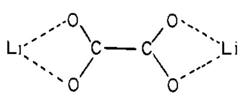
Table X. Comparison of Observed Product Band Positions (cm^{-1}) for Residue on Trapping Surface after CO_2 Is Sublimed away from ^6Li and CO_2 Matrix with Reported Frequencies for $Li_2C_2O_4$

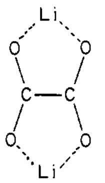
vibr mode	obsd frequency[a]	reported frequency[35]
$\nu(B_{3u})$, CO	1655 s	1650 vs
$\nu(B_{2u})$, CO	1315 m	1330 vs
$\nu(B_{2u})$, δ(OCO)	775 w	771 vs

[a] vs, very strong; s, strong; m, medium; w, weak.

further verified by comparing the observed product band positions for the residue left on the trapping surface after CO_2 is sublimed away from a ^6Li and CO_2 matrix with reported frequencies for $Li_2C_2O_4$ as shown in Table X. Two structures of D_{2h} symmetry are possible (I and II) for lithium oxalate molecules where the two lithiums are at equivalent positions and are equally interactive with two of the four oxygens. These structures seem reasonable as reflected from the values of the frequency assigned to the asymmetric stretching mode since if each lithium were interacting with one oxygen only, the frequency of this mode would have been at a higher value, namely, in the C=O stretching region of $LiCO_2(C_s)$. The second highest frequency is also due to a CO stretching mode, but it is a symmetric one. The third has been attributed to a δ(OCO) bending mode, and the lowest frequency is associated with a Li–O stretching mode. Again these assignments were based on carbon-13, oxygen-18, and lithium-6 isotopic frequency shifts.



I



II

X-ray diffraction studies[33] have shown that lithium oxalate has structure II in the solid phase where two of the CO bonds in the trans position are equal and slightly shorter than their counterparts (compare 1.252 vs. 1.264 Å). The carbon–carbon bond length is calculated to be 1.561 Å, which is greater than a typical value for a single bond. The $Li^+\cdots O$ distances vary between 1.931 and 2.071 Å in the crystal structure of $Li_2C_2O_4$. Our observations do not allow us to distinguish between the two structural isomers. However, recently Jordan[32] has carried out preliminary calculations on stabilities and structures of $Li_2C_2O_4$ and has concluded that species II is more stable than I.

Acknowledgment. Funds from the Robert A. Welch Foundation and from the National Science Foundation have supported this study.

Registry No. Li, 7439-93-2; CO_2, 124-38-9; Ar, 7440-37-1; $LiCO_2$, 80480-95-1; Li_2CO_2, 85355-11-9; LiC_2O_4, 85355-12-0; $Li_2C_2O_4$, 553-91-3; ^{13}C, 14762-74-4; ^{18}O, 14797-71-8; Xe, 7440-63-3.

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Asymmetric Synthesis of (+)-2,2,3-Trimethylhex-4-enal via Nucleophilic Attack on η^3-1,3-Dimethylallyl Complexes of Molybdenum

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Abstract: Nucleophilic attack on mixtures of endo and exo isomers of (neomenthylcyclopentadienyl)carbonylnitrosyl(η^3-1,3-dimethylallyl)molybdenum complexes (NM = neomenthyl) provide facile routes to optically pure allylically substituted olefins. A given configuration at the metal center controls the configuration at the allylic center because the exo isomer is attacked preferentially and attack occurs cis to the nitrosyl. Thus, reaction of an enamine of isobutyraldehyde with (*S*)-[NMCpMo(CO)(NO)(η^3-1,3-dimethylallyl)] cation yields (+)-(*R*)-2,2,3-trimethylhex-4-enal upon liberation of the olefin from the complex. The crystal and molecular structure of (*S*)-[(η^5-$C_{15}H_{23}$)Mo(CO)(NO)(η^2-$C_8H_{15}CHO$)] was determined by X-ray crystallographic analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ (D_2^4) (No. 19) with lattice constants a = 10.331 (2) Å, b = 13.571 (3) Å, c = 17.968 (7) Å, and Z = 4. Full-matrix least-squares refinement using anisotropic thermal parameters for the molybdenum and isotropic thermal parameters for the remaining non-hydrogen atoms converged to the final residuals $R_1 = 0.069$ and $R_2 = 0.066$.

Since Tsuji's original studies of nucleophilic reactions with (η^3-allyl)palladium complexes,[1] extensive applications to organic syntheses have been developed,[2] particularly by Trost.[3] The use of allylic moieties bound to metal complexes offers the potential of enhanced activity, greater selectivity, and the possibility of control of S_N2 vs. S_N2' attack. The control of regiochemistry and stereochemistry using the palladium systems was exploited originally in stoichiometric reactions, and subsequently, catalytic approaches were developed. The effectiveness of these systems in alkylations suggested that they might be useful in asymmetric synthesis. Considering the high optical yields achieved in asymmetric catalytic hydrogenation using chiral phosphines,[4] these palladium allyls offered a potential route to effective asymmetric allylic alkylations. The stoichiometric reactions using optically active chelating phosphines such as DIOP met with modest success

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(up to 24% ee with 1,3-dimethylallyl) in asymmetric formation of carbon–carbon bonds.[5] Improvements in optical purity (up to 46% ee (enantiomeric excess) with cyclopentyl) were obtained by using the catalytic approach.[6,7] Bosnich, upon detailed consideration of rearrangement mechanisms available to palladium allyls[8] and the diastereomeric interactions with the phosphines, recently devised systems which give higher optical yields (up to 86% ee).[9]

The nucleophilic additions are generally presumed to involve attack on an η^3-allyl trans to the metal; however, cis additions occur in some cases[10] and σ intermediates are obtained with high ligand concentrations[11] and become important reactants in some situations.[12] Although this mechanism can be open to debate,[13] empirically, one observes that the selectivity can vary or even be reversed by variations in solvent, substrate concentration or ligand concentration.[7] Our recent success in the preparation of readily resolvable allylmolybdenum complexes containing the neomenthylcyclopentadienyl group[14,15] suggested to us that these complexes might provide a complementary approach for asymmetric syntheses.

The molybdenum system appeared attractive relative to stoichiometric palladium reactions on the basis of cost. It also had potential advantages relative to the catalytic palladium system because the molybdenum complexes are less prone to form σ-allyls, are coordinately saturated and do not contain labile ligands. These features limit the mechanistic paths for rearrangement and lessen the chance of prior additions of the nucleophile to the metal and subsequent transfer to the allyl. We have shown previously that attack of a nucleophile occurs on the face opposite to the metal and cis to nitrosyl in the exo isomer of the [CpMo(NO)(CO)(1,3-dimethylallyl)] cations.[16] The Cp, NO, CO, and allyl substituents on the molybdenum center render it chiral; thus, attachment of a neomenthyl group to the cyclopentadienyl ring provides a pair of diastereomers, which fortunately can be separated readily. With substituted allyl groups, therefore, one has a straightforward method of producing complexes of allylically substituted olefins of predictable configuration in very high optical purity.

Experimental Section

General Synthetic Procedures. All operations involving the handling of organometallic complexes in solution were carried out by using inert-atmosphere techniques under an atmosphere of nitrogen. THF was distilled from sodium benzophenone ketyl before use. Other solvents were deoxygenated with a stream of dry nitrogen. Neomenthylcyclopentadiene was prepared according the method of Cesarotti, Kagan, et al.[17] with the exception that the reflux period with NaCp was increased to 10 h.

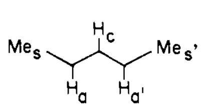
NMR spectra were obtained with Bruker spectrometers operating at 270 and 500 MHz. The chemical shifts are reported as parts per million downfield from Me_4Si are at 270 MHz unless indicated otherwise. Optical rotations were measured with a Perkin-Elmer 241 polarimeter with a thermostated cell. Sample concentrations were measured by weighing the complex on a microbalance (±1 μg), weighing the solvent, and converting to g/100 cm^3 using the density of the solvent.

Preparation of NMCpMo(CO)$_2$(1,3-dimethylallyl). Two grams (7.58 mmol) of $Mo(CO)_6$ was suspended in 75 mL of CH_3CN. The solution was refluxed for 3 h, and then 1.36 g (7.58 mmol) of 4-bromo-2-pentene was added whereby a large quantity of yellow precipitate was produced. The solvent was removed completely under reduced pressure, and freshly distilled THF (75 mL) was added. Lithium neomenthylcyclopentadienide was prepared from a solution of 1.55 g (7.58 mmol) of NMCpH in 20 mL of THF by the addition of 4.7 mL of 1.6 M *n*-BuLi in hexane. The resulting suspension was added via syringe to the solution of $Mo(CO)_2(CH_3CN)_2$(1,3-dimethylallyl)Br. After the mixture was stirred for 10 h at 25 °C, removal of the solvent on a rotary flash evaporator left an orange-red crystalline residue. The crude orange-red product was extracted with a CH_2Cl_2–pentane (1:1) mixture and was chromatographed on a 2.5 × 12 cm column of alumina. Removal of solvent from the yellow eluant gave 2.41 g (75%) of a yellow crystalline product. Recrystallization from pentane yielded a product melting at 54–56 °C and having a rotation $[\alpha]_D$ +49.5° (*c* 0.112). The 500-MHz ^{1}H NMR exhibited resonances for the major conformer (*syn,syn-exo*-1,3-dimethylallyl), which was present to the extent of 85%, at ($CDCl_3$, 25 °C): δ 5.41, 5.24, 5.05, 5.01 (m, 4 CpH of NMCp), 3.98 (t, H_2, J = 9.5 Hz), 1.76, 1.73 (d, 2 Me, J = 6.3, 6.3 Hz), 0.94, 0.93, 0.71 (d, 3 Me of NMCp, J = 6.3, 6.0, 5.9 Hz). The anti protons at the 1- and 3-positions of the allyl were obscured by the neomenthyl resonances. Carbonyl bands were observed in cyclohexane solution at 1948 and 1872 cm^{-1}. Anal. Calcd for $MoC_{22}H_{32}O_2$: C, 62.26; H, 7.60. Found: C, 62.18; H, 7.57.

Preparation of [NMCpMo(NO)(CO)(1,3-dimethylallyl)]PF$_6$. NMCpMo(CO)$_2$(1,3-dimethylallyl), 200 mg (0.47 mmol), was dissolved in 10 mL of CH_3CN at 0 °C. Nitrosonium hexafluorophosphate (83 mg, 0.47 mmol) was added to the solution, which turned dark brown and effervesced owing to CO evolution. After 5 min at 0 °C the mixture was added dropwise into cold ether. The yellow precipitate, which formed immediately, was separated by centrifugation and crystallized twice from CH_2Cl_2–pentane mixtures. This crude product with $[\alpha]_D{}^{25}$ +66 (*c* 0.033, $CHCl_3$) was obtained in 80% yield (220 mg) and melted at 142–145 °C dec and the IR showed two bands at 2071 and 1716 cm^{-1} (CH_2Cl_2). The ^{1}H NMR ($CDCl_3$) showed four sets of resonances, suggesting the presence of four isomers, which were assigned to the endo and exo isomers of both diastereomers arising from *R* and *S* configurations at the metal center. Anal. Calcd for $MoC_{21}H_{32}NO_2PF_6$: C, 44.14, H, 5.64. Found: C, 44.98, H, 5.73.

Preparation of (−)$_D$-(*S*)-[NMCpMo(NO)(CO)(1,3-dimethylallyl)]BPh$_4$. An isomeric mixture of [NMCpMo(NO)(CO)(1,3-dimethylallyl)]PF$_6$ (40 mg, 0.073 mmol) was dissolved in 15 mL of acetone, 25 mg (0.073 mmol) of $NaBPh_4$ was added, the mixture was stirred for 30 min, and the solvent was removed. The residue was extracted with CH_2Cl_2, and the solution was evaporated to yield a yellow precipitate which was recrystallized from a CH_2Cl_2–pentane and washed with pentane to yield light yellow crystals (31 mg, 60%). This BPh_4^- salt had a rotation of $[\alpha]^{25}{}_D$ −68° (*c* 0.167, acetone), and the IR showed two bands at 2075 and 1720 cm^{-1} (CH_2Cl_2). It melted at 98–100 °C dec. The ^{1}H NMR (acetone-d_6, 25 °C) showed only two sets of resonances indicating the presence of exo and endo conformers of a single CpMo(NO)(CO) configuration in a ratio of 2:1. The exo isomer exhibited the following resonances: δ 7.33, 6.94, 6.77 (m, 20 H, Ph), 6.59, 6.27, 6.01, 5.96 (m, 4 CpH of NMCp), 5.41 (t, H_c, J_{ca} = 12.4 Hz, $J_{ca'}$ = 12.4 Hz), 4.04 (dq, H_a, J_{ac} = 12.4 Hz, J_{as} = 6.3 Hz), 3.58 (dq, $H_{a'}$, $J_{a'c}$ = 12.4 Hz, $J_{a's}$ = 6.2 Hz), 2.434 (d, Me_s, J_{sa} = 6.3 Hz), 2.198 (d, $Me_{s'}$, $J_{s'a'}$ = 6.2 Hz), 0.970, 0.929, 0.753 (d, 3 Me of NMCp).

The endo isomer exhibited the following: δ 7.33, 6.94, 6.77 (m, 20 H Ph), 6.46, 6.42, 6.10, 5.89 (m, 4 CpH of NMCp), 5.45 (t, H_c, J_{ca} = 12.8 Hz, $J_{ca'}$ = 12.8 Hz), 4.38 (dq, H_a, J_{ac} = 12.8 Hz, J_{as} = 6.6 Hz), $H_{a'}$ unobserved, 2.443 (d, Me_s, J_{sa} = 6.6 Hz), 2.186 (d, $Me_{s'}$, $J_{s'a'}$ = 6.2 Hz), 0.970, 0.929, 0.753 (d, 3 Me of NMCp).



Forty milligrams (0.054 mmol) of (−)$_D$-[NMCpMo(NO)(CO)(1,3-dimethylallyl)]BPh$_4$ was dissolved in 15 mL of CH_3CN at 0 °C. The 1-pyrollidino-2-methylpropene (7.5 μL, 0.054 mmol) was added to the

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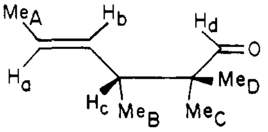
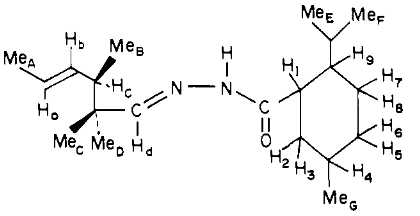
solution and the mixture allowed stir for 1 h. Several drops of water were added, and the mixture was passed through acidic alumina to remove the base. The solvent was evaporated and the residue crystallized from CH_2Cl_2–pentane. The complex had a rotation of $[\alpha]^{25}_{D}$ +64° (c 0.055, $CHCl_3$) gave three intense IR bands at 1969, 1722, and 1633 cm^{-1} (CH_2Cl_2) and melted at 120–122 °C dec. The ^1H NMR (25 °C, $CDCl_3$) showed the following resonances: δ 9.496 (s, CHO), 5.88, 5.58, 5.49, 4.66 (m, 4 CpH of NMCp), 2.980 (dq, H$_a$, J_{aA} = 6.1 Hz, J_{ab} = 11.5 Hz), 2.885 (dd, J_{ba} = 11.5 Hz, J_{bc} = 9.5 Hz), 1.424 (d, Me$_A$, J_{Aa} = 6.1 Hz), 1.192 (d, Me$_B$, J_{Bc} = 7.0 Hz), 1.138, 1.093 (s, Me$_C$, Me$_D$), 0.984, 0.925, 0.775 (d, 3 Me of NMCp). This complex was shown to be (*S*)-NMCpMo(NO)(CO)[(*S*)-2,2,3-trimethylhex-4-enal] by single-crystal X-ray structural analysis (see below).



Preparation and Resolution of (+)$_D$- and (−)$_D$-NMCpMo(NO)(CO)(2,2,3-trimethylhex-4-enal). Following the procedure for the tetraphenylborate, 40 mg (0.072 mmol) of the diastereomeric mixture of [NMCpMo(NO)(CO)(1,3-dimethylallyl)]PF_6 was dissolved in 15 mL of CH_3CN at 0 °C and 0.01 mL of 1-pyrrollidino-2-methylpropene (0.072 mmol) was added to the solution. Evaporation of the eluent from chromatography on acidic alumina gave 28 mg (80%) of a mixture of diastereomers; i.e., 48% yield of a major isomer and 32% of a minor isomer. Three crystallizations from CH_2Cl_2–pentane yielded the pure major isomer $[\alpha]_D$ +64°, with an NMR spectrum identical with that obtained from the single isomer obtained from the BPh_4^- salt. The more soluble minor isomer exhibited resonances (25 °C, $CDCl_3$): δ 9.50 (s, CHO), 6.04, 5.69, 5.37, 4.55 (m, 4 CpH of NMCp), 3.05 (m, Ha), 2.96 (m, Hb), 1.46 (d, Me$_A$, J = 6.1 Hz), 1.21 (d, Me$_B$, J = 7.0 Hz), 1.15, 1.11 (s, Me$_C$, Me$_D$), 0.93, 0.91, 0.78 (d, 3 Me of NMCp).

Preparation of Optically Pure (+)-2,2,3-Trimethylhex-4-enal. Pure (+)$_D$-NMCpMo(NO)(CO)(2,2,3-trimethyl-4-hexenal) (33 mg, 0.067 mmol) was dissolved in 10 mL of $CDCl_3$ in the air and the solution allowed to stand for 10 days, after which the metal complex had decomposed completely. Addition of 1 g of neutral alumina and filtration separated the decomposed metal complex and left only the free ligand in the solution, as verified by ^1H NMR spectroscopy. The aldehyde had rotations of $[\alpha]^{25}_{D}$ +20° and $[\alpha]^{25}_{365}$ +97° (c 0.015, $CDCl_3$), and the IR showed one band at 1750 cm^{-1} ($CDCl_3$). The ^1H NMR exhibited the following resonances (25 °C, $CDCl_3$): δ 9.432 (s, CHO), 5.464 (dq, H$_a$, J_{ab} = 15.4 Hz, J_{aA} = 6.2 Hz), 5.266 (ddq, H$_b$, J_{ba} = 15.4 Hz, J_{bc} = 8.4 Hz, J_{bA} = 1.5 Hz), 2.245 (dq, H$_c$, J_{cb} = 8.4 Hz, J_{cB} = 7.0 Hz), 1.642 (dd, Me$_A$, J_{Aa} = 6.2 Hz, J_{Ab} = 1.5 Hz), 0.956, 0.954 (s, Me$_C$, Me$_D$), 0.911 (d, Me$_B$, J_{Bc} = 7.0 Hz). This compound was obtained in greater than 97% ee based on derivatization (see below).

Preparation of the *l*-Menthyl Hydrazide of 2,2,3-Trimethylhex-4-enal. Two hundred milligrams (1.43 mmol) of racemic 2,2,3-trimethylhex-4-enal was dissolved in 15 mL of THF, and 283 mg (1.43 mmol) of *l*-menthyl hydrazide was added. After the mixture was stirred for 2 h, the solvent was removed and the residue was washed with pentane and recrystallized from CH_2Cl_2–pentane. The yield was 382 mg (90%) of crystals melting at 88–90 °C. The IR showed bands at 1715 and 1693 cm^{-1} (pentane). Anal. Calcd for $C_{20}H_{36}N_2O$: C, 74.95; H, 11.32. Found: C, 75.24; H, 11.07. The ^1H NMR of the diastereomeric mixture exhibited the following resonances at 25 °C: ($CDCl_3$) δ 7.769 (s, NH), 7.089 (s, H$_d$), 5.414 (dq, H$_a$, J_{aA} = 5.6 Hz, J_{ab} = 14.9 Hz), 5.308 (dd, H$_b$, J_{ba} = 14.9 Hz, J_{bc} = 7.6 Hz), 4.638 (td, H$_1$, J_{12} = 4.6 Hz, J_{19} = 10.6 Hz, J_{13} = 10.6 Hz), 1.642 (d, Me$_A$, J_{Aa} = 5.6 Hz), 1.040, 1.035 (s, Me$_C$, Me$_D$), 0.882 (d, Me$_E$, Me$_F$, J = 7.3 Hz), 0.786 (d, Me$_G$). Diastereomeric differences in shifts were more readily observed in benzene-d_6: δ 7.150 (s, NH), 6.704 (s, H$_d$), 5.24 (m, 2 H, H$_a$, H$_b$), 4.902 (td, H$_1$, J_{12} = 4.4 Hz, J_{19} = 11.0 Hz, J_{13} = 11.0 Hz), 1.545 (d, Me$_A$, J_{Aa} = 4.0 Hz), 1.002, 0.991 (s, Me$_C$, Me$_D$, isomer A), 0.985, 0.976 (s, Me$_{C'}$, Me$_{D'}$, isomer B), 0.891 (d, Me$_E$, Me$_F$, J = 7.0 Hz), 0.878 (d, Me$_B$, J_{Bc} = 6.9 Hz, isomer A), 0.874 (d, Me$_{B'}$, $J_{B'c}$ = 6.9 Hz, isomer B), 0.758 (d, Me$_G$, J_{G4} = 6.2 Hz).



Preparation of the (2,4-Dinitrophenyl)hydrazone Derivative of (+)$_D$-NMCpMo(NO)(CO)(2,2,3-trimethylhex-4-enal). Pure (+)$_D$-NMCPMo(NO)(CO)(2,2,3-trimethylhex-4-enal) (33.2 mg, 0.066 mmol) was dissolved in 30 mL of absolute ethanol, and 13.2 mg of 2,4-DNPH (0.066 mmol) was added to the solution. After the addition of 1.5 mL of concentrated HCl, the solution was stirred for 4 h. The solvent was removed and the residue taken up in CH_2Cl_2. Chromatography on silica gel yielded a yellow band which was concentrated to yield orange crystals. Recrystallization from CH_2Cl_2–pentane yielded 42 mg (95%) of the hydrazone melting at 123–125 °C dec. The IR showed bands at 1970, 1705, 1617 cm^{-1} (CH_2Cl_2). It gave a rotation of $[\alpha]_D$ +53° (c 0.077, CH_2Cl_2), and its ^1H NMR (25 °C, $CDCl_3$) showed the following resonances: δ 11.001 (s, H$_d$), 9.140 (d, H of DNP, J = 2.6 Hz), 8.31 (dd, H of DNP, J = 2.6, 9.5 Hz), 7.954 (d, H of DNP, J = 9.5 Hz), 7.464 (s, NH of DNP), 5.890, 5.583, 5.502, 4.660 (m, 4 H of Cp of NMCp), 2.975 (dq, H$_a$, J_{ab} = 12.0 Hz, J_{aA} = 6.2 Hz), 2.861 (dd, H$_b$, J_{ba} = 12.0 Hz, J_{bc} = 9.5 Hz), H$_3$ not observed, 1.494 (d, Me$_A$, J_{Aa} = 6.2 Hz), 1.292, 1.252 (s, Me$_C$, Me$_D$), 0.976, 0.913, 0.767 (d, 3 Me of NMCp); 0.868 (d, Me$_B$ = J 6.6 Hz).

Preparation of the (2,4-Dinitrophenyl)hydrazone Derivative of the (+) Enantiomer of 2,2,3-Trimethylhex-4-enal. The (+)-NMCpMo(NO)(CO)(2,2,3-trimethylhex-4-enal–2,4-DNPH) complex (68 mg, 0.10 mmol) was dissolved in 30 mL of absolute ethanol, 40 mg (0.25 mmol) of $FeCl_3$ was added to the solution, and the mixture was stirred for 12 h. After removal of the solvent, the residue was extracted with CH_2Cl_2 and chromatography on silica gel gave a well-resolved yellow band. Evaporation and recrystallization of the residue from CH_2Cl_2 yielded the 2,4-DNPH derivative, melting at 143–145 °C dec and exhibiting an IR band at 1705 cm^{-1} (CH_2Cl_2). The hydrazone had a rotation of $[\alpha]_D$ −10° (c 0.038, acetone). The mass spectrum showed a parent peak at *m*/*e* 320, and major fragments were observed at *m*/*e* 274 (M − NO_2), 251 (M − C_5H_9), and 69 (C_5H_9). The ^1H NMR yielded the following resonances (25 °C, $CDCl_3$): δ 11.001 (s, H$_d$), 9.133 (d, H of DNP, J = 2.6 Hz), 8.307 (dd, H of DNP, J = 2.6, 9.5 Hz), 7.936 (d, H of DNP, J = 9.5 Hz), 7.415 (s, NH of DNP), 5.491 (dq, H$_a$, J_{aA} = 6.2 Hz, J_{ab} = 15.4 Hz), 5.359 (dd, H$_b$, J_{ba} = 15.4 Hz, J_{bc} = 8.4 Hz), 2.207 (dq, H$_c$, J_{cb} = 8.4 Hz, J_{cB} = 6.6 Hz), 1.694 (d, Me$_A$, J$_{Aa}$ = 6.2 Hz), 1.148 (s, Me$_C$, Me$_D$), 0.994 (d, Me$_B$, J_{Bc} = 6.6 Hz). Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29. Found: 56.31; H, 6.17.

Crystallographic Analyses. Crystals of (+)-NMCpMo(NO)(CO)-[2,2,3-trimethylhex-4-enal] were grown from methylene chloride–pentane solution by cooling. All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. The unit cell was determined from 2k randomly selected reflections by using the CAD-4 automatic search, center, index, and least-squares routines. The space group was determined from the systematic absences $h00$, $h = 2n$, $0k0$, $k = 2n$, and $00l$, $l = 2n$, observed during data collection.

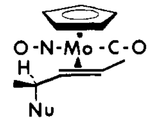
All calculations were performed on a Digital PDP 11/23 computer using the Enraf-Nonius SDP program library. The structure was solved by the heavy-atom method. Anomalous dispersion corrections[12a] were added to the neutral-atom scattering factors.[12b] Full-matrix least-squares refinements minimized the function $\sum w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F^2)$, $\sigma(F) = \sigma(F_o)^2/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (pF_o^2)^2]^{1/2}/Lp$. Crystallographic data for the structure are listed in Table I.

A crystal of dimensions 0.2 mm × 0.2 mm × 0.2 mm was selected and mounted in a thin-walled glass capillary. From a total of 2537 reflections including absences collected, 961 reflections ($F^2 > 2\sigma(F^2)$) were used in the structure solution and refinement. Hydrogen atoms were not included in the refinement. The proper absolute configuration was obtained by reference to the known configuration of the neomenthyl group.[8,9] The distinction between CO and NO was made by refining both C and N as carbon atoms. The atom identified as nitrogen refined to yield an isotropic thermal parameter of 2.05 Å^2 compared to that of 5.36 Å^2 for carbon. Additional features that confirm this assignment are the shorter Mo–N bond length (Mo–N = 1.72 Å; Mo–C = 1.92 Å) and the greater linearity of the M–C–O bond (M–C–O = 177°; M–N–O = 171°). The largest peak in the final difference Fourier synthesis was 0.66 e/Å^3 and was in the vicinity of the metal atom. The largest value of the shift/error parameter on the final cycle of refinement was 0.01. The error in an observation of unit weight was 1.714. Final atomic coordinates and thermal parameters are listed in Table II. Selected bond distances and angles with errors from the inverse matrix obtained on the final cycle of least-squares refinement are listed in the supplementary material.

Results

Owing to the high directing effect of the nitrosyl group,[10,13,14] a single enantiomeric product would be expected from a reaction on a given enantiomer of a η^3-1,3,-dimethylallyl complex (eq 1).[21]

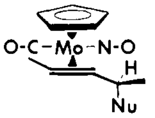
(*R*)-[CpMo(NO)(CO)(1,3-dimethylallyl)]$^+$ $\xrightarrow{\text{Nu}}$



(1a)

(R,R)

(*S*)-[CpMo(NO)(CO)(1,3-dimethylallyl)]$^+$ $\xrightarrow{\text{Nu}}$

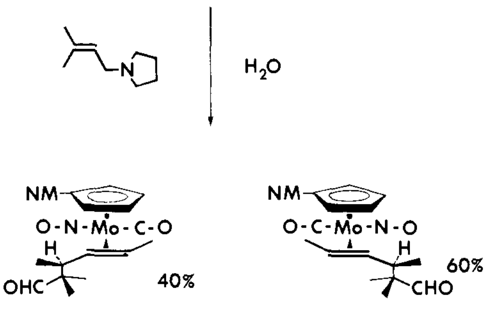


(1b)

(S,S)

Attachment of a neomenthyl group to the cyclopentadienyl ring has proved valuable in this system as a method of producing diastereomers of significantly different physical properties.[16] Thus, we anticipated the diastereomeric NMCpMo(NO)(CO)(allyl) and -(olefin) complexes to be readily distinguishable by NMR spectroscopy and separable by crystallization. If one takes the diastereomeric mixture produced by the addition of $NOPF_6$ to $NMCpMo(CO)_2$(1,3-dimethylallyl) and adds the nucleophile, 1-pyrrolidino-2-methylpropene, two diastereomeric aldehydes are obtained (eq 2). The configurations at the metal center and at

(*R*)- and (*S*)-[NMCpMo(NO)(CO)(1,3-dimethylallyl)]$^+$
1



(R,R)-2 (S,S)-2

(2)

the 3-carbon of the aldehydes of major isomer, (+)-(*S*,*S*)-**2**, were verified by X-ray diffraction analysis as shown in Figure 1.[21]

Resolution of the 1,3-dimethylallyl cation (*S*)-**1** could be achieved readily by recrystallization with the tetraphenylborate counterion. Reaction of the pure enantiomer with the enamine gave a single product, (+)-(*S*)-**2**. Alternatively, a mixture of (*R*)-**1** and (*S*)-**1** could be treated with the enamine and the products easily separated to yield pure (+)-(*S*)-**2**. Thus, two convenient routes to a complex containing the pure (+)-2,2,3-trimethylhex-4-enal, **3**, were developed.

Several methods are available for the removal of the unsaturated moiety from the metal. The choice is dependent on the sensitivity of product to decomposition and nature of the intended use of the product. The mildest procedure found was the exposure of a chloroform solution of the complex to air and allowing the solution to stand for several days. After this time the oxidized molybdenum complexes could be removed by adsorption on alumina and filtration. This provided a chloroform solution of the pure olefinic ligand. This procedure was especially useful for small quantities of liquid products and for subsequent physical studies to establish enantiomeric purity before treatments which might alter the ee (eq 3).

Removal appears to occur with less than 2% racemization. Unfortunately chiral shift reagents were ineffective in producing

Table I. Experimental Data for X-ray Diffraction Study of (+)-(*S*)-(Neomenthylcyclopentadienyl)carbonylnitrosyl-(2,2,3-trimethylhex-4-enal)molybdenum

(A) Crystal Parameters at 24 (2) °C

space group	$P2_12_12_1$	V, Å	2519 (2)
a, Å	10.331 (2)	Z	4
b, Å	13.571 (3)	mol wt	497.53
c, Å	17.968 (7)	ρ_{calcd}, g/cm	1.312

(B) Measurement of Intensity Data

radiation Mo Kα	0.710 73 Å
monochromator	graphite
detector aperture	horizontal, $A + B \tan \theta$ (A = 3.0 mm, B = 1.0 mm); vertical, 4.0 mm
reflctns measd	$+h, +k, +l$
max 2θ, deg	50
scan type	moving crystal–stationary counter
ω scan rate, deg/min	max, 10; min, 1.82
ω scan width, deg	1.1
background	one-fourth additional scan at each end of scan
std reflctns	three measured after each 90 min; showing only random fluctuations of ±2%
reflctns measd	2537 including absences
data used ($F^2 > 2\sigma(F^2)$)	961

(C) Treatment of Data

abs coeff μ, cm^{-1}	5.388
p factor	0.03
final residuals R_1, R_2	0.069, 0.066
esd of unit weight	1.714

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo	−0.1587 (2)	−0.3342 (1)	−0.2285 (1)	*b*
O1	−0.126 (2)	−0.551 (1)	−0.2237 (9)	6.7 (4)
O2	−0.330 (2)	−0.327 (1)	−0.0873 (8)	7.1 (4)
O3	0.456 (2)	−0.455 (1)	−0.2095 (10)	7.6 (5)
N	−0.136 (2)	−0.459 (1)	−0.220 (1)	4.8 (4)
C	−0.262 (2)	−0.330 (2)	−0.1394 (12)	5.2 (6)
Cp1	−0.225 (2)	−0.340 (2)	−0.3583 (10)	2.5 (4)
Cp2	−0.113 (2)	−0.273 (2)	−0.3520 (12)	3.4 (6)
Cp3	−0.156 (2)	−0.189 (1)	−0.3057 (9)	3.1 (5)
Cp4	−0.286 (2)	−0.206 (1)	−0.2793 (13)	4.2 (6)
Cp5	−0.332 (2)	−0.302 (1)	−0.3126 (10)	3.4 (5)
C1	0.352 (3)	−0.442 (2)	−0.1753 (13)	6.6 (7)
C2	0.286 (2)	−0.350 (2)	−0.1713 (11)	3.6 (5)
C3	0.146 (2)	−0.380 (1)	−0.2029 (10)	3.3 (5)
C4	0.052 (2)	−0.296 (1)	−0.1970 (11)	2.9 (5)
C5	−0.025 (2)	−0.277 (2)	−0.1319 (13)	3.8 (6)
C6	−0.048 (2)	−0.173 (2)	−0.1060 (12)	5.5 (6)
C7	0.345 (3)	−0.263 (1)	−0.2132 (12)	4.8 (6)
C8	0.272 (2)	−0.324 (2)	−0.0840 (12)	5.4 (6)
C9	0.157 (3)	−0.419 (1)	−0.2858 (11)	4.5 (5)
Cm1	−0.224 (2)	−0.438 (1)	−0.4036 (11)	2.5 (5)
Cm2	−0.218 (2)	−0.420 (2)	−0.4883 (11)	3.4 (6)
Cm3	−0.356 (2)	−0.372 (2)	−0.5141 (11)	4.2 (6)
Cm4	−0.462 (3)	−0.455 (2)	−0.4020 (13)	4.8 (6)
Cm5	−0.474 (3)	−0.471 (2)	−0.4130 (14)	5.4 (7)
Cm6	−0.340 (3)	−0.507 (1)	−0.3852 (10)	3.6 (5)
Cm7	−0.095 (2)	−0.365 (2)	−0.5153 (11)	3.6 (6)
Cm8	0.029 (2)	−0.415 (2)	−0.4976 (14)	5.0 (7)
Cm9	−0.105 (2)	−0.348 (2)	−0.6031 (12)	5.1 (6)
Cm10	−0.567 (3)	−0.557 (2)	−0.4045 (14)	6.1 (7)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)]$, where $B(1,1)$ = 2.70 (6), $B(2,2)$ = 2.77 (7), $B(3,3)$ = 3.03 (6), $B(1,2)$ = 0.3 (1), $B(1,3)$ = 0.1 (1), and $B(2,3)$ = 0.1 (1).

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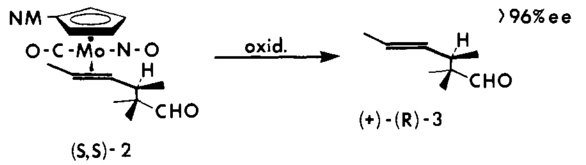
(21) Although the neomenthyl group and the olefinic ligand contain several chiral centers, we will often specify only the chirality at the metal center. If two centers are specified, the first is the metal center and the second is the 3-carbon of the hexenal. Priorities for the metal center are established by assuming that the ligands are pseudo atoms of atomic number equal to the sum of those bound to the metal [cf. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–6600. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1–36]. Note that the descriptor of the chirality at the 3-carbon of 2,2,3-trimethylhexen-4-al ligand in (*S*)-**2** shown in Figure 1 is *S*; however, when the ligand is free, the 3-carbon descriptor is *R* even though the absolute configuration at that center is the same.



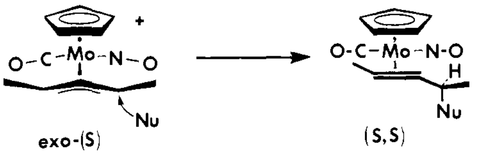
(3)

diastereomeric shifts in the NMR spectrum to establish enantiomeric purity. Preparation of the *l*-menthyl hydrazide of the racemic aldehyde provided diastereomers which showed sufficient differences in the NMR spectrum to allow analysis of the enantiomeric ratio. The hydrazide prepared from the aldehyde released from (+)-(*S*)-**2** was enantiomerically pure within the accuracy of the NMR experiment.

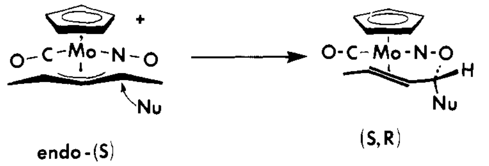
Alternatively, a derivative could be prepared of the complexed aldehyde and more stringent conditions applied to removing the metal. For example, the 2,4-DNPH derivative was prepared of (+)-(*S*)-**2** and oxidatively cleaved from the molybdenum complex by ferric ion.

Discussion

Studies with substituted CpMo(NO)(CO)(allyl) cations have shown that not only does nucleophilic attack occur cis to nitrosyl in the exo isomer but also cis to nitrosyl in the endo isomer, as well.[22,23] Hence, one would expect different products to be obtained from *exo*-(*S*)-**2** and *endo*-(*S*)-**2** (eq 4). Most importantly, these products would yield different enantiomers of 2,2,3-trimethylhex-4-enal upon release from the metal.[21,24] Therefore, the observation that only a single product is obtained by nucleophilic addition to the endo, the exo, or endo–exo mixtures of 1,3-dimethylallyls complexed to the CpMo(NO)(CO) or (*S*)-NMCpMo(NO)CO) moieties is surprising.



(4a)



(4b)

The source of the high selectivity can be traced to the relative rates of exo–endo interconversion and the rates of nucleophilic substitution of exo and endo isomers. With η^3-cyclooctenyl systems the exo–endo reactant interconversion rate can be made negligible relative to the nucleophilic substitution rate. Hence, the product stereochemistry depends on the starting isomer; i.e., exo-(*S*) yields the (*S*,*S*) product, whereas endo-(*S*) yields the (*S*,*R*) product.[23] It also appears that the reaction rates of the exo isomers are generally ten to several hundred times faster than those of the analogous endo isomers. Thus, for the [CpMo(NO)(CO)(η^3-cyclooctentyl)]$^+$ cation one finds $k_{2x}[\mathrm{Nu}] > k_{2n}[\mathrm{Nu}] \gg k_{1n} > k_{1x}$ (eq 5).

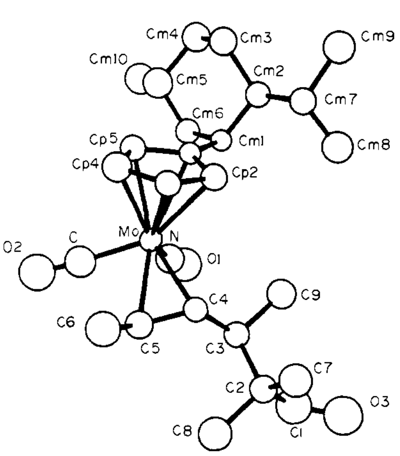


Figure 1. An ORTEP plot showing 50% probability ellipsoids of (+)-(*S*)-NMCpMo(NO)(CO)[2,2,3-trimethylhex-4-enal].

$$\begin{tikzcd} \text{exo-(S) reactant} \arrow[r, "\mathrm{Nu}", "k_{2x}"'] \arrow[d, shift left, "k_{1x}"] & (S,S)\text{ product} \\ \text{endo-(S) reactant} \arrow[r, "\mathrm{Nu}", "k_{2n}"'] \arrow[u, shift left, "k_{1n}"] & (S,R)\text{ product} \end{tikzcd} \tag{5}$$

For the 1,3-dimethylallyl complex, the exo–endo interconversion rate is faster and the exo reaction rate is much faster than that of the endo isomer. Furthermore, it appears that the exo–endo interconversion is catalyzed by the nucleophile. Thus, very little product is obtained directly from the endo isomer. The endo isomer is consumed by conversion to the exo isomer and subsequent reaction with the nucleophile. This path results from relative rates of $k_{2x}[\mathrm{Nu}] > k_{1n} > k_{1x} \gg k_{2n}[\mathrm{Nu}]$.

This complex kinetic system can be studied by variations in concentration and temperature to allow dominance of a particular rate.[17] Although this was only investigated qualitatively for the 1,3-dimethylallyl system. Low-temperature NMR studies of an exo–endo mixture in the presence of nucleophile showed cleanly the disappearance of *exo*-(*S*)-**2** and formation of (*S*,*S*)-product resonances without significant change in *endo*-(*S*)-**2** signal intensity.

Conclusions

These complexes provide a route for allylic alkylations in high optical yield. Owing to the formation of different diastereomers from exo to endo isomers, one has the opportunity to prepare either enantiomer under appropriate conditions. Understanding of the mechanism and rate laws can allow control of the product, but for most situations conversion of the cation to the exo isomer, or a mixture predominately the exo isomer, is sufficient to yield a single diastereomer of predictable configuration. Since the exo cation predominates at equilibrium in cases when there is no substituent on the 2-carbon of the allyl, most experiments will yield a single diastereomer if equilibrated starting cations are used.

A large number of nucleophilic reagents can be used in these reactions,[23,25-27] and we are pursuing these methods on cyclic allyls and unsymmetrical acyclic allyls. It appears that these molybdenum systems may provide an alternate route to many of the syntheses based on allylic palladium systems.[1-6,28]

Acknowledgment. This research was supported by National Science Foundation Grant CHE82-08042. We also wish to thank

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(22) The increase in exo–endo interconversion rate which occurs only in the presence of nucleophile was not understood in the initial studies with the unsubstituted allyl.[16,20] Thus the catalyst was consumed by the reaction. This produced results in control and kinetic experiments which were misinterpreted as requiring trans attack in the endo isomer. Theoretical results on charge distribution and overlaps clearly predicted cis attack in the exo isomer but showed a marginal reversal in the endo isomer.[20]

(23) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organomet. Chem.*, to be submitted for publication.

(24) One might also note that the chiral centers at carbon atoms attaching the double bond to the metal atom are different in the isomers arising from endo and exo reactants. Hence, when Nu = $\mathrm{CMe_2CHO}$, the (*S*)-CpMo(NO)(CO) fragment is attached to a (3*S*,4*R*,5*R*)-olefin when made from exo-(*S*), but a (3*R*,4*S*,5*S*)-olefin when made from endo-(*S*).

(25) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388–3390.

(26) McCleverty, J. A.; Murray, A. J. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 273–285.

(27) McCleverty, J. A.; Murray, A. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1424–1429.

(28) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310–1315.

the National Science Foundation for its support of the NSF Northeast Regional NMR Facility (Grant CHE79-16210).

Registry No. NMCpMo(CO)$_2$B (B = 1,3-dimethylallyl), 85565-44-2; [NMCpMo(NO)(CO)B]PF$_6$ (B = 1,3-dimethylallyl) (isomer 1), 85565-46-4; [NMCpMo(NO)(CO)B]PF$_6$ (B = 1,3-dimethylallyl) (isomer 2), 85646-37-3; [NMCpMo(NO)(CO)B]PF$_6$ (B = 1,3-dimethylallyl) (isomer 3), 85646-35-1; [NMCpMo(NO)(CO)B]PF$_6$ (B = 1,3-dimethylallyl) (isomer 4), 85646-39-5; [NMCpMo(NO)(CO)B]BPh$_4$ (B = 1,3-dimethylallyl) (isomer 1), 85699-63-4; [NMCpMo(NO)(CO)B]-BPh$_4$ (B = 1,3-dimethylallyl) (isomer 2), 85646-40-8; NMCpMo(NO)(CO)B (B = (*R*)-2,2,3-trimethylhex-4-enal) (isomer 1), 85565-47-5; NMCpMo(NO)(CO)B (B = (*R*)-2,2,3-trimethylhex-4-enal) (isomer 2), 85646-41-9; (+)$_D$-NMCpMo(NO)(CO)B (B = 2,2,3-trimethylhex-4-enal) ((2,4-dinitrophenyl)hydrazone), 85565-48-6; Mo(CO)$_6$, 13939-06-5; M(CO)$_2$(CH$_3$CN)$_2$(B)Br (B = 1,3-dimethyl)allyl), 85565-49-7; NMCpH, 69165-85-1; (+)-2,2,3-trimethylhex-4-enal, 85553-69-1; 2,2,3-trimethylhex-4-enal (*l*-menthyl hydrazide) (isomer 1), 85553-70-4; 2,2,3-trimethylhex-4-enol (*l*-menthyl hydrazide) (isomer 2), 85611-53-6; (+)-2,2,3-trimethylhex-4-enal ((2,4-dinitrophenyl)-hydrazone), 85553-71-5; 4-bromo-2-pentene, 1809-26-3; 1-pyrrolidino-2-methylpropene, 2403-57-8; *l*-menthyl hydrazide, 85553-68-0.

Supplementary Material Available: Tables of selected bond distances and angles and structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Synthesis and Decay Kinetics of Ni(CO)$_3$N$_2$ in Liquid Krypton: Approximate Determination of the Ni–N$_2$ Bond Dissociation Energy

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Abstract: The unstable species Ni(CO)$_3$N$_2$ is generated in solution by UV photolysis of Ni(CO)$_4$ in N$_2$-doped liquid Kr in a specially designed high-pressure cell. We have used IR spectroscopy to follow the subsequent thermal reaction of Ni(CO)$_3$N$_2$ with dissolved CO to reform Ni(CO)$_4$. The reaction rate has been monitored over the temperature range 112–127 K. The rate shows a first-order dependence on the concentration of Ni(CO)$_3$N$_2$ and a more complex dependence on the concentrations of CO and N$_2$. The reaction involves two simultaneous paths, one dissociative and the other probably associative. From the dissociative path, we have estimated the Ni–N$_2$ bond dissociation energy to be 10 kcal mol^{-1}.

Introduction

Kinetic measurements on unstable inorganic species in solution have been obtained either by "instantaneous" techniques such as flash photolysis[2a] and pulse radiolysis or by pseudo-steady-state methods such as stopped flow.[2b] Unfortunately, these techniques generally provide rather poor structural information about the unstable species. By contrast, matrix isolation can provide excellent structural data about reactive and even highly unstable species, trapped in low-temperature solids,[3,4] but kinetic measurements on these species are generally impossible, except in unusual circumstances.[5] Recently[6] we have used liquefied xenon at −80 °C as a solvent for the photochemical generation of the molecules Cr(CO)$_{6-x}$(N$_2$)$_x$, all previously unknown outside low-temperature matrices. The compounds were identified from their IR spectra in specially designed low-temperature/high-pressure cells.[7,8] During this work we also found that the thermal stabilities of the different Cr(CO)$_{6-x}$(N$_2$)$_x$ species could be estimated by using a *conventional* IR spectrometer (e.g., for Cr(CO)$_3$(N$_2$)$_3$, $t_{1/2} \sim 15$ min at −79 °C).

In this paper, we describe the photochemical generation of a thermally much less stable compound, Ni(CO)$_3$N$_2$, in liquid krypton. Ni(CO)$_3$N$_2$ has previously been identified only in low-temperature matrices either by photolysis[9] of Ni(CO)$_4$ in solid N$_2$ or by co-condensation of Ni atoms with CO/N$_2$ mixtures.[10] Furthermore, we present quantitative kinetic measurements for the thermal decay reaction

$$\mathrm{Ni(CO)_3N_2 + CO \rightarrow Ni(CO)_4 + N_2}$$

over the temperature range 112.5–127 K (which represents a change in kT equivalent to a temperature rise of 40 °C at room temperature).

This type of ligand replacement reaction in substituted metal carbonyl complexes has received considerable attention.[11,12] In particular, tetrahedral nickel (Ni^0, d^{10}) complexes such as Ni(CO)$_4$ obey a single-term rate law in which the ligand substitution process appears to be purely dissociative (D) in character.[13] The bimolecular pathway is predominant,[14-16] however, for the isoelectronic d^{10} species Co(CO)$_3$NO, Fe(CO)$_2$(NO)$_2$, and Mn(NO)$_3$CO. In the case of the group 6B M(CO)$_5$(amine) compounds the situation is more complicated.

Substitution of amine by a Lewis base such as PR$_3$ generally follows a two-term rate law:

$$\mathrm{M(CO)_5A + L \rightarrow M(CO)_5L + A}$$

whence, in the absence of added free amine (A)

$$k_{\text{obsd}} = k_1 + k_2[\mathrm{L}] \qquad \mathrm{L} = \text{phosphine} \tag{1}$$

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