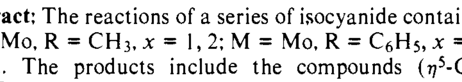
# Isocyanide Insertion Reactions. 1. The Importance of $\eta^2$-Iminoacyl Ligands as Intermediates[1]

**Richard D. Adams* and Daniel F. Chodosh**

*Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520.* *Received April 20, 1977*

**Abstract:** The reactions of a series of isocyanide containing organometallic anions of the type $(\eta^5\text{-}C_5H_5)M(CO)_{3-x}(CNR)_x^-$, M = Mo, R = $CH_3$, $x$ = 1, 2; M = Mo, R = $C_6H_5$, $x$ = 1; and M = W, R = $CH_3$, $x$ = 1, with methyl iodide have been investigated. The products include the compounds $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (IV) and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (V), which contain novel dihapto iminoacyl ligands. Reaction of the tungsten anion produces the complex $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)(CH_3)$ (VI), in which the methyl group is attached to the tungsten atom. Complexes IV and V readily add the ligands tetracyanoethylene, trimethyl phosphite, and triphenylphosphine to the metal atoms in a process that converts the $\eta^2$-iminoacyl group into an $\eta^1$-iminoacyl group. Addition of iodide ion to IV ultimately leads to formation of the complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(I)[C(CH_3)(N(H)(CH_3)]$ (XI), which contains a methyl methylaminocarbene ligand. Reaction of the anion, $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$, with methyl iodide produces the complex $(\eta^5\text{-}C_5H_5)Mo(CO)I[C(N(CH_3)_2)C(CH_3)N(CH_3)]$ (XII). This compound was investigated by crystal structure analysis. Space group: $P\bar{1}\text{-}C_i^1$, $a = 8.296$ (4), $b = 7.492$ (4), $c = 13.945$ (8) Å, $\alpha = 85.95$ (4)°, $\beta = 72.01$ (3)°, $\gamma = 63.46$ (3)°; $Z = 2$, $\rho_{calcd} = 1.98$ g/cm$^3$, $\rho_{obsd} = 1.98$ g/cm$^3$. Refinement on 1803 reflections with $F_o^2 > 3\sigma(F_o^2)$ has yielded the final discrepancy indices, $R = 0.025$ and $R_w = 0.027$. Attached to the molybdenum atom is a slightly skewed *pentahapto* cyclopentadienyl ring, a linear carbonyl group, and an iodine atom. The most interesting feature is a complex polyhapto carbon–nitrogen containing ligand that has been interpreted as an iminodimethylaminocarbene. All the reaction products have been explained through a scheme that involves a uniform series of additions and facile isocyanide insertion rearrangements.

As one of the most important rearrangements known to organometallic chemistry, the "insertion" rearrangement has been the subject of diverse and detailed scrutiny. Although a large number of molecules will engage in these rearrangements,[2] certainly the most familiar example is the insertion of carbon monoxide into the metal–carbon (R) bond,[3] eq 1. The intramolecular nature of the rearrangement has been verified and careful labeling experiments have revealed subtle details of the stereochemical transformations that occur at both the metal[4] and carbon[5] atoms. A supplementary ligand is usually added to the metal to accommodate the electronic changes that accompany the formation of the acyl group.

(1) 

$$L_x\overset{\overset{\displaystyle O}{\overset{\displaystyle C}{|}}}{M}\text{-}R \xrightarrow{+L'} L_x(L')M\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R$$

Isocyanide molecules are structurally similar and isoelectronic to carbon monoxide. They are also known to engage in insertion rearrangements;[6] however, detailed mechanistic studies have not been done. In this and the accompanying paper[7] we report the results of our studies of the reactions of some organometallic anions containing isocyanide ligands with methyl iodide. They show a characteristic pattern of facile isocyanide insertions. The products show new and unusual structural forms which may help clarify the details of the isocyanide insertion rearrangement and may provide a new perspective for discussing the carbonyl and other insertion rearrangements.

## Experimental Section

**General.** All reactions were performed under an inert nitrogen atmosphere. The anions $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)^-$ and $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$ were prepared as previously described.[8] $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNC_6H_5)^-$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)^-$ were prepared similarly from $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNC_6H_5)I$ and $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)Cl$. $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNC_6H_5)I$ was prepared according to the method of Pauson.[9] $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ was prepared according to the method of Wilkinson for the preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$.[10] $CNCH_3$[11] and $CNC_6H_5$[12] were prepared by established procedures. $CH_3I$ was obtained commercially and used without further purification. The solvents THF, toluene, and hexanes were dried just prior to use by refluxing over sodium–benzophenone and distilling under nitrogen.

**Measurements.** Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer and calibrated with polystyrene, 1601.4 cm$^{-1}$. $^1$H NMR spectra were obtained with a Perkin-Elmer R32 equipped with a variable temperature accessory operating in unlocked mode and calibrated with $Me_4Si$. Variable temperature spectra of XII were recorded in *o*-dichlorobenzene-toluene-$d_8$ (1:1 solvent). Temperatures were calibrated with ethylene glycol. Line shape calculations were performed using the program EXCHSYS,[13] and treating the exchange processes as a 1:1 exchange of uncoupled sites.

Samples were prepared by placing solid samples in serum cap adaptable NMR tubes under nitrogen and injecting the appropriate amount of a degassed solvent through the serum cap via syringe. Melting points were obtained in capillaries sealed under nitrogen on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Mass spectra were obtained on a Perkin-Elmer RMU-6D mass spectrometer operated at 40 or 70 eV ionizing voltage and using direct inlet sample additions. Elemental microanalyses were performed by Midwest Microanalytical Laboratory, Indianapolis, Ind.

**Reactions.** In Table I are listed important physical properties of the compounds that have been prepared, as well as the method of purification, percent yields, and microanalytical data. Representative reactions are reported below.

**$(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)Cl$.** $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ (4.0 g, 10.86 mmol) and 0.65 mL (11.95 mmol) of $CNCH_3$ were placed in 100 mL of THF in a 200-mL round-bottom flask equipped with a nitrogen inlet. With stirring, UV irradiation was applied for 3 h. During this time a yellow precipitate began to form and the solution turned darker red. After this period the solvent was removed in vacuo. The residue was taken up in benzene-THF (10:1) and chromatographed over $Al_2O_3\cdot6\%H_2O$. A small band of $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ was followed by a large red band of $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)Cl$. The latter was collected. Solvent again was removed in vacuo and the residue crystallized from toluene-hexane (1:2) at −20 °C, yield 1.58 g.

**$(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (IV), $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (V), and $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)(CH_3)$ (VI).** To ~1-mmol quantities of the anion, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)^-$, in THF solvent at −78 °C was added an equivalent amount of methyl iodide. After addition the reaction mixture was allowed to warm to room temperature and stir for an additional 2 h. Solvent was then removed in vacuo. The residue was extracted with hexanes and filtered. The filtrate was concentrated and cooled to −78 °C. This led to the crystallization of the product, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (IV). $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (V) was prepared

Table I

| Compd | Color | Mp, °C | Method of purification (solvent used) | Yield, % | Exptl (calcd) anal., % C | H | N | I |
|---|---|---|---|---|---|---|---|---|
| $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)Cl$ | Red | 98.0-103.5 | C[b] (benzene) | 38 | 28.41<br>(28.34) | 2.21<br>(2.11) | 3.72<br>(3.67) | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (IV) | Red | 94-101 | E (hexanes) | 51 | 44.02<br>(43.96) | 4.31<br>(4.06) | 5.31<br>(5.15) | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (V) | Red | 84-87.5 | E (hexanes) | 79 | c | | | |
| $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)(CH_3)$ (VI) | Red-orange | 117-118 | C (benzene) | 34 | 33.34<br>(33.27) | 3.08<br>(3.07) | 3.86<br>(3.88) | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(TCNE)(\eta^1\text{-}CH_3CNCH_3)$ (VII) | Orange | 160-170 dec | C[a] (THF) | 89 | 47.86<br>(47.89) | 2.90<br>(2.76) | 17.36<br>(17.45) | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(TCNE)(\eta^1\text{-}CH_3CNC_6H_5)$ (VIII) | Orange | 165-170 dec | C[a] (benzene-THF) | 30 | 54.16<br>(54.44) | 2.70<br>(2.83) | 14.74<br>(15.12) | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3(\eta^1\text{-}CH_3CNC_6H_5)$ (IX) | Yellow | 82.5-83.0 | C[a] (benzene-THF) | 25 | c | | | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(C_6H_5)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (X) | Yellow | 128-130 | E | 75 | 65.72<br>(66.34) | 4.72<br>(4.72) | 2.03<br>(2.34) | |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(I)[C(CH_3)N(H)(CH_3)]$ (XI) | Red | 121.5-123.5 | C[f] (benzene) | 24 | 30.39<br>(29.95) | 3.04<br>(3.02) | 3.42<br>(3.49) | 30.85<br>(31.64) |
| $(\eta^5\text{-}C_5H_5)Mo(CO)(I)[C(N(CH_3)_2C(CH_3)N\text{-}(CH_3)]$ (XII) | Red-brown | 182-183 | C[a] (benzene-THF) | 23 | 34.44[c]<br>(33.67) | 4.25<br>(4.00) | 6.33<br>(6.54) | 29.28<br>(29.64) |

[a] C = chromatography on $Al_2O_3$·6% $H_2O$. [b] E = solvent extraction. [c] Analysis by crystal structure.[7] [d] TCNE = tetracyanoethylene. [e] Crystallizes from reaction solution. [f] Chromatography over Florisil.

similarly. The anion, $(\eta^5\text{-}C_5H_5)W(CO)_2CNCH_3^-$, was considerably less reactive. Reaction mixtures with this anion required a 4-5 h reflux period. Purification of $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)(CH_3)$ was by chromatography followed by crystallization from toluene-hexane solvent at −78 °C.

**$(\eta^5\text{-}C_5H_5)Mo(CO)_2I[C(CH_3)N(H)(CH_3)]$ (XI).** A THF solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)^-$, prepared from 2.6 mmol of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)$ (I), and 26.0 mmol of methyl iodide was refluxed for 38 h. IR spectra taken during the reaction period showed that compound IV was formed initially and was slowly converted into the new compound XI. Upon disappearance of IV the reaction was stopped. Solvent was removed in vacuo. The residue was taken up in benzene, and chromatographed over Florisil. A large red brown band was eluted and collected. Solvent was removed and the residue crystallized from toluene-hexane (1:1) to give 0.231 g of pure XI. The mass spectrum taken at 70 eV showed the following: ions (*m/e*, rel abundance) $C_5H_5Mo(CO)_2(I)[C(CH_3)N(H)(CH_3)]^+$ (405, 8), parent ion; $C_5H_5Mo(CO)(I)[C(CH_3)N(H)(CH_3)]^+$ (376, 19); $C_5H_5Mo(CO)(I)(CNCH_3)^+$ (361, 13); $C_5H_5Mo(I)[C(CH_3)N(CH_3)]^+$ (348, 58); $C_5H_5Mo(CO)I^+$ (320, 13); $C_5H_5MoI^+$ (292, 100); $C_5H_5Mo^+$ (165, 43).[14]

**$(\eta^5\text{-}C_5H_5)Mo(CO)(I)[C(N(CH_3)_2)C(CH_3)N(CH_3)]$ (XII).** To a THF solution of 1.0 mmol of $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$ at −78 °C was added an excess of methyl iodide. The solution was then warmed to room temperature. After 2 h of stirring the solution had turned dark red. Solvent was removed and the residue chromatographed over $Al_2O_3$·6%$H_2O$. A large red-brown band eluted (1:1, $C_6H_6$-THF). The solvent was again removed and the compound, XII, crystallized from toluene-hexane (1:1) solvent. The mass spectrum at 40 eV showed the following: ions (*m/e*, rel intensity) $C_5H_5Mo(CO)I(CH_3)_2(CNCH_3)_2^+$ (432, 19), parent ion; $C_5H_5Mo(I)(CH_3)_2(CNCH_3)_2^+$ (404, 100); $C_5H_5Mo(I)(CH_3)(CNCH_3)_2^+$ (389, 6); $C_5H_5MoI(CH_3)_2(CNCH_3)^+$ (363, 6); $C_5H_5Mo(I)(CH_3)(CNCH_3)^+$ (348, 56); $C_5H_5Mo(I)(CNCH_3)^+$ (333, 16); $C_5H_5Mo(I)(CH_3)_2^+$ (322, 35); $C_5H_5Mo(I)(CH_3)^+$ (307, 13); $C_5H_5Mo(I)^+$ (292, 39).[14]

**Reactions of IV and V with Ligands.** IV (0.2 g, 0.73 mmol) and 0.1 g (0.78 mmol) of tetracyanoethylene (TCNE) were placed in a 200-mL flask under nitrogen. Approximately 75 mL of THF was then added at room temperature. An immediate reaction was indicated by a color change to dark orange. The solution was concentrated and chromatographed ($Al_2O_3$·6%$H_2O$) with THF. An orange band was collected. The elutant was concentrated and the product $(\eta^5\text{-}C_5H_5)Mo(CO)_2(TCNE)(\eta^1\text{-}CH_3CNCH_3)$ (VII) was crystallized by addition of pentane, yield 0.26 g.

Compounds VIII, IX, and X were prepared similarly. However, X was prepared in hexane solvent and it crystallized from the reaction mixture. It was purified by recrystallization alone. Compound VIII may undergo substantial (if not complete) decomposition during chromatography on alumina. It is best obtained by filtering a THF solution over a 3-4 in. column of alumina with additional purification by crystallization.

**Structure of $(\eta^5\text{-}C_5H_5)Mo(CO)I[C(N(CH_3)_2)C(CH_3)N(CH_3)]$ (XII). Data Collection and Reduction.** Crystals of XII suitable for diffraction studies were obtained by crystallization from toluene-hexane solutions by cooling to −20 °C. A crystalline plate of approximate dimensions 0.18 × 0.15 × 0.06 mm was mounted and sealed in a glass capillary. Preliminary precession and Weissenberg photographs indicated triclinic symmetry. On this basis the crystal faces were identified as {100}, {001}, 011, and $0\bar{1}0$. In a random mount orientation, accurate cell parameters were obtained through the centering and least-squares refinement of 12 high-angle reflections ($2\theta > 19°$) on a Picker FACS-1 four-circle automatic diffractometer, using graphite monochromatized Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å). Cell parameters are $a = 8.296$ (4) Å, $b = 7.492$ (4) Å, $c = 13.945$ (8) Å, $\alpha = 85.95$ (4)°, $\beta = 72.01$ (3)°, $\gamma = 63.46$ (3)°, $\rho_{calcd} = 1.98$ g/cm³, $\rho_{obsd} = 1.98$ g/cm³ (by flotation in $CCl_4$ and $CH_3I$ solution), $Z = 2$. Crystal mosaicity produced $\omega$-scan peak widths at half-height, generally, of 0.1°. At 21 ± 2°, a unique set of data was collected in the scan range $2\theta = 0\text{-}54°$ by the $\theta$-$2\theta$ scan technique. Data were collected in the scan range $K\alpha 1 - 0.6°$ to $K\alpha 2 + 0.6°$, where $K\alpha 1$ and $K\alpha 2$ are the calculated peak positions, at a scan rate of 2.0° per minute. Stationary backgrounds were measured for 4 s at each end of the scan range. A total of 3231 reflections was obtained. Three standard reflections, monitored every 100 reflections, showed only random fluctuation throughout the entire data collection process. Raw intensities, $I$, and backgrounds, $B$, were converted from decacounts to counts by the relations $I_{counts} = 10I_{decacounts} + 4.5$ and $B = 10B_{decacounts} + 4.5$. Intensities were then 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.[15] After correction for Lorentz and polarization effects[16] a total of 1801 reflections was found to conform to the relation $F^2 > 3\sigma(F^2)$. Only these reflections were used in the structure solution and refinement. The linear absorption coefficient for Mo $K\alpha$ radiation is 30.6. An absorption correction was applied to the data, using the Gaussian integration method and a grid of 8 × 8 × 4. The maximum and minimum transmission coefficients were 0.842 and 0.715, respectively.

**Solution and Refinement of the Structure.** The structure was solved by heavy atom methods. A three-dimensional Patterson synthesis clearly revealed the positions of the molybdenum and iodine atoms. Refinement on these two atoms with isotropic temperature factors

Table II. Atomic Coordinates for Crystalline $(\eta^5\text{-}C_5H_5)Mo(CO)(I)[C(N(CH_3)_2)C(CH_3)N(CH_3)]$

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | Atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|---|---|---|---|
| Iodine | −0.18016 (5) | 0.00862 (6) | 0.19815 (3) | Mo | 0.18780 (5) | −0.09304 (6) | 0.20864 (3) |
| O | 0.0372 (7) | −0.2146 (7) | 0.4215 (3) | N1 | 0.1435 (6) | 0.2136 (6) | 0.1579 (3) |
| N2 | 0.3070 (6) | 0.0826 (6) | 0.3641 (3) | C1 | 0.4178 (8) | −0.2042 (9) | 0.0438 (4) |
| C2 | 0.3101 (8) | −0.3053 (8) | 0.0577 (4) | C3 | 0.3271 (8) | −0.4146 (8) | 0.1431 (4) |
| C4 | 0.4535 (8) | −0.3833 (8) | 0.1804 (5) | C5 | 0.5055 (8) | −0.2486 (9) | 0.1198 (5) |
| C6 | 0.0965 (7) | 0.2410 (7) | 0.2580 (4) | C7 | 0.2342 (7) | 0.0750 (7) | 0.2948 (4) |
| C8 | 0.0119 (10) | 0.3517 (10) | 0.1073 (6) | C9 | −0.0821 (9) | 0.4033 (10) | 0.3262 (6) |
| C10 | 0.2995 (10) | 0.2668 (10) | 0.3989 (5) | C11 | 0.4146 (11) | −0.0989 (11) | 0.4061 (6) |
| C12 | 0.0868 (8) | −0.1672 (8) | 0.3422 (5) | H1 | 0.428 (9) | −0.120 (9) | −0.006 (4) |
| H2 | 0.228 (8) | −0.292 (8) | 0.018 (4) | H3 | 0.286 (8) | −0.508 (8) | 0.165 (4) |
| H4 | 0.484 (8) | −0.437 (9) | 0.232 (5) | H5 | 0.576 (8) | −0.204 (9) | 0.129 (5) |
| H81 | 0.075 (8) | 0.293 (8) | 0.038 (5) | H82 | −0.116 (9) | 0.377 (9) | 0.136 (4) |
| H83 | 0.019 (9) | 0.470 (9) | 0.106 (4) | H91 | −0.188 (9) | 0.426 (9) | 0.317 (5) |
| H92 | −0.071 (9) | 0.527 (9) | 0.303 (4) | H93 | −0.100 (8) | 0.377 (9) | 0.396 (5) |
| H101 | 0.423 (9) | 0.261 (8) | 0.384 (4) | H102 | 0.218 (8) | 0.394 (9) | 0.373 (4) |
| H103 | 0.234 (8) | 0.288 (9) | 0.471 (5) | H111 | 0.361 (8) | −0.081 (9) | 0.473 (5) |
| H112 | 0.425 (8) | −0.217 (9) | 0.369 (4) | H113 | 0.537 (9) | −0.120 (9) | 0.392 (5) |

Table III. Thermal Parameters for Crystalline $(\eta^5\text{-}C_5H_5)Mo(CO)(I)[C(N(CH_3)_2)C(CH_3)N(CH_3)]$

| Atom | $\beta(1,1)^{a,b}$ | $\beta(2,2)$ | $\beta(3,3)$ | $\beta(1,2)$ | $\beta(1,3)$ | $\beta(2,3)$ |
|---|---|---|---|---|---|---|
| Iodine | 0.1386 (9) | 0.2440 (12) | 0.0967 (4) | −0.0890 (9) | −0.0493 (5) | 0.0064 (5) |
| Mo | 0.1064 (9) | 0.1148 (10) | 0.0350 (3) | −0.0441 (8) | −0.0193 (4) | 0.0003 (4) |
| O | 0.399 (16) | 0.327 (14) | 0.049 (3) | −0.189 (12) | −0.005 (5) | 0.032 (5) |
| N1 | 0.156 (10) | 0.139 (10) | 0.042 (3) | −0.076 (8) | −0.038 (4) | 0.020 (4) |
| N2 | 0.188 (10) | 0.182 (11) | 0.044 (3) | −0.069 (9) | −0.052 (5) | 0.020 (4) |
| C1 | 0.187 (13) | 0.194 (15) | 0.039 (4) | −0.070 (12) | 0.007 (6) | −0.009 (6) |
| C2 | 0.170 (13) | 0.205 (15) | 0.042 (4) | −0.067 (12) | −0.011 (6) | −0.026 (6) |
| C3 | 0.159 (12) | 0.134 (13) | 0.052 (4) | −0.058 (10) | −0.003 (5) | −0.024 (6) |
| C4 | 0.124 (10) | 0.154 (13) | 0.056 (4) | −0.020 (10) | −0.022 (6) | −0.001 (6) |
| C5 | 0.110 (12) | 0.193 (15) | 0.072 (5) | −0.056 (10) | −0.004 (6) | −0.021 (7) |
| C6 | 0.150 (11) | 0.121 (11) | 0.049 (4) | −0.063 (10) | −0.040 (5) | 0.005 (5) |
| C7 | 0.126 (11) | 0.149 (12) | 0.035 (3) | −0.059 (9) | −0.022 (5) | 0.009 (5) |
| C8 | 0.250 (16) | 0.197 (16) | 0.067 (5) | −0.107 (15) | −0.077 (7) | 0.051 (7) |
| C9 | 0.166 (14) | 0.192 (16) | 0.071 (5) | −0.019 (13) | −0.027 (7) | −0.012 (7) |
| C10 | 0.231 (16) | 0.239 (17) | 0.059 (5) | −0.123 (14) | −0.053 (7) | −0.010 (7) |
| C11 | 0.306 (19) | 0.266 (19) | 0.060 (5) | −0.088 (17) | −0.094 (9) | 0.026 (8) |
| C12 | 0.184 (14) | 0.175 (14) | 0.057 (4) | −0.077 (12) | −0.021 (6) | 0.004 (6) |

[a] The form of the expression for the anisotropic temperature factors 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] All hydrogen atoms were assigned isotropic temperature factors of 5.0. This value was not refined.

produced the residuals

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

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

of 0.20 and 0.28, respectively. The weights, *w*, were taken as $4F_o^2/\sigma^2(F_o^2)$, and the function minimized in least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. Neutral atom scattering factors were calculated using the analytical expressions of Cromer and Waber.[17] Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, were made for the molybdenum and iodine atoms.[18] A difference Fourier syntheses at this time revealed the positions of all remaining nonhydrogen atoms. Initially, the central atom of the trihapto ligand was assumed to be nitrogen while the two external atoms were assumed to be carbon. Two cycles of full matrix least-squares refinement with all atoms having isotropic temperature factors produced the residuals $R = 0.107$ and $R_w = 0.127$. However, the external carbon atom which was later reassigned as nitrogen atom, N1, produced a negative temperature factor. This temperature factor was reset to 4.0 and another least-squares cycle with anisotropic temperature factors for the molybdenum and iodine atoms produced the indices $R = 0.050$ and $R_w = 0.058$. Once again, the temperature factor of the same external carbon atom went negative. At this time, the central atom was reassigned as carbon, C6, and the unsatisfactory external carbon atom was reassigned as nitrogen, N1 (cf. Figure 1). Two cycles of refinement on the new assignments produced the indices $R = 0.042$ and $R_w = 0.051$. The temperature factors for both atoms C6 and N1 were then 2.5. Assuming the reassignment as correct, two cycles of refinement with all atoms having anisotropic temperature factors produced the indices $R = 0.032$ and $R_w = 0.041$. A difference Fourier synthesis next revealed the positions of all hydrogen atoms. The refinement converged after three additional least-squares cycles with anisotropic temperature factors on all nonhydrogen atoms and coordinate refinement on all hydrogen atoms. The final values of the residuals were $R = 0.025$ and $R_w = 0.027$. The goodness of fit, error in an observation of unit weight, was 0.80.

The largest peak in the final difference Fourier synthesis was 0.7 e/Å$^3$ (approximately the size of a hydrogen atom) in the immediate vicinity of the iodine atom. All other peaks were less than 0.37 e/Å$^3$.

The positional and thermal parameters, as well as errors (calculated from elements of the inverse matrix obtained from the final cycle of refinement) are listed in Tables II and III, respectively. A table of final observed and calculated structure factor amplitudes has been reported previously.[1]

## Results

Each of the anions, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)^-$ (I), $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNC_6H_5)^-$ (II), and $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)^-$ (III), reacts with one molecule of methyl iodide to form the neutral molecules, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNCH_3)$ (IV), $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNC_6H_5)$ (V), and $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)CH_3$, (VI), respectively. The infrared and $^1$H NMR spectra of the compounds are listed in Table IV. The infrared absorptions at 1915, 1810, and 2120 cm$^1$ in VI establish that it contains

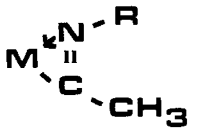
Table IV

| Compd | IR (CO and CN region), $cm^{-1}$ | $^1H$ NMR, ppm |
|---|---|---|
| $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)Cl$ | 2188 m,[a] 1980 w (sh), 1965 s, 1905 m (sh), 1885 s | 5.05 $(C_5H_5)$,* 4.90 $(C_5H_5)$, 2.55 $(CH_3)$, 2.53 $(CH_3)$*[b,c] |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNCH_3)$ (IV) | 1930 s, 1825 s, 1720 w | 5.03 $(C_5H_5)$,[b] 2.44 $(CH_3)$, 1.98 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$ (V) | 1945 s,[d] 1850 s, 1670 m, 1585 m[e] | 5.59 $(C_5H_5)$,[j] 7.25–7.50 $(C_6H_5)$, 3.09 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)(CH_3)$ (VI) | 2120 w,[a] 1915 s, 1810 s | 5.12 $(C_5H_5)$,[b] 2.51 $(CH_3)$, 1.98 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(TCNE)(\eta^1\text{-}CH_3CNCH_3)$ (VII) | 2215 w,[f] 1970 s, 1885 s, 1630 w | 5.89 $(C_5H_5)$,[j] 3.86 $(CH_3)$, 2.68 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(TCNE)(\eta^1\text{-}CH_3CNC_6H_5)$ (VIII) | 2205 w,[f] 1970 s, 1885 s, 1615 w (br) | 5.52 $(C_5H_5$,[j] 7.0–7.6 $(C_6H_5)$, 2.45 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (IX) | 1970 w (sh),[g] 1955 m, 1895 m (sh), 1880 s, 1570 w (sh), 1550 m[e] | 5.24 $(C_5H_5, J_{P\text{-}C_5H_5} = 1.8$ Hz),[j] 6.5–7.2 $(C_6H_5)$, 3.61 $(OCH_3, J_{P\text{-}OCH_3} = 5.9$ Hz), 2.24 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(C_6H_5)_3)(\eta^1\text{-}CH_3CNC_6H_5)$ (X) | 1940 m,[a] 1855 s, 1575 w (sh), 1545 m[e] | 5.00 $(C_5H_5, J_{P\text{-}C_5H_5} = 1.0$ Hz),[k] 7.0–7.5 $(C_6H_5)$, 2.30 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_2(I)[C(CH_3)N(H)\text{-}(CH_3)]$ (XI) | 1955 s,[h] 1865 s, 1550 m[i] | 5.00 $(C_5H_5)$,[b] 2.75 $(CH_3, J = 5.0$ Hz), 2.17 $(CH_3)$ |
| $(\eta^5\text{-}C_5H_5)Mo(CO)(I)[C(N(CH_3)_2C\text{-}(CH_3)N(CH_3)]$ (XII) | 1900 s,[a] 1555 m | 4.93 $(C_5H_5)$,[b] 3.43 $(NCH_3)$, 2.60 (br, $NCH_3$), 2.37 (br, $NCH_3$), 1.72 $(CH_3)$ |

[a] In THF. [b] In $C_6H_6$, [c] Mixture of isomer, * = major isomer. [d] In pentane. [e] $C_6H_5$ ring vibrational mode. [f] In $CH_3CN$. [g] In hexanes. [h] In $C_6D_6$. [i] N–H at 3255 m in $CD_3CN$. [j] In acetone-$d_6$. [k] THF-$d_8$.

two cis-positioned carbonyl groups and a normal terminal isocyanide ligand, and indicate that methylation has taken place at the tungsten atom. Compounds IV and V each show two carbonyl absorptions but do not show an isocyanide absorption in the normal region. Instead, weak absorptions were found at 1720 and 1680 $cm^{-1}$ for IV and V, respectively. These low-energy positions are only slightly higher than those which occur for iminoacyl ligands (e.g., 1580–1620 $cm^{-1}$).[19] This suggests that in these complexes methylation may have occurred at the carbon atom of the isocyanide ligand and has resulted in the formation of an iminoacyl ligand. In the absence of other ligands, only the structural arrangements, **1**, which contains an $\eta^1$-iminoacyl ligand and an electron-deficient (16 e) metal atom, or **2**, which contains a novel dihapto-($\eta^2$-)iminoacyl ligand, seem plausible. Although 16 electron, $\eta^1$-iminoacyl configurations have been observed in complexes of the noble metals, 16 electron configurations of carbonyl complexes of molybdenum are very rare. For this reason, we favor the dihapto structure, II. This is supported by spectral studies and has now been confirmed crystallographically.[7]

1



2

Compounds IV and V readily add donor ligands, such as $P(C_6H_5)_3$, $P(OCH_3)_3$, and tetracyanoethylene (TCNE), to produce the new molecules VII–X, which also contain iminoacyl ligands. For these molecules the C–N stretching vibrations have lowered to the region normally expected for the $\eta^1$-iminoacyl ligands. A second product, XI, was isolated from the reaction which produces IV. Its yield is enhanced at the expense of IV by using a reflux period. A combination of IR, $^1H$ NMR, mass spectra, and elemental analyses has established its formula as $(\eta^5\text{-}C_5H_5)Mo(CO)_2(I)[C(CH_3)\text{-}N(H)(CH_3)]$. A very low field $^{13}C$ NMR resonance at 264.2 ppm[20] and infrared absorptions at 3255[21] and 1550 $cm^{-1}$ [22] are both characteristic of metal coordinated aminocarbenes. Accordingly, we have formulated XI as a methyl methylaminocarbene complex with cis-positioned carbonyl groups, a coordinated iodine atom, and a *pentahapto*cyclopentadienyl ring. Although the proton attached to the nitrogen atom is not directly observed in the $^1H$ NMR spectra, its immediate presence is indicated by coupling to one of the methyl groups.

The reaction of the anion, $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$ with methyl iodide produced the compound XII, whose molecular formula was tentatively established as $(\eta^5\text{-}C_5H_5)\text{-}Mo(CO)(CNCH_3)_2(CH_3)_2(I)$. The $^1H$ NMR spectrum shows a cyclopentadienyl resonance and four individual methyl resonances. Interestingly, two of the methyl resonances show temperature-dependent changes. As the temperature is raised, they broaden, merge (coalescence at 46 °C), and sharpen to a singlet (intensity 6) at 70 °C. Line-shape analysis of the broadened spectra has produced exchange rates which obey the Arrhenius and Eyring equations and has yielded the activation parameters $E_a = 17.3 \pm 0.3$ kcal/mol, $\log A = 12.5 \pm 0.4$, $\Delta H^{\ddagger} = 16.7 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -3.3 \pm 0.8$ eu, and $\Delta G^{\ddagger}_{298} = 17.7 \pm 0.3$ kcal/mol. The absence of isocyanide C–N absorptions in the infrared spectra has prompted us to further investigate this compound by crystal structure analysis.

**Structure Analysis of $(\eta^5\text{-}C_5H_5)Mo(CO)(I)[C(N(CH_3)_2\text{-}C(CH_3)N(CH_3)]$, XII.** The molecular structure of compound XII is shown in Figure 1. In Table V are listed important bond distances and angles. The molecule contains a slightly skewed *pentahapto*cyclopentadienyl ring with molybdenum–carbon bond lengths ranging from 2.246 (5) to 2.400 (6) Å. Although the skewing is significant, it is not uncommon in complexes of this type.[23] Thus, it does not seem appropriate at the present time to attempt to attribute it to any unusual features of this particular complex. A linearly coordinated carbonyl group (angle Mo–C–O = 176.1 (5)°), and coordinated iodine atom (Mo–I = 2.846 (2) Å), appear to be normal.[24] The most interesting feature is a complex, polyhapto arrangement of carbon and nitrogen atoms, C6–C11 and N1–N2. We have chosen to describe this ligand as an iminodimethylaminocarbene with C7 being the carbenoid carbon. The Mo–C7 distance of 2.027 (5) Å is short, but similar to the molybdenum–carbene distance of 2.09 Å found in the complex $(\eta^5\text{-}C_5H_5)Mo\text{-}(CO)_2(N(H)NC(CO_2C_2H_5)COH)$, which also contains a heterocyclic carbene chelating ligand.[26] As is characteristic of aminocarbenes, the nitrogen atom, N2, is planar and the angle between the methyl groups C10 and C11 at N2 is 115.8

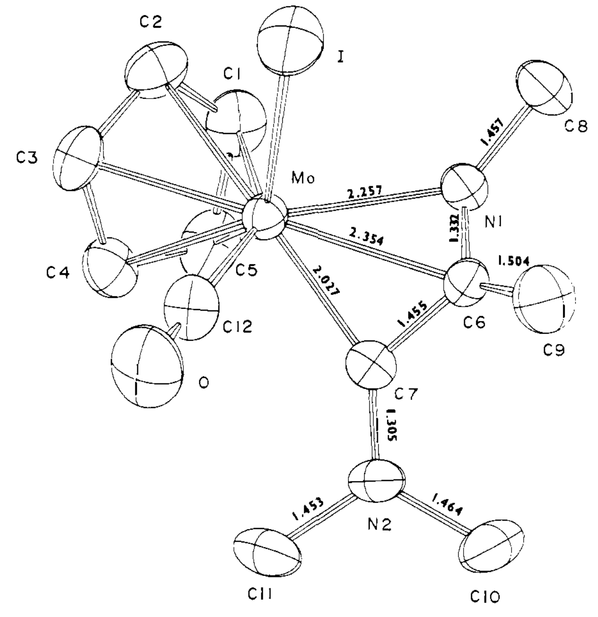


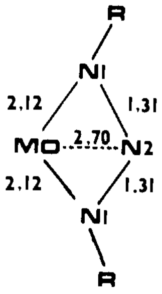
**Figure 1.** An ORTEP diagram of the molecule $\eta^5$-$C_5H_5$)Mo(CO)(I)[C(N($CH_3$)$_2$C($CH_3$)N($CH_3$)] (XII), excluding hydrogen atoms; 50% probability ellipsoids are shown.

Table V. Selected Bond Distances (Å) and Angles (deg)

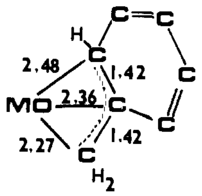
| | | | |
|---|---|---|---|
| Mo-I | 2.846 (2) | C7-Mo-N1 | 64.0 (2) |
| Mo-C12 | 1.945 (6) | C6-Mo-N1 | 33.5 (2) |
| Mo-C1 | 2.400 (6) | C6-Mo-C7 | 37.9 (2) |
| Mo-C2 | 2.387 (6) | I-Mo-C12 | 82.5 (2) |
| Mo-C3 | 2.268 (5) | C7-Mo-C12 | 81.1 (2) |
| Mo-C4 | 2.246 (5) | N1-Mo-C12 | 128.8 (2) |
| Mo-C5 | 2.298 (6) | I-Mo-C7 | 122.2 (2) |
| Mo-C6 | 2.354 (5) | I-Mo-N1 | 87.0 (1) |
| Mo-C7 | 2.027 (5) | C1-Mo-C2 | 33.3 (2) |
| Mo-N1 | 2.257 (4) | C2-Mo-C3 | 35.0 (2) |
| C1-C2 | 1.373 (8) | C3-Mo-C4 | 36.5 (2) |
| C2-C3 | 1.404 (8) | C4-Mo-C5 | 35.9 (2) |
| C3-C4 | 1.414 (8) | C5-Mo-C1 | 34.7 (2) |
| C4-C5 | 1.400 (8) | Mo-C12-O | 176.1 (5) |
| C5-C1 | 1.404 (8) | C8-N1-C6 | 118.4 (5) |
| C12-O | 1.146 (6) | N1-C6-C9 | 126.3 (5) |
| C6-C7 | 1.455 (6) | C7-C6-N1 | 109.7 (4) |
| C6-N1 | 1.332 (6) | C9-C6-C7 | 123.6 (5) |
| C6-C9 | 1.504 (8) | C6-C7-N2 | 127.8 (5) |
| C7-N2 | 1.305 (6) | C7-N2-C10 | 123.3 (5) |
| N1-C8 | 1.457 (7) | C7-N2-C11 | 120.7 (5) |
| N2-C10 | 1.464 (7) | C10-N2-C11 | 115.8 (5) |
| N2-C11 | 1.453 (7) | C5-C1-C2 | 108.6 (6) |
| | | C1-C2-C3 | 108.4 (6) |
| | | C2-C3-C4 | 107.7 (5) |
| | | C3-C4-C5 | 107.2 (5) |
| | | C4-C5-C1 | 108.0 (5) |

(5)°. The short C7-N2 internuclear distance of 1.305 (6) Å is normal[27] and reflects the partial multiple bonding that occurs in heteronuclear carbene ligands. The short C6-N1 distance of 1.332 (6) Å also indicates multiple bonding between these atoms. This group can formally be regarded as a coordinated imine and the C-N distance is only slightly longer than the 1.29-1.31 Å generally accepted for the C-N double bond.[28,29] The Mo-C6 = 2.354 (5) and Mo-N1 = 2.257 (4) Å distances indicate that both C6 and N1 are bonded to the metal atom. Although it is somewhat distorted, this could formally be viewed as a $\pi$ donation from the imine to the metal atom. The only previous example of a coordinated imine was for the compound {($\eta^5$-$C_5H_5$)$_2$Mo($NH_3$)[(HNC($CH_3$)($C_2H_5$)}($PF_6$)$_2$.[31] In this case the monohapto imine was bonded to the molybdenum atom through the nitrogen atom only with Mo-N = 2.192 (5) Å and C=N = 1.30 (1) Å. In the present case the imino function is fused to the carbenoid function through a bond between atoms C6 and C7. The C6-C7 distance of 1.455 (7) Å is slightly shorter than the normal C($sp^3$)-C(carbene) bond distance of 1.51 (2) Å[27] and may reflect a partial electron delocalization between the two functions. The combined functions produce a trihapto ligating unit, which in order to preserve the 18 electron configuration at the metal atom, must serve as a four-electron donor. Formally, two of these electrons are provided by the carbenoid carbon, C7, and two by the imino function, C6-N1.

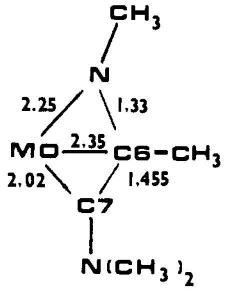
This trihapto, C7-C6-N1, unit contrasts significantly to the dihapto, triazenido Mo-$N_3$ unit found in the complex ($\eta^5$-$C_5H_5$)Mo(CO)$_2$($N_3$($C_6H_3$-3,5-$CF_3$)$_2$).[32] In that case the triazenido ligand bonds as a chelate, A, through the two external nitrogen atoms. The Mo-$N_3$ unit is planar and the long Mo-N2 distance of 2.70 indicates little or no bonding to the central nitrogen atom. Perhaps the best comparison is with the molecule ($\eta^5$-$C_5H_5$)Mo(CO)$_2$($\eta^3$-$CH_2C_6H_5$), which contains a *trihapto*-benzyl group.[33] Structure B shows this arrangement. These metal-carbon bond distances are similar to those reported here, C, except for our shorter metal-carbene distance.



**A**



**B**



**C**

Table VI contains a list of least-squares planes calculated for several pertinent atomic groupings. The group C7, C6, C9, N1, C8 (plane 1) is essentially planar, but does not include the dimethylamino group (plane 2). Nitrogen atom N2 lies 0.61 Å from plane 1 on the side opposite the metal atom and the entire amino group is tipped 54.3° with respect to it. Plane 1 is essentially perpendicular to the plane of the cyclopentadienyl ring, plane 3. There are no abnormally short intermolecular distances. The shortest distance between nonhydrogen atoms was between two cyclopentadienyl carbons at 3.217 Å.[34]

## Discussion

The formation of all of the compounds prepared in this study can be readily understood on the basis of a uniform series of addition and isocyanide insertion rearrangements. We have previously shown that the anions I and II do, in general, react with alkyl group 4 halides by nucleophilic displacement and yield addition of the group 4 substituent to the metal atom.[8] As shown in Scheme I, this may be assumed as the initial step (step 1) in the reaction of all the anions reported here with methyl iodide. This may then be followed by step 2: (a) an isocyanide insertion rearrangement which results in transfer of the methyl group from the metal atom to the isocyanide carbon and (b) a rearrangement which leads to incorporation of the nitrogen atom into the coordination sphere of the metal atom. This produces the $\eta^2$-iminoacyl group. Steps 2a and 2b might occur either individually or in concert. It is important to point out those cases where insertion does not occur. For example, it is known that tungsten carbonyl complexes resist carbonyl insertion.[3] Similarly, we find no evidence for isocy-

**Table VI.** Various Unweighted Least-Squares Planes

| Plane no. | Atoms | Distance from plane |
|---|---|---|
| 1 | C7 | −0.041 |
| | C6 | 0.048 |
| | C9 | −0.007 |
| | N1 | 0.037 |
| | C8 | −0.037 |
| | N2[a] | 0.610 |
| 2 | C7 | 0.009 |
| | N2 | −0.024 |
| | C10 | 0.008 |
| | C11 | 0.008 |
| 3 | C1 | 0.003 |
| | C2 | 0.006 |
| | C3 | −0.012 |
| | C4 | 0.014 |
| | C5 | −0.011 |
| | Mo[a] | 1.985 |

Dihedral Angles between Planes

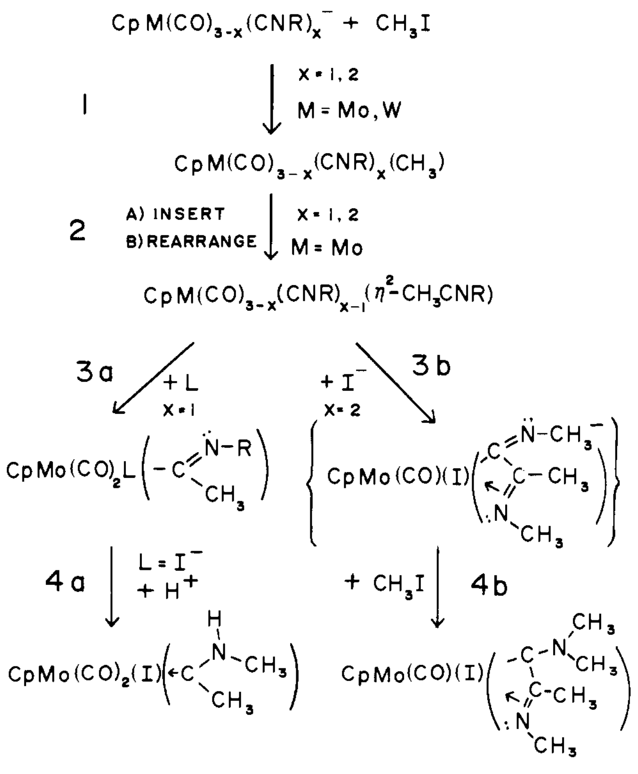
| Planes | Angle, deg |
|---|---|
| 1-2 | 54.3 |
| 1-3 | 85.9 |
| 2-3 | 43.3 |

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

| Plane | $A$ | $B$ | $C$ | $D$ |
|---|---|---|---|---|
| 1 | 0.8201 | 0.5620 | −0.1073 | 9.0843 |
| 2 | 0.6802 | −0.0940 | −0.7270 | 1.1419 |
| 3 | 0.3369 | −0.7323 | −0.5918 | −2.0893 |

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

**Scheme I**



anide insertion in the tungsten complex, VI. Accordingly, the reaction sequence is aborted upon methylation at the metal atom. It is also known that electron-withdrawing alkyl groups resist insertion reactions,[3] and we have previously shown that the reactions of anions I and II with chloroacetonitrile lead to the formation of complexes containing a cyanomethylene group attached to the molybdenum atoms.[8] They show no evidence toward isocyanide insertion even under forcing conditions.

The $\eta^2$-iminoacyl dicarbonyl complexes readily add nucleophiles, L, to the metal atoms in a step which also converts the $\eta^2$-iminoacyl ligand into an $\eta^1$-iminoacyl ligand, step 3a. This leads to the formation of complexes VII–X. Accordingly, we observe a shift to lower energy of the C–N stretching vibration into the region that is characteristic of the monohapto structural arrangement. If L is an iodide ion, the $\eta^1$-iminoacyl complex is negatively charged and is subject to protonation, step 4a. This occurs at the nitrogen atom of the iminoacyl group and produces the carbene ligand as found in complex XI.

On the other hand, if after step 2 there are additional isocyanide ligands in the coordination sphere of the metal atom, the addition of iodide is accompanied by a second isocyanide insertion, step 3b. Multiple isocyanide insertion rearrangements have been noted on several previous occasions.[35] It is possible that this insertion may occur directly upon the $\eta^2$-iminoacyl ligand.[36] The $\eta^2$-iminoacyl ligand is converted into an $\eta^2$-imino group and is joined to the inserting isocyanide which becomes an $\eta^1$-imino group. The entire complex is negatively charged and subsequently reacts with an additional molecule of methyl iodide, step 4b. Methylation occurs at the lone pair on the nitrogen atom of the $\eta^1$-imino grouping and converts it into the dimethylaminocarbene group. The observed temperature-dependent $^1$H NMR spectra are a result of averaging of these aminomethyl groups due to hindered rotation about this aminocarbene C–N bond.

The comparative ease of isocyanide insertion is a notable feature and can be demonstrated from two sources.[38] For example, even under optimum conditions it is known that carbonyl insertions in related complexes generally require a reflux period of several hours in THF solvent.[39] In the present systems the insertions are usually complete within 15 min at room temperature although longer reaction periods were permitted. However, more direct evidence may be obtained from these present systems, per se. We observe that the initial insertion, step 1, always involves an isocyanide ligand, yet carbonyl ligands are contained within the coordination sphere of the metal atom and could, in principle, insert if it were energetically more favorable. We have found no evidence whatsoever for carbonyl insertions occurring in any of the systems studied here.

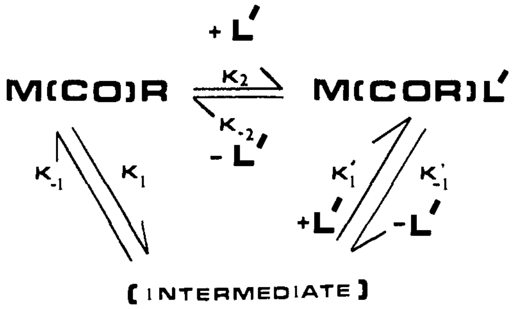
Facile isocyanide insertions may be a general property of molybdenum complexes and such processes have already been invoked to explain the formation of $C_2$ and $C_3$ hydrocarbons in the reduction of isocyanides by nitrogenase and molybdothiol model systems.[40]

The most important feature of the present work is the isolation and characterization of the first $\eta^2$-iminoacyl ligands. They, undoubtedly, demonstrate the importance of this structural arrangement, not only as an intermediate, but even as a ground state in the overall scheme of isocyanide insertions. Their scope probably goes far beyond the few systems studied here. Recently, Otsuka et al.[41] in their studies of isocyanide insertion into alkyl palladium bonds observed an intermediate which was described as "a highly coordinatively unsaturated species having an iminoalkyl ligand". This may well be another example of an $\eta^2$-iminoacyl ligand.

It seems appropriate that we compare what we now know about isocyanide insertion reactions with what is already known about the carbonyl insertion reactions. As is represented by eq 1, kinetic and mechanistic studies have shown that the insertion and addition of L′ can follow either of two pathways, Scheme II.[3]

The $k_2$ pathway follows second-order kinetics, and it is believed that L′ is added to the complex in conjunction with the

Scheme II



formation of the acyl group. Through the $k_1$ pathway, a slow formation of an intermediate is followed by a rapid addition of L′ to give the product. Rearrangement rates via this pathway are frequently sensitive to the coordinating ability of the solvent, and it has been proposed that the intermediate is a solvent coordinated acyl complex.[3,42] In some cases, however, rates via the $k_1$ pathway have been shown to be solvent independent.[43] In these cases, the structural character of the intermediate is even less certain. Coordinatively, unsaturated and $\eta^2$- or $\pi$-acyl species have been proposed.[3,44] Recently, the first structural verification of an $\eta^2$-acyl ligand has been reported.[45]

Our studies of the isocyanide insertion reaction shows that it also proceeds via the formation of an intermediate. In the absence of coordinating ligands, the intermediate may be isolated and carefully studied.[7] It possesses a dihapto structural arrangement, and its great stability can only buttress those arguments which support the $\eta^2$-acyl ligand as the structure of some intermediates for carbonyl insertions.

Another important feature is the facility of the $\eta^2 - \eta^1$ transformation. This may be important in catalyst design and development, and has already been invoked on numerous occasions to explain the stereospecific cyclization and oligomerization of acetylenes by metal atoms.[46]

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

**Supplementary Material Available:** Root mean square amplitudes of thermal vibration, selected intermolecular distances, and crystal packing diagram (4 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) Preliminary report: R. D. Adams and D. F. Chodosh, *J. Am. Chem. Soc.*, **98**, 5391 (1976).
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