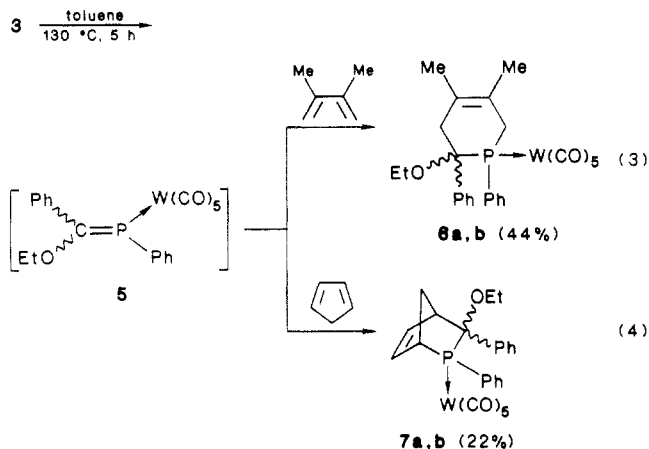and 7,[9] both as mixtures of two isomers (eq 3 and 4). These [4 + 2] cycloadditions are typical of either free or P-complexed P=C double bonds.[10,11]

6a,b (44%)

7a,b (22%)

We are currently exploring the various possibilities offered by these preliminary results.

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(9) Complexes 7a,b were separated by chromatography on silica gel at −10 °C (eluent pentane/CH$_2$Cl$_2$, 7/1). 7a: mp ~115 °C; ^{31}P NMR (CDCl$_3$) δ +55.4; ^{1}H{^{31}P} NMR (CDCl$_3$) δ 1.32 (t, 3 H, CH$_3$), 2.14 (m, ^2J(H−H) = 10.3 Hz, 1 H, bridge CH$_2$), 2.66 (m, 1 H, bridge CH$_2$), 3.38 (m, 1 H, OCH$_2$), 3.60 (m, 1 H, OCH$_2$), 3.70 (m, 2 H, bridgehead CH), 6.16 (m, ^3J(H−H) = 5.6 Hz, 1 H, =CH), 6.31 (m, ^3J(H−H) = 5.6 Hz, 1 H, =CH), 6.45−7.54 (m, 10 H, Ph); IR (CH$_2$Cl$_2$) ν(CO) 2072 (m), 1940 (vs) cm^{-1}; MS (EI, 20 eV, ^{184}W) m/z (relative intensity) 632 (M, 47), 548 (M − 3CO, 100), 492 (M − 5CO, 89). Anal. Calcd for C$_{25}$H$_{21}$O$_6$PW: C, 47.48; H, 3.32; O, 15.19; P, 4.90; W, 29.09. Found: C, 47.79; H, 3.35; O, 15.34; P, 4.43; W, 28.90. 7b (major isomer) mp 147−150 °C; ^{31}P NMR (CDCl$_3$) δ +44.6 (^1J(^{31}P−^{183}W) = 239 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 14.70 (s, Me), 42.83 (d, ^2J(C−P) = 15 Hz, bridge CH$_2$), 48.61 (d, ^1J(C−P) = 14 Hz, CH−P), 49.65 (d, ^2J(C−P) = 4 Hz, CH), 61.12 (d, ^3J(C−P) = 4 Hz, OCH$_2$), 90.27 (d, ^1J(C−P) = 34 Hz, O−C−P), 196.61 (d, ^2J(C−P) = 5 Hz, cis CO), 199.52 (d, ^2J(C−P) = 23 Hz, trans CO); ^{1}H{^{31}P} NMR δ 0.90 (t, 3 H, CH$_3$), 2.31 (m, 2 H, bridge CH$_2$), 3.08 (q, 2 H, OCH$_2$), 3.86 (m, 2H, bridgehead CH), 6.05 (dd, ^3J(H−H) = 5.6 and 3.2 Hz, 1 H, =CH), 6.45 (dd, ^3J(H−H) = 5.6 and 2.9 Hz, 1 H, =CH), 7.24−7.60 (m, 10 H, Ph); IR (CH$_2$Cl$_2$) ν(CO) 2072 (m), 1940 (vs) cm^{-1}; MS (EI, 20 eV, ^{184}W) m/z (relative intensity) 632 (M, 47), 548 (M − 3CO, 100), 492 (M − 5CO, 65). Anal. Found: C, 47.24; H, 3.45; O, 15.25; P, 4.05; W, 28.90. We suggest that in the minor isomer 7a, the OCH$_2$ is cis to the W(CO)$_5$ group, thus explaining the deshielding and the inequivalency of these protons (hindered rotation); conversely, one of the bridge protons of 7a is shielded by the phenyl C substituent.

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## Asymmetric Recognition between Triosmium Clusters and Their μ-Acyl Ligands

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Summary: The triosmium clusters Os$_3$(1,2-μ-H)[1,2-μ-O=C(CHMeR)](CO)$_{10}$ (R = Et (1), Ph (2), or cyclohexyl (3)) exist as diastereomers resulting from the combined cluster-centered asymmetry and the asymmetry of the α-acyl carbon. The diastereomeric excesses (de) of the triosmium clusters, as synthesized, are 18%, 81%, and 15%, respectively. The diastereomers of 3 are separable by thin-layer chromatography. Each diastereomer of 3 independently equilibrates to a de of 20% when heated in the presence of 1,4-diazabicyclo[2.2.2]octane. Clusters 1 and 2 give thermodynamic de's of 8% and 58%, respectively, under the same equilibrating conditions.

When a heterobidentate ligand is bound to a trinuclear cluster, such as in structure A, the compound exists as a pair of enantiomers as a result of the cluster-centered asymmetry. A variety of such di- and trimetal complexes containing heterobidentate ligands have been reported.[1-7] When the ligand is also asymmetric, diastereomers result that may have significantly different stabilities due to interactions between the metal cluster moiety and the bridging ligand; see structure B. These energy differences

A

B
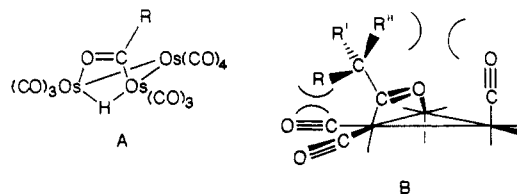
will determine the suitability of clusters for asymmetric synthesis and catalysis and for the use of chiral clusters as mechanistic probes for cluster integrity under catalytic conditions. We now report results which demonstrate the cooperative asymmetric recognition between triosmium clusters and their μ-acyl ligands. Stepwise asymmetric induction has recently been reported on mononuclear titanium,[8] iron,[9-12] rhenium,[13] and cobalt,[14] complexes. Asymmetric syntheses using mononuclear organometallic catalysts have been reviewed.[15]

Cluster 1 was prepared by the method of Mayr[16] by titrating Os$_3$(CO)$_{12}$ in dry tetrahydrofuran with *sec*-BuLi (1.3 M in cyclohexane) while monitoring by IR ν(CO). The resulting anion was protonated with F$_3$CC(O)OH to yield 1. Clusters 2 and 3 were synthesized by the reaction of Os$_3$(NCMe)$_2$(CO)$_{10}$[4] with an excess of either (±)-2-phenylpropionaldehyde (Oxford) or (±)-2-cyclohexylpropionaldehyde, respectively[17] in dibutyl ether at 80 °C

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Table I. Diastereomeric Excesses and Spectroscopic Data for $Os_3[1,2\text{-}\mu\text{-H};1,2\text{-}\mu\text{-O}=C(CHMeR)](CO)_{10}$
(R = Et (1), Ph (2), and Cyclohexyl (3))[a]

	de/%			
compd	I[b]	II[c]	isomer	^{1}H NMR[d]
1	18	8	1a	1.7–0.7 (m), –13.74 (s)
			1b	1.7–0.7 (m), –13.84 (s)
2	81	58	2a	7.4–6.9 (m, 5), 3.42 (quart, 1, J = 7 Hz), 1.35 (d, 3 J = 7 Hz), –14.00 (s, 1)
			2b	7.4–6.9 (m, 5), 3.67 (quart, 1, J = 7 Hz), 1.18 (d, 3, J = 7 Hz), –14.15 (s, 1)
3	15	20	3a	2.55 (quint, 1, J = 7 Hz), 1.9–0.9 (m, 11), 0.78 (d, 3, J = 7 Hz), –14.08 (s, 1)
			3b	2.00 (quint, 1, J = 7 Hz), 1.9–0.9 (m, 11), 1.07 (d, 3, J = 7 Hz), –13.90 (s, 1)

[a] IR (cm^{-1}, hexane, ν(CO)): 1, 2109 w, 2070 s, 2057 s, 2028 s, 2014 s, 1997 m, 1982 w; 2, 2108 w, 2069 s, 2058 s, 2027 s, 2011 s, 1998 m, 1983 w; 3, 2109, w, 2069 s, 2058 s, 2028 s, 2014 s, 1999 w, 1981 m. MS; ^{192}Os parent ion: 1, m/e 942; 3, m/e 996. [b] Synthetic Diastereomeric excess. [c] Thermodynamic Diastereomeric excess. [d] Chemical shifts are reported in parts per million downfield from Me$_4$Si; 1 in acetone-d_6; 2 and 3 in CDCl$_3$.

for 4 h. 2-Cyclohexylpropionaldehyde was prepared by oxidizing 2-cyclohexyl-1-propanol (Wiley) with pyridinium chlorochromate.[18] Clusters 1, 2, and 3 were purified by 4% ethyl acetate/hexane elution of reaction residues on silica thin-layer chromatography plates.

1

2

3
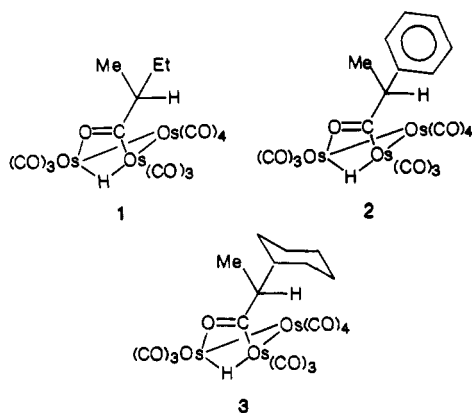
Diastereomeric excesses (de) and spectroscopic data for 1, 2, and 3 are reported in Table I. The de's were determined by integrations of the diastereomeric hydride signals in the ^{1}H NMR spectra. Cluster 1 has a de of 18% when isolated from the reaction mixture. This reflects the subtle discrimination between H, Me, and Et groups of the μ-acyl ligand. Methods to equilibrate the diastereomers of 1 were developed to establish whether the above de represented thermodynamic or kinetic ratios determined during synthesis (see below). The amine base 1,4-diaza-bicyclo[2.2.2]octane (Dabco) was found to facilitate H/D exchange of the μ-acyl α-protons with deuterons from acetone-d_6 but not the exchange of the bridging hydride. In fact, when 1 was treated with Dabco in toluene-d_8 at 96 °C for 45 min, a new de (8%) was established, indicating that this is the thermodynamically favored de under these conditions.

In cluster 2 the Et group of 1 has been replaced by the more bulky phenyl. The de of 2 (81%) is expectedly greater than that of 1 (18%) presumably resulting from the more pronounced discrimination between H, Me, and Ph. Diastereomers of 2 were equilibrated as described for 1 above. The thermodynamic de for 2 was established in 45 min and was found to be 58%. Arce's carboxamido cluster 4[19,20] differs from 2 by having (–NH–) situated between the bridging carbonyl carbon and the alkyl group. This places the chiral carbon center one bond length
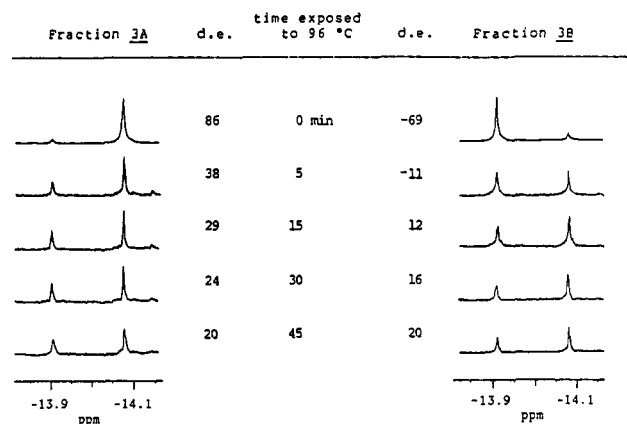
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Figure 1. Ambient-temperature ^{1}H NMR spectra of the thermal equilibrations of the separated diastereomers of 3 in toluene-d_8.

farther from the triosmium moiety than in the corresponding μ-acyl cluster 2. As a result of the closer in-

4

5
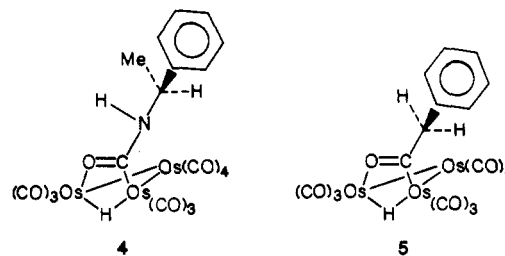
teraction of the asymmetric centers in 2, both de's of 2 (synthetic 81%, thermodynamic 58%) are greater than that of 4 (30%). An earlier X-ray structure of the benzyl μ-acyl cluster 5 indicates that the phenyl group occupies a position that points away from the cluster.[17] The phenyl group in 2 probably also favors this conformation. The preferred position of the methyl is less predictable.

The third substituent studied was cyclohexyl, i.e., cluster 3. The ^{1}H NMR spectrum of 3 has two close resonances in the hydride region of similar integrated areas which indicate a de of 15%. The diasteromers of 3 are separable by preparative silica thin-layer chromatography (eluant, 4% ethyl acetate in hexane). Each diastereomer was *independently* equilibrated at 96 °C in toluene-d_8 with Dabco to a final de of 20%. The ^{1}H NMR spectra of these equilibrations, the respective de's, and the exposure times to 96 °C are shown in Figure 1. These data prove that this equilibrated de of 3 is, in fact, the thermodynamic de. Since the final de's for 1 and 2 were obtained by equilibrating each under identical conditions as 3 and heating was stopped only well after no further isomer ratio changes were observed, these values reflect thermodynamic de's with reasonable certainty.

We have demonstrated that the asymmetry arising from heterobidentate ligand bonding to transition-metal clusters can be stereospecifically translated into ligand configuration. The initially observed (synthetic) de's are different than those obtained under equilibrating conditions. These results indicate the magnitudes of diastereomeric excesses that can reasonably be expected in similar cluster systems and the sensitivity of observed de's to substituents. Our observations set good precedent for the utility of the broad variety of asymmetric clusters now available[1-7,21] in asymmetric synthesis and catalysis.[22]
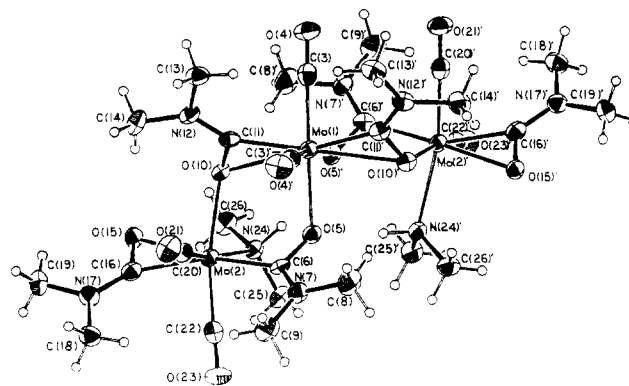
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Mo₃[C(O)NMe₂]₆(CO)₆(HNMe₂)₂. An Unexpected Product Formed in the Carbonylation of Mo(NMe₂)₄ Displaying Three Distinct Modes of Carbamoyl–Molybdenum Bonding

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Summary: From the reaction between Mo(NMe₂)₄ and CO (>4 equiv) in hydrocarbon solvents, the yellow crystalline compound Mo₃[C(O)NMe₂]₆(CO)₆(HNMe₂)₂ has been obtained and characterized. In the solid state, the molecule has C_2 symmetry. There are three *cis*-Mo(CO)₂ units, two related by symmetry. Each molybdenum atom has 18 valence shell electrons and may be ascribed as oxidation state +2 in a distorted octahedral geometry considering the η²-carbamoyl ligands are uninegative, occupy one coordination site, and donate four electrons. The Mo₃ chain is held together by two pairs of bridging carbamoyl ligands, one of which is η²-(CO)-bonded to the central molybdenum atom Mo(1) and η¹, oxygen-bonded to the outer molybdenum atoms Mo(2) and Mo(2)'; the other pair are η²-(CO)-bonded to Mo(2)/Mo(2)' and Mo(1), respectively. NMR data indicate that the trimeric unit is retained and relatively rigid in solution.

The d² group 4–6 metal complexes or fragments are known to be capable of binding π-acceptor ligands such as alkynes, olefins, carbon monoxide, diazoalkanes, and, even in some instances, dinitrogen. Well-known examples include Cp₂Ti(CO)₂,[1] [Cp*₂Zr(N₂)]₂(μ-N₂),[2] Cp*₂Ta-(H)(C₂H₄),[3] Mo(O-*t*-Bu)₄(N₂CAr₂),[4] and [WCl₄(Ph₂C₂)]₂.[5] We are currently examining the reactivity of the coordi-

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Figure 1. An ORTEP view of the Mo₃[C(O)NMe₂]₆(CO)₆(HNMe₂)₂ molecule giving the atomic number scheme used in the tables.

natively unsaturated, π-donor-stabilized, d² complex Mo-(NMe₂)₄[6] toward π-acid molecules[7] and wish to report here our discovery of an unexpected and unusual product formed in the reaction involving carbon monoxide.

The intense purple color of hydrocarbon solutions containing the extremely air- and moisture-sensitive compound Mo(NMe₂)₄ changes virtually instantaneously to brown upon exposure to carbon monoxide (>4 equiv). By ¹H and ¹³C NMR spectroscopy the main diamagnetic product formed is 1,1,3,3-tetramethylurea that suggests a reaction pathway involving (i) CO insertion to give a Mo[C(O)NMe₂] moiety and (ii) reductive elimination by C–N bond formation "Mo(IV)[C(O)NMe₂](NMe₂)" → "Mo(II)" + (Me₂N)₂CO. When pentane is used as the solvent, an inhomogenous brown solution results. Filtering this powder and reducing the volume of the filtrate yield the only isolable pure metal-containing compound Mo₃-[C(O)NMe₂]₆(HNMe₂)₂,[8] 5–20% yield.

The infrared spectrum was suggestive of (i) ν(NH) at 3225 cm⁻¹ for the coordinated Me₂NH ligand, (ii) *cis*-Mo(CO)₂ units, ν(CO) = 1948 and 1925 cm⁻¹ in the integral ratio 0.68,[9] and (iii) carbamoyl ligands[10] having ν(NCO) bands at 1585, 1530, and 1500 cm⁻¹. The ¹H NMR spectrum allowed the identification of a bound HNMe₂ ligand having diastereotopic methyl groups and three different carbamoyl ligands, each with two N*Me* carbons, implying restricted rotation about the Me₂N—CO bond. Even when the temperature is increased to 60 °C, all resonances in the ¹H NMR spectrum are well-defined with no noticable line broadening as might have been anticipated for a fluxional molecule. The ¹³C{¹H} spectrum of the ¹³CO-labeled compound was complicated by ¹³C–¹³C coupling between carbamoyl–carbamoyl, carbonyl–carbonyl, and carbamoyl–carbonyl carbon atoms. Identification of the carbamoyl carbon atoms, Me₂N-*C*O, was made possible by the fact that $^3J_{^{13}C-^1H}$ coupling causes broadening in the proton-coupled ¹³C NMR spectra. Three of the six signals

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(7) A reaction involving 2,6-dimethylphenyl isocyanide, CNAr (4 equiv), has been found to give a tetrakis(η²-amidino) complex Mo(η²-C-(NMe₂)N(Ar)₄): Chisholm, M. H.; Hammond, C. E.; Huffman, J. C.; Ho, D., submitted for publication in *J. Am. Chem. Soc.*

(8) Anal. Calcd (Found): C, 34.37 (34.57); H, 5.15 (5.04); N, 11.45 (11.47). ¹H NMR data (toluene-d₈ at 22 °C): δ 3.61 (septet, 2 H, *H*NMe₂), 3.16 (s, 6 H, N*Me₂*), 3.13 (s, 6 H, N*Me₂*), 3.06 (s, 6 H, N*Me₂*), 3.05 (s, 6 H, N*Me₂*), 2.98 (s, 6 H, N*Me₂*), 2.97 (s, 6 H, N*Me₂*), 2.61 (d, 6 H, HN*Me₂*), 2.44 (d, 6 H, HN*Me₂*). ¹³C{¹H}NMR spectral data using ¹³CO (CDCl₃ at 22 °C): δ 240.76 (m, 2 C, carbonyl), 239.05 (m, 2 C, carbamoyl), 235.63 (t, 2 C, carbonyl), 233.93 (m, 2 C, carbonyl), 230.24 (t, 2 C, carbamoyl), 210.47 (m, 2 C, carbamoyl).

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