0.042 (5)	0.024 (7)
CP2	0.138 (9)	0.350 (20)	0.019 (1)	−0.020 (20)	0.027 (5)	−0.016 (8)
CP3	0.133 (9)	0.320 (20)	0.020 (1)	0.130 (20)	0.018 (5)	−0.014 (7)
CP4	0.187 (11)	0.320 (20)	0.018 (1)	0.030 (20)	0.028 (5)	−0.051 (7)
CP5	0.175 (10)	0.470 (20)	0.012 (1)	0.070 (30)	0.007 (5)	−0.025 (8)
C11	0.151 (9)	0.130 (10)	0.012 (1)	0.050 (20)	0.012 (4)	0.009 (5)
C12	0.200 (11)	0.250 (10)	0.013 (1)	−0.060 (20)	0.001 (5)	0.028 (6)
C13	0.214 (12)	0.280 (20)	0.019 (1)	−0.050 (30)	−0.030 (6)	0.011 (8)
C14	0.275 (13)	0.250 (20)	0.012 (1)	0.150 (20)	−0.008 (6)	0.004 (6)
C15	0.280 (13)	0.290 (20)	0.016 (1)	0.010 (30)	0.043 (6)	0.056 (7)
C16	0.215 (11)	0.230 (10)	0.018 (1)	−0.090 (20)	0.016 (6)	0.029 (7)

[a] The form of the expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Anisotropic temperature factors multiplied by 10.0. [c] All hydrogen atoms were assigned isotropic temperature factors of 5.0. This value was not refined.

set of data consisting initially of 5318 reflections was collected. The raw data were processed as before (vide supra). $\sigma(I)$ was calculated employing a p factor of 0.04. After data reduction,[9] a total of 2621 reflections were found to conform to the relation $F^2 > 3\sigma(F^2)$. These data were used in the structure solution and refinement. The linear absorption coefficient for III is 7.70 and no absorption correction was applied.

Solution and Refinement of the Structure of III. The structure was solved by heavy-atom methods. A three-dimensional Patterson synthesis provided the coordinates of the molybdenum atom. Three cycles of least-squares refinement with an isotropic temperature factor provided values for the unweighted and weighted residuals, R and R_w, as 0.319 and 0.415, respectively. The weights, w, were based on the relation $4F_o^2/\sigma^2(F_o^2)$, and the function minimized was $\sum w_i(|F_o| - |F_c|)^2$. Neutral atom scattering factors were calculated,[10] and anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were made for the molybdenum atom.[11] A difference Fourier synthesis next revealed the position of the phosphorus atom, and two cycles of refinement with isotropic temperature factors produced the residuals $R = 0.257$ and $R_w = 0.365$. A difference Fourier synthesis at this time revealed the location of all remaining nonhydrogen atoms in chemically reasonable positions. However, subsequent refinement produced uncomfortably large temperature factors on the oxygen atoms of two of the methoxyl groups. An additional cycle was performed omitting all three methoxyl groups on the phosphorus atom. At this time the residuals were $R = 0.161$ and $R_w = 0.247$. A difference Fourier next revealed the nature of the refinement problem of the methoxyl groups. While one methoxyl group appeared to be normal, the other two showed a disorder phenomenon in which each oxygen atom occupied two different sites while the methyl groups attached to them occupied one and the same site (i.e., the methyl groups appeared as ordered). The relative intensities of the disordered oxygen atoms indicated that the disorder was not equal but approximately 2:1 in each case. A model was devised in which each disorder was treated equivalently and the occupancies conformed to the relation α and $1 - \alpha$. Two cycles of least-squares refinement were performed on the methoxyl groups with isotropic temperature factors and an occupancy factor α, starting at a value of 0.66 for the oxygen atoms labeled A, see Figure 3. This refinement proceeded adequately and produced credible temperature factors. The value of α changed to 0.63. The residuals at this stage were $R = 0.099$ and $R_w = 0.114$. Two further cycles of refinement with anisotropic temperature factors for all atoms produced residuals of $R = 0.065$ and $R_w = 0.076$. However, atom C3 on the seemingly undistorted methoxyl group developed a negative temperature factor. This atom had previously maintained a relatively large isotropic temperature factor (approximately 9.5), and we now suspected an unresolved disorder. As a result of the accumulating difficulties, we decided that subsequently we would refine all three methoxyl groups with isotropic temperature factors, yet allow the occupancy factor, α, to vary. Hydrogen atom positions were calculated for the cyclopentadienyl and phenyl rings. A difference Fourier synthesis showed that many of the calculated hydrogen positions corresponded to the positions of peaks in a list of the 50 largest peaks in this Fourier. Two peaks close to the methyl carbon, C7, were accepted as hydrogen atoms and were used to calculate the position of the third, assuming a tetrahedral geometry about the carbon. Hydrogen atoms were added to the least-squares calculation, using isotropic temperature factors of 5.0, but were not refined. No attempt was made to place hydrogen atoms on the methoxyl groups. Refinement converged with two additional cycles (isotropic temperature factors on methoxyl groups) and gave the final reliability indices, $R = 0.067$ and $R_w = 0.075$. The final value for α was 0.66. The error in an observation of unit weight was 1.78. The largest shift vs. error value on the final cycle of refinement was 0.16 among all atoms excluding the methoxyl groups and 0.52 for those of the methoxyl groups. The largest peaks in a final difference Fourier synthesis were approximately 1.4 e/Å^3 and were in the immediate vicinity of the phosphite ligand. No further attempts to sort out residual disorder, locate methoxyl hydrogens, or achieve anisotropic refinement on the methoxyl atoms were made. The positional and thermal parameters with errors (obtained from the elements of the inverse matrix on the final cycle of least squares) are listed in Table IV and V. A table of final observed and calculated structure factor amplitudes and a packing diagram are available.

Results

Description of the Structure of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (II). The molecular structure of II is shown in Figure 1. Intramolecular bond distances and angles are listed in Table VI. The compound contains a normal η^5-cyclopentadienyl ring and two linear carbonyl groups, but the most interesting feature is a well-defined dihapto, $CH_3CNC_6H_5$, iminoacyl ligand. The internuclear distance Mo–C3 = 2.106 (5) Å compares favorably with the Mo–C distances of 2.157 (6) and 2.135 (6) Å that were recently found for a η^2-acetylene in the compound $(\eta^5\text{-}C_5H_5)Mo(CF_3C_2CF_3)[C(CF_3){=}C(CF_3)C_5H_5]$.[14] The Mo–N distance of 2.143 (4) Å is similar to the Mo–N distances of 2.134 (3) and 2.184 (3) Å that were found for a η^2-hydrazine ligand in the complex, $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NH_2NHC_6H_5)][BF_4]$[15] and the 2.114 (9) and 2.126 (8) Å Mo–N distances found for the η^2-triazenido ligand in the complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2[(3,5\text{-}(CH_3)_2C_6H_3)_2N_3]$.[16] The short C3–N distance of 1.233 (6) Å is considerably shorter than the 1.29–1.31 Å generally accepted for an uncoordinated double bond[17,18] but also significantly longer than the 1.16 Å found for C–N triple bonds in organonitriles.[20] The phenyl and methyl groups are folded away from the metal atom with the angles C4–C3–N and C11–N–C3 being 134.7 (5) and 138.9 (6)°, respectively. The planar phenyl ring appears to be normal with a mean C–C

Table IV. Atomic Coordinates for Crystalline $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNC_6H_5)(P(OCH_3)_3)^a$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Mo	0.46292 (10)	0.21121 (8)	0.19334 (8)	C3	0.7899 (21)	0.5510 (15)	0.1791 (14)
P	0.6997 (3)	0.3159 (3)	0.1830 (2)	O4A	0.8267 (14)	0.2675 (11)	0.2503 (10)
O1	0.7282 (9)	0.9761 (7)	0.1882 (8)	O4B	0.7645 (23)	0.3298 (18)	0.3092 (17)
C1	0.6355 (12)	0.0642 (10)	0.1903 (9)	C4	0.7974 (16)	0.2291 (12)	0.3684 (12)
O2	0.3683 (10)	0.3361 (7)	0.4410 (6)	O5A	0.8262 (15)	0.3257 (12)	0.0547 (11)
C2	0.4090 (12)	0.2848 (9)	0.3525 (10)	O5B	0.8725 (22)	0.2555 (17)	0.1031 (15)
CP1	0.2273 (13)	0.3036 (17)	0.1474 (11)	C5	0.1027 (15)	0.7851 (12)	0.0160 (11)
CP2	0.3450 (17)	0.3801 (10)	0.1036 (11)	H1	0.129	0.333	0.211
CP3	0.4636 (14)	0.3084 (14)	0.0173 (10)	H2	0.349	0.468	0.127
CP4	0.5818 (18)	0.8077 (12)	−0.0076 (10)	H3	0.563	0.340	−0.027
CP5	0.2688 (21)	0.1890 (15)	0.0906 (15)	H4	0.480	0.124	−0.046
C11	0.2369 (14)	0.8556 (9)	0.2862 (8)	H5	0.201	0.121	0.108
C12	0.3327 (16)	0.7454 (11)	0.3000 (10)	H12	0.454	−0.255	0.284
C13	0.2644 (24)	0.6398 (14)	0.3376 (13)	H13	0.337	−0.439	0.348
C14	0.1068 (30)	0.6353 (15)	0.3632 (14)	H14	0.059	−0.444	0.390
C15	0.0009 (20)	0.7441 (17)	0.3495 (12)	H15	−0.122	−0.258	0.366
C16	0.0675 (16)	0.8542 (12)	0.3099 (11)	H16	−0.009	−0.067	0.301
C6	0.3496 (12)	0.0474 (9)	0.2949 (9)	H6	0.238	−0.024	0.464
C7	0.3160 (21)	0.0376 (13)	0.4259 (10)	H7	0.299	0.115	0.458
N	0.3086 (11)	0.9630 (8)	0.2372 (7)	H8	0.428	0.002	0.428
O3	0.6630 (11)	0.4619 (8)	0.1920 (7)				

[a] Hydrogen atom positions were not refined.

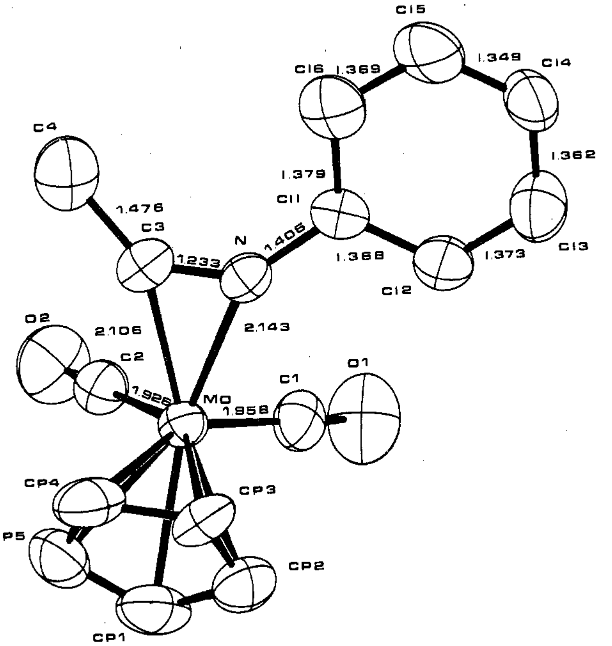


Figure 1. An ORTEP diagram of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$, showing 50% probability ellipsoids. Hydrogen atoms have been omitted.

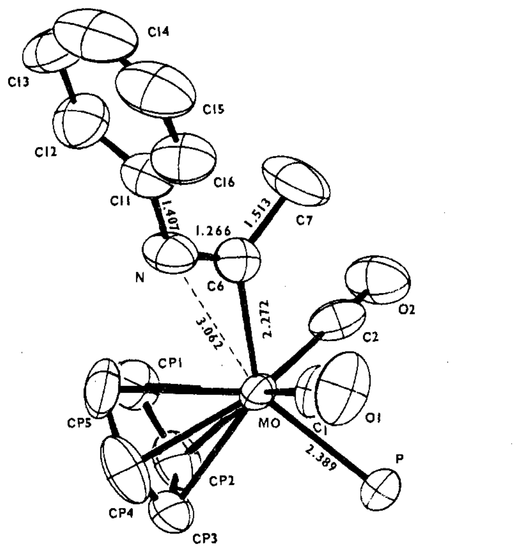


Figure 2. An ORTEP diagram of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ minus the methoxyl groups and hydrogen atoms. The 50% probability ellipsoids are shown.

bond distance of 1.367 Å. The maximum deviation of an atom from its least-squares plane is only 0.003 Å (cf. Table VII). The ring is essentially coplanar with the plane of the iminoacyl ligand formed by atoms C4–C3–N–C11. The dihedral angle between the planes is only 5.4°. There are no abnormally short intermolecular contacts. The shortest distance between nonhydrogen atoms is between a carbonyl oxygen and an iminoacyl nitrogen at 3.169 Å.[13]

Description of the Structure of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (III). The molecular structure of III minus the methoxyl groups of the phosphite ligand is shown in Figure 2. Important intramolecular distances and angles are listed in Table VIII. The compound contains a regular η^5-cyclopentadienyl ring, two linear carbonyl groups, a phosphite ligand, and an η^1-iminoacyl ligand. The gross geometry conforms to that characteristic of the molecules $(\eta^5\text{-}C_5H_5)MoL_4$, which has been described as pseudo square pyramidal with the cyclopentadienyl ring occupying a single coordination site at the apex. In this case, the carbonyl groups lie on opposite sides of the square base in what is frequently referred to as the trans configuration. The C1–Mo–C2 angle of 105.0 (5)° is typical of these complexes.[21-23] The Mo–P distance of 2.389 (3) Å is very similar to the Mo–P distances of 2.406 (9) and 2.388 (8) Å that were found for the structurally analogous complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)I$ and $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_2(P(OCH_3)_3)I$.[23] The η^1-iminoacyl ligand has no unusual distortions. The bonding Mo–C6 distance of 2.272 (10) Å and the nonbonding Mo···N distance of 3.062 (9) Å are essentially equal to the bonding Mo–C = 2.264 (10) Å and nonbonding Mo···O = 3.068 (10) Å distances that were found for the η^1-acetyl ligand in the complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(C_6H_5)_3)(\eta^1\text{-}COCH_3)$.[21] The nonbonding Mo···N distance is also very similar to the nonbonding Pt···N distance of 3.042 (10) Å that was found for the η^1-iminoacyl group in the complex *trans*-$Pt(I)[C(CH_3){=}N(C_6H_4Cl)](P(C_2H_5)_3)_2$ (V).[3] The C–N distance of 1.266 (12) Å is appreciably longer than the corresponding distance in the η^2-iminoacyl ligand (vide supra) but similar to the 1.287(13) Å found for the η^1-iminoacyl ligand in V.[3] As indicated in Table IX, the iminoacyl group, as defined by atoms C7, C6, N, and C11, the phenyl ring, and the cyclopentadienyl ring

Table V. Thermal Parameters for Crystalline (η^5-C_5H_5)Mo(CO)$_2$($CH_3CNC_6H_5$)(P(OCH_3)$_3$)

Atom	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.0804 (12)	0.0722 (8)	0.0621 (7)	−0.0172 (8)	−0.0215 (7)	−0.0103 (7)
P	0.107 (4)	0.104 (3)	0.077 (3)	−0.032 (3)	−0.029 (3)	0.009 (2)
O1	0.173 (15)	0.107 (9)	0.201 (11)	0.050 (10)	−0.092 (11)	−0.020 (8)
C1	0.113 (17)	0.095 (12)	0.097 (10)	−0.005 (12)	−0.050 (11)	−0.004 (9)
O2	0.278 (19)	0.125 (10)	0.078 (7)	−0.037 (11)	0.011 (10)	−0.019 (7)
C2	0.134 (18)	0.067 (10)	0.097 (11)	−0.015 (12)	0.005 (12)	0.006 (9)
CP1	0.082 (17)	0.270 (25)	0.099 (13)	0.020 (19)	−0.032 (12)	0.050 (15)
CP2	0.248 (27)	0.092 (13)	0.107 (13)	0.016 (16)	−0.088 (16)	0.013 (10)
CP3	0.158 (22)	0.184 (18)	0.083 (11)	−0.043 (17)	−0.055 (13)	0.062 (12)
CP4	0.304 (32)	0.096 (13)	0.093 (12)	0.071 (18)	−0.104 (17)	−0.021 (11)
CP5	0.318 (35)	0.173 (19)	0.181 (20)	−0.165 (23)	−0.191 (23)	0.106 (16)
C11	0.231 (24)	0.067 (11)	0.069 (9)	−0.024 (14)	−0.022 (13)	−0.002 (8)
C12	0.267 (28)	0.092 (13)	0.111 (13)	−0.021 (17)	−0.013 (15)	0.006 (11)
C13	0.497 (51)	0.097 (16)	0.121 (15)	−0.050 (25)	−0.029 (24)	0.018 (12)
C14	0.690 (74)	0.114 (18)	0.103 (15)	−0.200 (34)	−0.017 (28)	−0.010 (14)
C15	0.356 (40)	0.239 (25)	0.105 (14)	−0.214 (28)	0.010 (18)	−0.022 (16)
C16	0.258 (29)	0.127 (16)	0.123 (14)	−0.064 (18)	−0.045 (17)	−0.006 (12)
C6	0.137 (18)	0.080 (11)	0.076 (9)	−0.001 (12)	−0.026 (11)	0.007 (8)
C7	0.640 (53)	0.189 (19)	0.076 (11)	−0.230 (27)	−0.093 (20)	0.049 (12)
N	0.236 (19)	0.077 (9)	0.074 (8)	−0.043 (11)	−0.022 (10)	0.018 (7)

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
O3	7.46 (22)	O4B	3.67 (39)	O5B	3.45 (37)
C3	9.98 (45)	C4	6.82 (29)	C5	6.26 (29)
O4A	5.02 (38)	O5A	6.42 (29)		

[a] The form of the expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Anisotropic temperature factors multiplied by 10.0. [c] Thermal parameters for the hydrogen atoms were fixed at 5.0.

Table VI. Pertinent Bond Distances and Angles for (η^5-C_5H_5)Mo(CO)$_2$(η^2-$CH_3CNC_6H_5$)

Distance, Å			
Mo–C1	1.958 (6)	CP4–CP5	1.392 (9)
Mo–C2	1.926 (5)	C1–O1	1.148 (6)
Mo–C3	2.106 (5)	C2–O2	1.160 (6)
Mo–N	2.143 (4)	C3–C4	1.476 (8)
Mo–CP1	2.304 (5)	C3–N	1.233 (6)
Mo–CP2	2.338 (5)	N–C11	1.406 (6)
Mo–CP3	2.389 (5)	C11–C12	1.368 (7)
Mo–CP4	2.371 (6)	C11–C16	1.379 (7)
Mo–CP5	2.317 (6)	C12–C13	1.373 (7)
CP1–CP2	1.415 (8)	C13–C14	1.362 (8)
CP1–CP5	1.389 (9)	C14–C15	1.349 (9)
CP2–CP3	1.385 (8)	C15–C16	1.369 (8)
CP3–CP4	1.392 (8)		

Angle, Deg			
C1–Mo–C2	76.6 (2)	CP4–CP5–CP1	109.0 (6)
C3–Mo–N	33.7 (2)	C3–N–C11	138.9 (4)
Mo–C1–O1	176.8 (5)	N–C3–C4	134.7 (5)
Mo–C2–O2	178.8 (5)	N–C11–C12	117.6 (4)
Mo–C3–C4	150.3 (4)	N–C11–C16	123.9 (5)
Mo–C3–N	74.8 (3)	C12–C11–C16	118.6 (5)
Mo–N–C3	71.5 (3)	C11–C12–C13	121.0 (5)
Mo–N–C11	148.1 (3)	C12–C13–C14	119.9 (6)
CP2–CP1–CP5	106.8 (6)	C13–C14–C15	119.2 (6)
CP1–CP2–CP3	108.1 (6)	C14–C15–C16	121.8 (6)
CP2–CP3–CP4	108.5 (6)	C15–C16–C11	119.4 (6)
CP3–CP4–CP5	107.6 (6)		

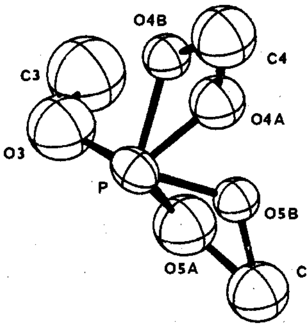


Figure 3. An ORTEP diagram of the phosphite ligand from (η^5-C_5H_5)Mo(CO)$_2$(P(OCH_3)$_3$)(η^1-$CH_3CNC_6H_5$) showing 50% probability ellipsoids.

Table VII. Various Weighted Least-Squares Planes for (η^5-C_5H_5)Mo(CO)$_2$(η^2-$CH_3CNC_6H_5$)

Plane no.	Atoms	Dist from plane, Å
1	C4	0.008 (6)
	C3	−0.021 (5)
	N	0.022 (4)
	C11	−0.009 (5)
2	C11	0.000 (5)
	C12	−0.001 (6)
	C13	0.002 (6)
	C14	−0.003 (6)
	C15	0.003 (6)
	C16	−0.001 (6)
3	CP1	0.001 (5)
	CP2	−0.003 (5)
	CP3	0.004 (5)
	CP4	−0.004 (6)
	CP5	0.002 (6)
	Mo[a]	2.019

Selected Dihedral Angles between Planes

Planes	Angles, deg	Planes	Angles, deg
1–2	5.4	2–3	38.7
1–3	41.5		

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	0.4318	−0.8678	−0.2458	−0.9681
2	0.5145	−0.8234	−0.2391	−0.8130
3	0.6210	−0.3569	−0.6979	0.6844

[a] These atoms were not used in the calculation of the plane.

are each planar. However, unlike the configuration in II, the phenyl ring in III is rotated 85.6° from the plane of the iminoacyl group.

The phosphite ligand showed disorder in two of the three methoxyl groups. The nature of this disorder is shown in Figure 3. The disorder is such that the oxygen atoms are disordered while the methyl groups attached to them are ordered. A similar order–disorder phenomenon was observed in one of the trimethyl phosphite ligands in the complex (η^5-C_5H_5)Mo(Cl)(P(OCH_3)$_3$)$_2$(C═C(CN)$_2$).[24] The crystal shows no unusually short intermolecular contacts. A table of

Table VIII. Intramolecular Atomic Distances and Bond Angles for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$

Distances, Å

Mo–C1	1.986 (10)	C13–C14	1.298 (23)
Mo–C2	1.969 (12)	C14–C15	1.401 (22)
Mo–C6	2.272 (10)	C15–C16	1.385 (17)
Mo···N	3.062 (9)	CP1–CP2	1.360 (17)
Mo–P	2.389 (3)	CP1–CP5	1.352 (18)
Mo–CP1	2.300 (10)	CP2–CP3	1.385 (15)
Mo–CP2	2.320 (10)	CP3–CP4	1.347 (16)
Mo–CP3	2.320 (10)	CP4–CP5	1.393 (18)
Mo–CP4	2.348 (11)	P–O3	1.534 (8)
Mo–CP5	2.324 (11)	P–O4A	1.535 (11)
C1–O1	1.134 (10)	P–O4B	1.739 (19)
C2–O2	1.136 (11)	P–O5A	1.631 (13)
C6–C7	1.513 (14)	P–O5B	1.581 (18)
C6–N	1.266 (12)	O3–C3	1.497 (18)
N–C11	1.407 (12)	O4A–C4	1.425 (15)
C11–C12	1.366 (14)	O4B–C4	1.310 (20)
C11–C16	1.391 (16)	O5A–C5	1.419 (15)
C12–C13	1.343 (17)	O5B–C5	1.437 (20)

Angles, Deg

C1–Mo–C2	105.0 (4)	O4B–P–O5B	96.4 (9)
C1–Mo–C6	69.8 (4)	P–O3–C3	125.1 (9)
C1–Mo–P	78.3 (3)	P–O4A–C4	128.3 (10)
C2–Mo–C6	80.4 (4)	P–O4B–C4	121.1 (15)
C2–Mo–P	79.4 (3)	P–O5A–C5	121.0 (10)
C6–Mo–P	135.9 (3)	P–O5B–C5	123.3 (13)
Mo–C1–O1	176.3 (9)	CP5–CP1–CP2	109.7 (12)
Mo–C2–O2	173.5 (9)	CP1–CP2–CP3	106.2 (11)
Mo–C6–C7	123.6 (8)	CP2–CP3–CP4	109.6 (11)
Mo–C6–N	116.9 (7)	CP3–CP4–CP5	106.9 (11)
Mo–P–O3	114.0 (4)	CP4–CP5–CP1	107.6 (12)
Mo–P–O4A	121.4 (4)	C7–C6–N	119.4 (9)
Mo–P–O4B	118.4 (6)	C6–N–C11	124.3 (9)
Mo–P–O5A	117.3 (5)	N–C11–C12	120.9 (11)
Mo–P–O5B	119.2 (7)	N–C11–C12	120.7 (11)
O3–P–O4A	110.6 (6)	C16–C11–C12	118.1 (11)
O3–P–O4B	84.9 (7)	C11–C12–C13	120.7 (14)
O3–P–O5A	89.9 (6)	C12–C13–C14	123.2 (17)
O3–P–O5B	117.6 (8)	C13–C14–C15	119.4 (15)
O4A–P–O5A	98.5 (6)	C14–C15–C16	118.9 (15)
O4A–P–O5B	65.7 (8)	C15–C16–C11	119.8 (13)
O4B–P–O5A	120.8 (8)		

Table IX. Various Unweighted Least-Squares Planes for $(\eta^5\text{-}C_5H_5)Mo(CO)_2P(OCH_3)_3(\eta^1\text{-}CH_3CNC_6H_5)$

Plane no.	Atoms	Dist from plane, Å
1	C7	0.0091
	C6	−0.0086
	N	0.0037
	C1	−0.0042
2	C11	0.0098
	C12	−0.0023
	C13	−0.0068
	C14	0.0076
	C15	0.0005
	C16	−0.0088
3	CP1	0.0016
	CP2	−0.0043
	CP3	0.0054
	CP4	−0.0044
	CP5	0.0016
	Mo[a]	2.0098

Dihedral Angle between the Planes

Planes	Angle, deg	Planes	Angle, deg
1–2	85.6	2–3	47.9
1–3	131.0		

Equations of the Planes of the Form $AX + BY + CZ = D$

Plane	A	B	C	D
1	−7.183	4.263	−1.431	−2.723
2	1.611	2.883	10.937	3.086
3	5.370	−2.825	9.621	1.780

[a] This atom was not used to define the plane.

Table X. 67.88-MHz ^{13}C NMR Spectra of Compounds I, III, and IV

Compd	Temp, °C	Shift (ppm vs. Me_4Si)
I	−10	18.88 (CH_3);[a] 36.65 (NCH_3); 93.91 (C_5H_5); 195.15 (C=N); 249.97 (CO); 252.63 (CO)
III	30	52.22 (CH_3),[b] $J_{P-C} = 4.5$ Hz; 94.61 (C_5H_5); 120.44 (OCH_3), $J_{P-C} =$ 156 Hz; 155.49 (C=N); 237.33 (CO), $J_{P-C} = 38.5$ Hz[c]
IV	−10	13.70 $(CpCH_3)$; 18.74 $(C\text{-}CH_3)$; 35.50 (NCH_3); 90.28, 90.64, 94.12, 94.81 $(C_4H_4CCH_3)$;[d] 114.55 $(C_4H_4CCH_3)$;[e] 196.99 (C=N); 250.90 (CO); 253.06 (CO)

[a] In toluene-d_8. [b] In C_6D_6. [c] Carbons of phenyl ring not observed, probably obscured by solvent. [d] Resonances from ring carbons containing hydrogen substituents. [e] Ring carbon containing methyl substituent.

intermolecular contacts and a packing diagram have been provided.[13]

^{13}C NMR Studies. Table X lists the chemical shifts and resonance assignments of compounds I, III, and IV. Although the chemical shifts of the cyclopentadienyl, carbonyl and methyl groups appear to be normal,[25,26] the shift of the imino carbon in compound III at 155.5 ppm is nearly 100 ppm upfield from the shift of the corresponding carbon in η^1-acyl ligands.[27] However, this is similar to the approximately 75 ppm upfield shifts that occur for coordinated carbene carbons when the substituents are changed from OR to NR_2.[25] Interestingly, the imino carbons of the η^2-iminoacyl ligands in I and IV are shifted approximately 40 ppm to lower field values than that of the η^1-iminoacyl ligand.

The most interesting aspect of the ^{13}C NMR of these compounds is the variable-temperature spectra of I and IV. Figure 1 clearly shows that the carbonyl groups of II are inequivalent. Spectroscopically, we have shown that compounds I and IV are structurally similar.[2,28] At −10 °C the spectrum of each compound shows a separate resonance for each of the carbonyl carbons. However, as the temperature is raised, the resonances broaden, coalesce, and re-form as sharp singlets at approximately +60 °C. The broadening is reversible, independent of concentration (over a factor of at least 2), and independent of solvent.[30] Labeling with the prochiral group, $C_5H_4CH_3$, as in IV, has provided additional and mechanistically significant information (vide infra). The variable-temperature spectra of the $(\eta^5\text{-}C_5H_4CH_3)$ and CO groups in IV are shown in Figure 4. The cyclopentadienyl (Cp) resonance labeled X is due to a portion of compound I present in the sample.[31] The asymmetry of molecule IV causes each carbon atom in the $C_5H_4CH_3$ ring to be chemically inequivalent, and as shown in the lowest temperature spectrum, a separate resonance is observed for each of those carbon atoms which bears a hydrogen substituent. As the temperature is raised, these four cyclopentadienyl resonances as well as the carbonyl resonances broaden. The cyclopentadienyl resonances coalesce in pairs and result in two singlets at higher temperatures. The carbonyl resonances coalesce at slightly higher temperatures. In addition, in sample mixtures, we find that in the fast-exchange limit there is no evidence for interchange of the carbonyl carbons or the carbons of the iminoacyl ligands between I and IV.

Discussion

The structure of II shows unequivocally that both the nitrogen and carbon atoms of the iminoacyl ligand are formally

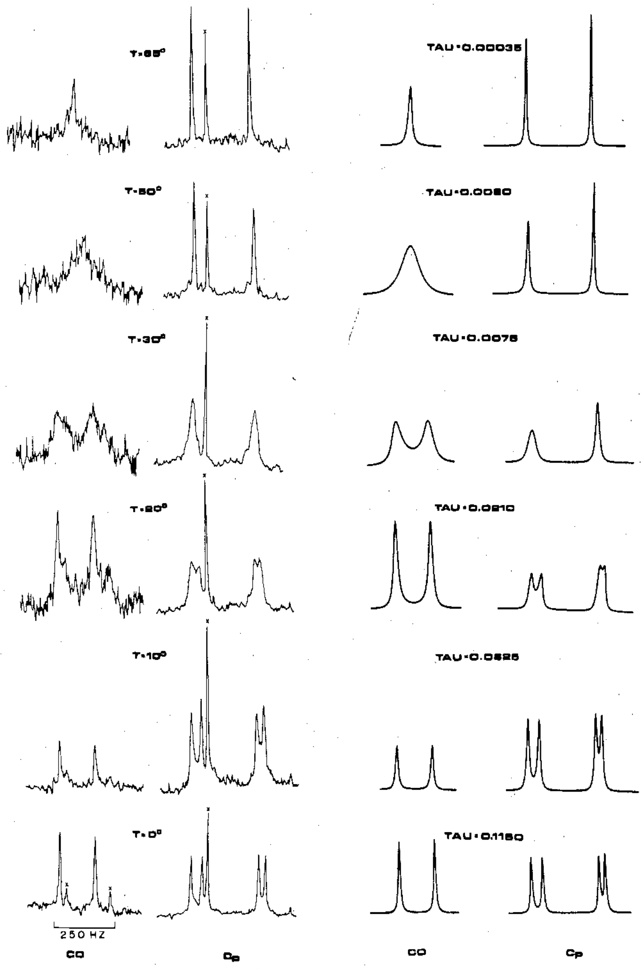
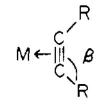
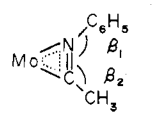


Figure 4. Variable-temperature 67.88-MHz ^{13}C NMR spectra of carbonyl and cyclopentadienyl carbons of $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ in toluene-d_8 solvent. Peaks labeled × are due to a small amount of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ impurity also present in the sample. Computer-simulated spectra with the indicated mean residence times in seconds are shown on the right-hand side.

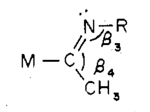
bonded to the molybdenum atom. This confirms the dihapto structure **1**. In this form the iminoacyl ligand can be viewed as a three-electron donor with the metal atom then achieving an 18-electron configuration. The ligand resembles that of a coordinated acetylene. It is well known that upon coordination the R substituents of the linear acetylene fold back away from the coordination site. The fold angle β as shown in A is known to range from 138 to 172°[32] but generally lies in the range 140–150°. This is similar to the angles β_1 and β_2 of 138.9 (4) and 134.7 (5)° found for the η^2-iminoacyl ligand of II, B. The corresponding angles β_3 and β_4 of η^1-iminoacyl ligands are still more acute, being 124.3 (9) and 119.4 (9) for III and 125.4 (10) and 115.4 (10)° for V,[3] C.



A



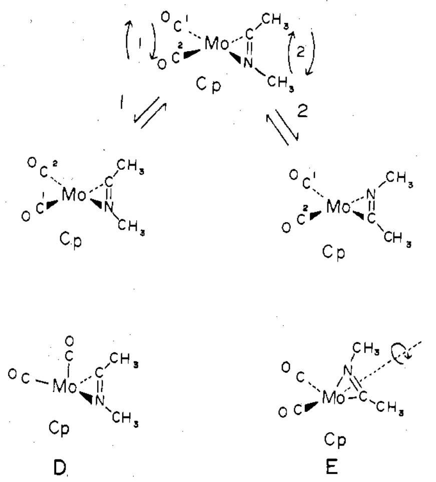
B



C

The imino C–N bond distance in the η^2-iminoacyl ligand is considerably shorter than the corresponding distance in the η^1-iminoacyl ligands of both III and V. In sum, it appears that $\eta^1 \rightarrow \eta^2$ transformation causes the ligand to become more acetylenic in character. The C–N bond is strengthened and the β angles increase and approach values typical of coordinated acetylenes. This strengthening of the C–N bond is also indicated by the C–N stretching vibration. The C–N stretching frequencies of I and II are 1720 and 1680 cm^{-1}, respectively. These are significantly higher than the corresponding frequencies found for η^1-iminoacyl ligands which generally lie in the range 1580–1620 cm^{-1}.[33] The C–N stretching vibration in III occurs at 1570 cm^{-1}.[2]

Scheme I



There have been scattered reports concerning the physical nature of η^2-acyl ligands. The only structure analysis[34a] shows that the C–O bond distance of 1.211(8) Å is essentially the same as that found for η^1-acyl ligands. Claims that the C–O stretching vibration of the η^2-acyl ligand lie at lower energy than those of the monohapto ligand contrast with our results. While this may be true, we feel that additional confirmations through more thorough investigations of the acyl system are necessary.

III, which contains a normal η^1-iminoacyl ligand, contains a phenyl ring which is nearly perpendicular to the plane of the iminoacyl group. It appears that the lone pair of electrons on the nitrogen atom may be interacting with the π system of the ring. In contrast, the plane of the phenyl ring in II is nearly parallel to the plane of the iminoacyl ligand. Evidently, the π system of the ring is now conjugated to the π system of the imino group. This difference is understandable since the lone pair on the nitrogen atom in II is coordinated to the metal atom and is thus not available for interaction with the ring.

The addition of donor molecules to I and II proceeds smoothly and produces new molecules containing η^1-iminoacyl ligands. Thus, the addition of another electron pair to the metal atom induces the release an electron pair to the nitrogen atom of the iminoacyl ligand and results in the dihapto to monohapto transformation. This transformation is demonstrated by the formation of III, where the added donor was trimethyl phosphite. Although the phosphite ligand is positioned trans to the iminoacyl ligand, one cannot conclude that initial attack of the phosphite on the metal atom also occurred at that site. Indeed, some studies have shown that phosphine-promoted carbonyl insertions do occur with a cis addition and this is followed by intramolecular isomerization to yield a trans product.[39]

The variable-temperature ^{13}C NMR spectra of I establish that the carbonyl ligands are rapidly exchanging their environments at room temperature. Topologically, the transformation can be represented by either of rearrangements **1** or **2** (Scheme I). Through rearrangement **1**, the exchange of carbonyl environments is accomplished through an interchange of the coordination sites of the carbonyl ligands. Mechanistically, this could occur via a polytopal rearrangement at the metal atom which might traverse an intermediate such as D. A thorough analysis of related rearrangements has been carried out for the molecules (η^5-C_5H_5)Mo(CO)$_2$(L)X (L = PR_3; X = H, R, Cl, Br, I).[5] Through rearrangement **2**, the carbonyl ligands remain fixed, but their environments are exchanged as a result of an interchange of the C and N coordination sites of the iminoacyl ligand. Three mechanisms which could account for this transformation are (a) a 180° rotation of the dihapto ligand about an axis defined by the metal atom and the center of the C–N bond, passing through an intermediate such as E, (b) a breaking of the Mo–N bond (i.e., conversion to a monophato ligand), a 180° rotation about the Mo–C bond, and a re-formation of the Mo–N bond, and (c) complete dissociation of the iminoacyl ligand, followed by a 180° rotation and reassociation.

The investigation of IV allows us to distinguish between rearrangements **1** and **2**. Figure 4 shows that the four diastereotopic carbon atoms, which bear the hydrogen substituents in the methylcyclopentadienyl ring, are averaged in sets of two at rates equivalent to those of the carbonyl interchange. This observation clearly allows us to rule out rearrangement **1** since this rearrangement would not produce a change in the environments of the carbon atoms in the ring. Within the framework of rearrangement **2**, we may also rule out mechanism **2c** since mixtures of I and IV showed no evidence of intermolecular exchange of the iminoacyl ligands.[40] The distinction between mechanisms **2a** and **2b** is based primarily on the degree to which the Mo–N bond is broken in the course of the 180° rotation. We might expect that if the Mo–N bond were completely broken the stability of the coordinatively unsaturated intermediate would be influenced by the coordinating ability of the solvent. This should effect the rate of the rearrangement. Since we found no evidence of a solvent effect, we prefer to describe the rearrangement by mechanism **2a** through which we would not expect to observe a significant solvent effect on the rearrangement rate. Although mechanism **2a** does fall within the scope of the polytopal rearrangement,[5] it is probably best compared to that of the rotational behavior of coordinated monoolefins.[41,42] Pertinent comparisons can be made to the acetylene complexes (η^5-C_5H_5)Cr(CO)(NO)(C_2H_2)[43] and [(η^5-C_5H_5)Mo(dppe)$C_2(CH_3)_2$]PF_6[44] which showed rotational behavior with activation barriers of $\Delta G^{\ddagger}_{T_c}$ = 12–14 kcal/mol. In contrast, however, is the dynamic activity of the complexes (η^5-C_5H_5)M(CO)$_2$[η^2-(3,5-$(CF_3)_2C_6H_3$)N_3(C_5H_4-4-CH_3)], M = Mo and W) which contain η^2-triazenido ligands and which were reported to rearrange by interchange of the carbonyl ligands (mechanism 1).[45]

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Registry No. I, 60954-80-5; II, 62200-85-5; III, 64440-73-9; IV, 64440-72-8.

Supplementary Material Available: Observed and calculated structure factor amplitudes, root mean square amplitudes of vibration, selected intermolecular contacts, crystal packing diagrams, and molecular diagrams showing all atoms for both structures (38 pages). Ordering information is given on any current masthead page.

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