Mixed-Metal Cluster Chemistry. 16.[1] Syntheses of Oligourethanes Containing Clusters in the Backbone

Nigel T. Lucas and Mark G. Humphrey*

Department of Chemistry, Australian National University, Canberra ACT 0200, Australia

A. David Rae

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

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ABSTRACT: Bis(hydroxyalkylcyclopentadienyl)-containing mixed molybdenum−iridium clusters $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_xOH\}_2$ [$x = 2$ (**1**), 10] react with alkyl or aryl 1,ω-diisocyanates OCNRNCO [R = $(CH_2)_y$ ($y = 4$, 6, 12), *trans*-1,4-cyclohexyl, or 4-$C_6H_4CH_2$-4-C_6H_4] to form oligourethanes with transition metal clusters in the oligomer backbone. Characterization of the cluster-containing oligourethanes is aided by spectral comparison with model cluster diurethanes $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)NHRH\}_2$ [R = $(CH_2)_y$ [$y = 4$ (**6**), 6, 12], *trans*-1,4-cyclohexyl] prepared from reaction between the cluster diol **1** and alkyl isocyanates HRNCO. The precursor diol cluster **1** and cluster diurethane **6** have been characterized by single-crystal X-ray diffraction studies. The extent of polymerization has been assessed by gel permeation chromatography, with little dependence on diisocyanate precursor linker R but strong dependence on alkylcyclopentadienyl linker length $(CH_2)_x$, suggesting that the steric influence of the bulky dimolybdenum−diiridium cluster core and co-ligands is the most important factor governing extent of polymerization. Supporting this assessment, the considerably more sterically hindered precursor 2-butyn-1,4-diol-substituted cluster $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}C_2(CH_2OH)_2\}(CO)_8(\eta\text{-}C_5H_5)_2$ fails to react to any significant extent with 1,6-diisocyanatohexane.

Introduction

Bimetallic clusters are of great significance; the presence of an M−M′ interaction in bimetallic clusters has led to their use as catalyst precursors for organic substrate transformations, some of which give products or product distributions not achievable utilizing the individual metal precursors. Well-defined, supported bimetallic clusters are of considerable interest as they can help enhance our understanding of these forms of catalysis. With this in mind, attention has focused on various supports to which bimetallic species may be attached and from which information may then be gleaned. Most studies have examined inorganic oxides or polymers as supports. Supporting bimetallic particles on inorganic oxides has successfully afforded catalytically active species; however, this procedure suffers from the problem of structurally nonuniform environments for the bimetallic species, which complicates interpretation of results and hence rational catalyst improvement. Supporting metal clusters on polymers has also attracted significant interest, with supported species catalytically active for ethylene hydrogenation.[2] While clusters have been stabilized by aminated polymers as ion pairs of cluster anions and ammonium cations,[3−9] almost all studies have examined coordinating metal clusters to prefunctionalized polymers, mainly through P-linkages,[10−13] but also via O-[14] C-,[15−17] and N-interactions.[18] Polymer supports of this type certainly afford greater structural control than is possible with inorganic oxide supports, but problems arise due to polycoordination,[19] resulting in a mixture of mono- and polysubstituted clusters, together with noncoordinated polymer bound ligands attached to the backbone.

A logical course of action which does not seem to have been widely exploited is to incorporate the metal cluster into the polymer backbone. Significant attention has been focused recently on incorporating transition metals in the polymer backbone[20−24] with ferrocene-based polymers in particular the subject of a considerable number of studies.[22,25] Despite these successes, and the attraction of cluster-containing analogues, few reports on polymer preparation with clusters in the backbone have appeared. Mixing $Co_4(CO)_{12}$ and dppe in varying ratios gave oligomeric structures containing Co_4 tetrahedra, with the largest being $Co_4(CO)_{11}\{(\mu\text{-dppe})Co_4(CO)_{10}\}_3(\mu\text{-dppe})Co_4(CO)_{11}$.[26] The mixed-metal polymeric $[(\mu\text{-}N,N'\text{-hexamethylenetetramine})Cu_2\{Co(CO)_4\}_2]_n$ with a butterfly Co_2Cu_2 cluster core has been prepared, although n was not estimated.[27] The cluster polymers $\{[\{Pt_3(\mu\text{-dppm})_3\}(\mu\text{-1,4-CNC}_6R_4NC)][PF_6]\}_n$, with triangular Pt_3 cores bridged by isocyanides, are only soluble in polar-coordinating solvents, possibly suggesting that the polymers break down under such conditions.[28] The polymeric $\{Ru_6(\mu_6\text{−}C)(CO)_{15}(Ph_2PC_2PPh_2)\}_n$ has been prepared, with n = ca. 1000 from electron microscopy, although the polymer was very beam-sensitive.[29] Existing cluster polymers are thus linked by P- and N-ligands and isocyanides, all of which can potentially be displaced, leading to polymer breakdown. None of the existing cluster polymers have afforded soluble polymeric structures except $\{Ru_6(\mu_6\text{−}C)(CO)_{15}(Ph_2PC_2PPh_2)\}_n$ which was reported while the present studies were in progress. New routes to soluble cluster-containing polymers are clearly required.

One particular problem with existing cluster-containing polymers is the ease of polymer breakdown. Replacing the P- or N-ligands with substituted cyclopentadienyl ligands, which are significantly more strongly bound to clusters, is expected to remedy this problem.

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* To whom correspondence should be addressed. E-mail: Mark.Humphrey@anu.edu.au.

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Tyler and co-workers have prepared polyamides, polyurethanes and polyureas containing $Mo_2(CO)_6(\eta\text{-}C_5H_4R)_2$ units along the polymer backbone.[30-36] This flexible methodology employing functionalized cyclopentadienyl rings was utilized to prepare photochemically reactive polymers; in the solid state, light and oxygen combine to cleave the Mo−Mo linkage and destroy the polymer, affording a visible light photodegradable polymer. Replacement of the photoactive $Mo_2(CO)_6(\eta\text{-}C_5H_4R)_2$ group with photostable cluster units is a logical procedure. We report herein the synthesis of a range of oligourethanes incorporating dimolybdenum−diiridium units in the oligomer backbone, and related "model" compounds, assessment of the size of these oligomers, and comment on the factors influencing the extent of polymerization.

Experimental Section

Materials. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All glassware used in reactions involving sodium, sodium hydride or isocyanates was flame-dried under vacuum before use. 2-Methoxypropene, $Mo(CO)_6$, 2-butyne-1,4-diol, dibutyltin diacetate, isocyanates, and diisocyanates (Aldrich), sodium metal, sodium hydride, and anhydrous potassium carbonate (BDH) were used without further purification. Liquid reactants were deoxygenated by purging with nitrogen prior to addition. Cyclopentadiene was distilled under nitrogen from cyclopentadiene dimer (Aldrich) immediately prior to use. The metal complex $IrCl(CO)_2(p\text{-toluidine})$[37] and cluster $Mo_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$[38] were prepared as described in the literature. Pyridinium *p*-toluenesulfonate was prepared from pyridine and *p*-toluenesulfonic acid according to a literature procedure.[39] The cyclopentadienylethanol ketal was prepared using a literature procedure.[30]

The reaction solvents THF (Unilab, LR grade) and *p*-dioxane (Aldrich) were distilled under argon from sodium benzophenone ketyl while CH_2Cl_2 (AR) was distilled from CaH_2 under argon; all other solvents were AR grade and used as received. Petroleum spirit refers to the petroleum fraction of boiling range 60−80 °C. The nonoligomer cluster compounds were purified by thin-layer chromatography (TLC) on 20 × 20 cm glass plates coated with Merck GF_{254} silica gel (0.5 mm). Column chromatography was performed using Merck silica gel 60 of particle size 0.040−0.063 mm (230−400 mesh ASTM).

Instruments. Infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in a solution cell with CaF_2 windows. ^1H NMR spectra were recorded in either $CDCl_3$, acetone-d_6 (Cambridge Isotope Laboratories), or THF-d_8 (Aldrich) using a Varian Gemini-300 FT spectrometer with residual nonperdeuterated solvent as an internal reference. Electron impact (EI) mass spectra (unit resolution and high resolution) were recorded using a VG Autospec instrument (70 eV electron energy, 8 kV accelerating potential) at the Research School of Chemistry, Australian National University. Secondary ion mass spectra (SIMS) were recorded using a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the Research School of Chemistry, Australian National University, or at the Department of Chemistry, University of Western Australia. All SIMS were calculated with the *m*/*z* based on ^{79}Br, ^{96}Mo, and ^{192}Ir assignments and are reported in the form: *m*/*z* (relative intensity) assignment. Elemental analyses were carried out by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University.

Polymer molecular weights were measured using a Spectra-Physics Analytical HPLC instrument (incorporating AS3000 auto sampler, P4000 pump with UV1000 detection). Experiments were run in THF (BDH HiperSolv, 99.7%) using toluene as an internal standard. The flow rate was maintained at 1.5 mL min^{-1}. The column was a 250 × 10 mm Jordi DVB Mixed-Bed with 5 μm particles. Polymers were detected with a UV−vis detector at 254 nm. Molecular weights were calculated using a standard curve calibrated from 0.37 to 130 K using polystyrene standards and were correlated with ^1H NMR results.

Synthesis of Diol Cluster $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OH\}_2$ (1). Sodium metal (108 mg, 4.70 mmol) was added to a flame-dried Schlenk tube containing cyclopentadienylethanol ketal (932 mg, 5.11 mmol) in 10 mL of THF. The mixture was stirred at room temperature until all the sodium had reacted (ca. 3 days). A further 10 mL of THF was added, followed by 1.00 g (1.53 mmol) of $Mo(CO)_6$, and the mixture heated at reflux for 24 h. After cooling, the THF was removed in vacuo and replaced with 30 mL of CH_2Cl_2. $IrCl(CO)_2(p\text{-toluidine})$ (201 mg, 0.514 mmol) was added to the stirred solution during which the color changed from pale pink to red-brown. After 1 h at room temperature, the excess metalate $[Mo(CO)_3\{\eta\text{-}C_5H_4(CH_2)_2OCMe_2(OMe)\}]^-$ was converted to the related chloride complex $MoCl(CO)_3\{\eta\text{-}C_5H_4(CH_2)_2OCMe_2(OMe)\}$ by addition of 0.5 mL of acetic acid, followed by 0.5 mL of CCl_4, and stirring another 15 min. The volume was reduced to 5 mL, and then acetone (10 mL) and water (0.5 mL) were added to effect deprotection to the alcohol over 1 h. The volatile materials were removed in vacuo, and the brown residue dissolved in 2 mL of CH_2Cl_2 and applied to preparative silica TLC plates. Elution with ethyl acetate/CH_2Cl_2 (1:1) afforded 4 bands. The products from the first three bands (in trace amounts) were identified by IR as $MoIr_3(CO)_{11}\{\eta\text{-}C_5H_4(CH_2)_2OH\}$ (orange, $R_f = 0.59$), $MoCl(CO)_3\{\eta\text{-}C_5H_4(CH_2)_2OH\}$ (orange, $R_f = 0.52$), and $Mo_2(CO)_6\{\eta\text{-}C_5H_4(CH_2)_2OH\}_2$ (red, $R_f = 0.43$),[30] respectively. The fourth and major band, $R_f = 0.27$, afforded 157 mg (0.146 mmol, 57%) of the desired diol cluster **1**. Diffusion of ethanol into a solution of **1** in toluene at 0 °C gave deep red-brown crystals.

IR (CH_2Cl_2): ν(O−H) 3619 w; ν(CO, cluster) 2060 vs, 2032 vs, 2006 vs, 1975 s, 1923 m, 1884 w, 1846 m, 1762 m; ν(C−O, alcohol) 1043 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.93−4.87 (m, 8H, cyclopentadienyl rings), 3.75 (t, J = 6 Hz, 4H, CH_2CH_2OH), 2.52 (t, J = 6 Hz, 4H, CH_2CH_2OH). MS (SIMS): 1074 (22) $[M]^+$. Anal. Calcd for $C_{24}H_{18}Ir_2Mo_2O_{12}$: C, 26.82; H, 1.69. Found: C, 27.22; H, 1.71.

Synthesis of 10-Bromodecanol Ketal, $Br(CH_2)_{10}OC(Me)_2OMe$ (2). A mixture of 10-bromodecanol (3.36 g, 14.1 mmol), 2-methoxypropene (3.00 mL, 31.3 mmol) and pyridinium *p*-toluenesulfonate (19 mg, 0.076 mmol) was stirred at 0 °C for 30 min and then for a further 1 h while allowing the mixture to warm to room temperature. The reaction mixture was gravity filtered into a separatory funnel and the paper washed with 20 mL of diethyl ether. The ethereal solution was washed twice with a brine solution and then dried over potassium carbonate. The ether and excess 2-methoxypropene were removed under reduced pressure (0.1 mmHg) to yield 3.79 g (12.3 mmol, 87%) of $Br(CH_2)_{10}OC(Me)_2OMe$ as a colorless liquid.

^1H NMR ($CDCl_3$): δ 3.61 (t, J = 7 Hz, 2H, CH_2O), 3.38 (t, J = 7 Hz, 2H, $BrCH_2$), 3.16 (s, 3H, OMe), 1.82 (quintet, J = 7 Hz, 2H, $BrCH_2CH_2$), 1.54 (quintet, J = 7 Hz, 2H, CH_2CH_2O), 1.31 (s, 6H, $C(Me)_2$), 1.27 (br s, 12H, $(CH_2)_6$. MS(EI): 293 (3) $[M - Me]^+$.

Synthesis of Cyclopentadienyldecanol Ketal, $C_5H_5(CH_2)_{10}OC(Me)_2OMe$ (3). Sodium metal (excess, 306 mg, 13.3 mmol) was added to a solution of freshly distilled cyclopentadiene (2.00 mL, 24.3 mmol) in THF (30 mL) and the resultant mixture stirred at room temperature for 6 h. The solution was separated from the unreacted sodium by transfer via cannula to a second Schlenk tube. The sodium cyclopentadienide solution was cooled to −78 °C, and a solution of 10-bromodecanol ketal (3.70 g, 12.0 mmol) in THF (15 mL) was added dropwise with the formation of a flocculant white precipitate. After being allowed to stand at 0 °C for 16 h, the solution was decanted from the precipitate which had settled, and 50 mL of diethyl ether was added. The ethereal solution was washed with brine solution (2 × 40 mL) and dried over potassium carbonate, and the volatile materials were removed in vacuo. The crude residue was added to a 30 cm silica column and eluted with 200 mL of petroleum spirit (containing 1% triethylamine). The solvent polarity of CH_2Cl_2/petroleum spirit mixtures was increased to finally neat CH_2Cl_2 as fractions were collected. The fractions were compared by analytical TLC and ^1H NMR, and identical fractions combined and the solvents removed under vacuum. The major band contained the cyclopentadienyldecanol ketal target compound **3** as a colorless liquid (mixture of isomers), 934 mg (3.17 mmol, 26% based on bromide precursor).

^1H NMR ($CDCl_3$): δ 6.41−5.96 (m, 3H, alkenyl), 3.62 (t, J = 7 Hz, 2H, CH_2O), 3.17 (s, 3H, OMe), 2.92 (m, 2H, allylic), 2.34 (m, 2H, $C_5H_5CH_2$), 1.52 (quintet, J = 7 Hz, 2H, CH_2CH_2O), 1.31 (s, 6H, $C(Me)_2$), 1.26 (br s, 14H, $(CH_2)_7$). MS(EI): 279 (4) $[M - Me]^+$. HR-MS(EI): Calculated $C_{18}H_{30}O$ 262.2297; Found 262.2296.

Synthesis of Diol Cluster $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_{10}OH\}_2$ (4). Sodium hydride (excess, 115 mg as a 60% dispersion in oil, 2.88 mmol) was added to a flame-dried Schlenk tube containing cyclopentadienyldecanol ketal (399 mg, 1.35 mmol) in 30 mL of THF. The mixture was stirred at room temperature for 18 h, and then the excess sodium hydride was allowed to settle. The pale pink solution was transferred to a second flame-dried Schlenk tube via a cannula. A 10 mL aliquot of THF used to wash the sodium hydride residue was also transferred into the second tube. The excess sodium hydride was carefully discarded. $Mo(CO)_6$ (373 mg, 1.41 mmol) was added and the mixture heated at reflux for 24 h. After cooling, the THF was removed in vacuo and replaced with 30 mL of CH_2Cl_2. $IrCl(CO)_2$(*p*-toluidine) (302 mg, 0.77 mmol) was added to the stirred solution, during which the color darkened. After 1 h at room temperature, the volume was reduced to 5 mL, and then acetone (10 mL), pyridinium *p*-toluenesulfonate (20 mg, 0.08 mmol), and water (0.5 mL) were added to effect deprotection of the alcohol over 1.5 h. The volatile materials were removed in vacuo, and the brown residue was dissolved in 2 mL of CH_2Cl_2 and applied to preparative silica TLC plates. Elution with ethyl acetate/CH_2Cl_2 (2:3) afforded 2 bands. The product from the first band (red, R_f = 0.50) was identified by IR as $Mo_2(CO)_6\{\eta\text{-}C_5H_4(CH_2)_{10}OH\}_2$. The product from the second and major band (R_f = 0.39) was isolated as a red-brown oil, and was identified as the diol cluster **4**, 180 mg (0.139 mmol, 36%).

IR (CH_2Cl_2): ν(O−H) 3617 w; ν(CO, cluster) 2060 vs, 2032 vs, 2006 vs, 1990 sh, 1973 m, 1925 m, 1884 w, 1850 m, 1760 m; ν(C−O, alcohol) 1045 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.85−4.76 (m, 8H, cyclopentadienyl rings), 3.61 (t, J = 7 Hz, 4H, $C_5H_4(CH_2)_9CH_2OH$), 2.23 (t, J = 8 Hz, 4H, $C_5H_4CH_2(CH_2)_9OH$), 1.53 (quintet, J = 7 Hz, 4H, $C_5H_4(CH_2)_8CH_2CH_2OH$), 1.25 (m, 28H, $C_5H_4CH_2(CH_2)_7CH_2CH_2OH$). MS(SIMS): 1298 (12) $[M]^+$.

Synthesis of Alkyne-Derived Diol Cluster $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}C_2(CH_2OH)_2\}(CO)_8(\eta\text{-}C_5H_5)_2$ (5). A mixture of $Mo_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$ (204 mg, 0.207 mmol) and 2-butyne-1,4-diol (88 mg, 1.02 mmol) in CH_2Cl_2 (40 mL) was heated at reflux for 1 h. After the reaction was cooled to room temperature, the solvent was removed in vacuo. The brown residue was dissolved in 2 mL of CH_2Cl_2 and applied to preparative silica TLC plates. Elution with ethyl acetate/CH_2Cl_2 (3:2) afforded two bands. The product from the first and major band (green, R_f = 0.49) was identified as the desired diol cluster **5**, 81 mg (0.080 mmol, 39%). The second band (R_f = 0.23) contained 23 mg of a green-brown compound that could not be identified.

IR (acetone-d_6): ν(CO) 2062 s, 2037 vs, 2011 m, 1991 w, 1812 m, 1777 m cm^{-1}. ^1H NMR (acetone-d_6): δ 5.33 (s, 10H, C_5H_5), 4.64 (t, J = 4 Hz, 2H, CH_2OH), 4.27 (d, J = 4 Hz, 4H, CH_2OH). MS (SIMS): 1016 (37) $[M]^+$.

Synthesis of Model Complex $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)N(H)(CH_2)_3CH_3\}_2$ (6). To a solution of diol cluster **1** (82.3 mg, 76.6 μmol) in 5 mL *p*-dioxane were added butyl isocyanate (80 μL, 765 μmol) and dibutyltin diacetate (DBTA) (4 μL, 15 μmol), and the mixture was stirred at room temperature for 18 h. Ethanol (ca. 0.3 mL, 5.5 mmol) was added and the mixture stirred for a further 1 h. All volatiles were removed in vacuo, and the dark red residue was dissolved in 1−2 mL of CH_2Cl_2 and applied to preparative TLC plates. Elution with ethyl acetate/petroleum spirit (2:3) gave a single band (red-brown, R_f = 0.51), the product from which was isolated and identified as **6** (70.2 mg, 55.1 μmol, 72%). Diffusion of methanol into a solution of **6** in CH_2Cl_2 at 3 °C gave deep red-brown crystals that were suitable for an X-ray structural study.

IR (CH_2Cl_2): ν(N−H) 3447 w; ν(CO, cluster) 2062 s, 2033 vs, 2007 vs, 1989 sh, 1969 m, 1926 ms, 1881 m, 1849 m, 1798 mw, 1762 ms; ν(C=O, urethane) 1723 s; δ(N−H) 1517 m; ν(C−N) 1218 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.86 (br s, 8H, C_5H_4), 4.13 (t, J = 6 Hz, 4H, $CH_2OC(O)N(H)$), 3.12 (br, 4H, $OC(O)N(H)CH_2$), 2.57 (t, J = 6 Hz, 4H, $C_5H_4CH_2$), 1.44 (quintet, J = 7 Hz, 4H, $N(H)CH_2CH_2CH_2CH_3$), 1.30 (sextet, J = 8 Hz, 4H, $N(H)CH_2CH_2CH_2CH_3$), 0.90 (t, J = 7 Hz, 6H, $N(H)CH_2CH_2CH_2CH_3$). MS(SIMS): 1272 (25) $[M]^+$. Anal. Calcd for $C_{34}H_{36}Ir_2Mo_2N_2O_{14}$: C, 32.08; H, 2.85; N, 2.20. Found: C, 32.05; H, 2.30; N, 2.40.

Synthesis of Model Complex $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)N(H)(CH_2)_5CH_3\}_2$ (7). To a solution of diol cluster **1** (42.0 mg, 39.1 μmol) in 5 mL pf *p*-dioxane were added hexyl isocyanate (20 μL, 124 μmol) and DBTA (4 μL, 15 μmol), and the mixture was stirred at 70 °C for 2 h. Ethanol (ca. 0.3 mL, 5.5 mmol) was added and the mixture stirred for a further 0.5 h. After cooling to room temperature, all volatiles were removed in vacuo, and the dark red residue was dissolved in 1−2 mL of CH_2Cl_2 and then applied to preparative TLC plates. Elution with ethyl acetate/petroleum spirit (2:3) gave a single band (red-brown, R_f = 0.54), the product from which was isolated and identified as **7** (37.4 mg, 28.1 μmol, 72%). Diffusion of methanol into a solution of **7** in CH_2Cl_2 at 3 °C gave deep red-brown crystals.

IR (CH_2Cl_2): ν(N−H) 3448 w; ν(CO, cluster) 2062 s, 2033 vs, 2007 vs, 1989 sh, 1968 m, 1926 ms, 1883 m, 1850 m, 1801 mw, 1761 ms; ν(C=O, urethane) 1723 s; δ(N−H) 1517 m; ν(C−N) 1239 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.89 (br s, 8H, C_5H_4), 4.12 (t, J = 6 Hz, 4H, $CH_2OC(O)N(H)$), 3.12 (br quartet, J = 7 Hz, 4H, $OC(O)N(H)CH_2$), 2.56 (t, J = 6 Hz, 4H, $C_5H_4CH_2$), 1.46 (br quintet, J = 7 Hz, 4H, $N(H)CH_2CH_2(CH_2)_3CH_3$), 1.26 (br s, 4H, $N(H)CH_2CH_2(CH_2)_3CH_3$), 0.86 (t, J = 7 Hz, 6H, $N(H)(CH_2)_5CH_3$). MS(SIMS): 1328 (10) $[M]^+$. Anal. Calcd for $C_{38}H_{44}Ir_2Mo_2N_2O_{14}$: C, 34.34; H, 3.34; N, 2.11. Found: C, 34.50; H, 3.48; N, 2.05.

Synthesis of Model Complex $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)N(H)(CH_2)_{11}CH_3\}_2$ (8). To a solution of diol cluster **1** (34.5 mg, 32.1 μmol) in 5 mL of *p*-dioxane were added dodecyl isocyanate (43.0 mg, 203 μmol) and DBTA (5 μL, 19 μmol), and the mixture was stirred at room temperature for 17 h. Ethanol (ca. 0.3 mL, 5.5 mmol) was added and the mixture stirred for a further 1 h. All volatiles were removed in vacuo, and the dark red residue was dissolved in 1−2 mL of CH_2Cl_2 and applied to preparative TLC plates. Elution with ethyl acetate/petroleum spirit (2:3) gave a single band (red-brown, R_f = 0.55), the product from which was isolated and identified as **8** (70.2 mg, 55.1 μmol, 72%). Diffusion of methanol into a solution of **8** in CH_2Cl_2 at 3 °C gave deep red-brown microcrystals.

IR (CH_2Cl_2): ν(N−H) 3447 w; ν(CO, cluster) 2062 s, 2033 vs, 2007 vs, 1989 sh, 1969 m, 1926 ms, 1883 m, 1850 m, 1800 w, 1760 m; ν(C=O, urethane) 1723 m; δ(N−H) 1517 m; ν(C−N) 1239 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.86 (s, 8H, C_5H_4), 4.12 (t, J = 6 Hz, 4H, $CH_2OC(O)N(H)$), 3.10 (t, J = 7 Hz, 4H, $OC(O)N(H)CH_2$), 2.56 (t, J = 6 Hz, 4H, $C_5H_4CH_2$), 1.44 (quintet, J = 7 Hz, 4H, $N(H)CH_2CH_2CH_2CH_3$), 1.23 (br s, 36H, $N(H)CH_2CH_2(CH_2)_9CH_3$), 0.86 (t, J = 7 Hz, 6H, $N(H)(CH_2)_{11}CH_3$). MS(SIMS): 1440 (5) $[M - 2CO]^+$. Anal. Calcd for $C_{34}H_{36}Ir_2Mo_2N_2O_{14}$: C, 40.11; H, 4.58; N, 1.87. Found: C, 40.26; H, 4.70; N, 2.27.

Synthesis of Model Complex $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)N(H)(C_6H_{11})\}_2$ (9). Cyclohexylisocyanate (22.0 μL, 172 μmol) and DBTA (5 μL, 19 μmol) were added to a solution of diol cluster **1** (40.9 mg, 38.1 μmol) in 5 mL of *p*-dioxane, and the mixture was stirred at room temperature for 17 h. Ethanol (ca. 0.3 mL, 5.5 mmol) was added and the mixture stirred for a further 2 h. All volatile materials were removed in vacuo, and the dark red residue was dissolved in 1−2 mL of CH_2Cl_2 and applied to preparative TLC plates.

Elution with ethyl acetate/petroleum spirit (1:3) gave two bands. The product from the first and major band (red-brown, $R_f = 0.29$) was isolated and identified as **9** (18.8 mg, 14.2 μmol, 37%). Diffusion of methanol into a solution of **9** in CH_2Cl_2 at 3 °C gave deep red-brown microcrystals.

IR (CH_2Cl_2): ν(N−H) 3328 w; ν(CO, cluster) 2061 s, 2032 vs, 2007 vs, 1989 m, 1970 sh, 1926 ms, 1884 m, 1850 m, 1800 w, 1760 m; ν(C=O, urethane) 1713 s; δ(N−H) 1517 m; ν(C−N) 1217 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.86 (s, 8H, C_5H_4), 4.12 (t, J = 6 Hz, 4H, $CH_2OC(O)N(H)$), 3.40 (br s, 2H, $OC(O)N(H)CH(CH_2)_5$), 2.56 (t, J = 6 Hz, 4H, $C_5H_4CH_2$), 1.92−1.53 (m, 20H, $OC(O)N(H)CH(CH_2)_5$). MS(SIMS): 1324 (3) [M]$^+$. Anal. Calcd for $C_{38}H_{40}Ir_2Mo_2N_2O_{14}$: C, 34.45; H, 3.04; N, 2.11. Found: C, 34.47; H, 3.01; N, 2.27.

The second band (red-brown, $R_f = 0.18$) was isolated and identified as $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)N(H)(C_6H_{11})\}\{\eta\text{-}C_5H_4(CH_2)_2OH\}$ (3.5 mg, 3.7 μmol, 10%).

IR (CH_2Cl_2): ν(O−H) 3613 w; ν(N−H) 3435 w; ν(CO, cluster) 2061 s, 2033 vs, 2007 vs, 1988 sh, 1968 m, 1926 ms, 1882 m, 1850 m, 1799 w, 1761 m; ν(C=O, urethane) 1717 s; δ(N−H) 1507 m; ν(C−N) 1217 m; ν(C−O) 1063 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.90−4.86 (m, 8H, C_5H_4), 4.12 (t, J = 6 Hz, 2H, $CH_2OC(O)N(H)$), 3.74 (t, J = 6 Hz, 2H, CH_2OH), 3.41 (br s, 1H, $OC(O)N(H)CH(CH_2)_5$), 2.55 (t, J = 6 Hz, 2H, $C_5H_4CH_2CH_2OC(O)N(H)$), 2.51 (t, J = 6 Hz, 4H, $C_5H_4CH_2CH_2OH$), 1.93−1.53 (m, 10H, $OC(O)N(H)CH(CH_2)_5$).

General Procedure for the Syntheses of Oligomer−Urethanes (10−14) from Cluster Diol 1, $[-O(CH_2)_2C_5H_4\{Mo_2Ir_2(CO)_{10}\}C_5H_4(CH_2)_2OC(O)N(H)RNHC(O)-]_n$. To a solution of diol cluster **1** (50−105 mg, 45−98 μmol) in 15 mL *p*-dioxane were added the diisocyanate (equimolar amount in 2 mL of *p*-dioxane) and DBTA (8 μL, 30 μmol), and the mixture was stirred at 40 °C for 24 h. Ethanol (ca. 0.3 mL, 5.5 mmol) was added and the mixture stirred for a further 30 min at 40 °C. After cooling to room temperature, all volatile materials were removed in vacuo, and the red residue stirred with 5−10 mL of CH_2Cl_2 for 1 h. After filtration into a vial, a layer of petroleum spirit was carefully added to the crude oligomer solution and the two layers allowed to diffuse together at 4 °C over 48 h. The mother liquor was decanted from the precipitate, and the diffusion/precipitation process repeated with THF and petroleum spirit. The isolated precipitate was dried in vacuo at room temperature for 24 h to yield the oligomer as a light red powder (27−71 mg, 46−84%).

R = $(CH_2)_4$ (**10**). Yield = 49%. IR (CH_2Cl_2): ν(N−H) 3448 w; ν(CO) 2061 s, 2032 vs, 2007 vs, 1989 sh, 1969 sh, 1925 ms, 1883 m, 1845 m, 1800 w, 1762 m; ν(C=O, urethane) 1717 s; δ(N−H) 1518 m; ν(C−N) 1238 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.88 (br d, 8H, C_5H_4), 4.14 (br, 4H, $CH_2OC(O)N(H)$), 3.16 (br, 4H, $OC(O)N(H)CH_2$), 2.57 (br, 4H, $C_5H_4CH_2$), 1.48 (br, 4H, $N(H)CH_2CH_2-$).

R = $(CH_2)_6$ (**11**). Yield = 47%. IR (CH_2Cl_2): ν(N−H) 3445 w; ν(CO) 2062 s, 2033 vs, 2007 vs, 1989 sh, 1970 m, 1925 ms, 1883 m, 1850 m, 1801 w, 1761 m; ν(C=O, urethane) 1717 s; δ(N−H) 1517 m; ν(C−N) 1235 m cm^{-1}. ^{1}H NMR: ($CDCl_3$): δ 4.86 (br s, 8H, C_5H_4), 4.12 (br, 4H, $CH_2OC(O)N(H)$), 3.12 (br, 4H, $OC(O)N(H)CH_2$), 2.58 (br, 4H, $C_5H_4CH_2$), 1.47 (br, 4H, $N(H)CH_2CH_2CH_2-$), 1.30 (br, 4H, $N(H)CH_2CH_2CH_2-$).

R = $(CH_2)_{12}$ (**12**). Yield = 65%. IR (CH_2Cl_2): ν(N−H) 3448 w; ν(CO) 2062 s, 2033 vs, 2007 vs, 1989 sh, 1970 m, 1926 ms, 1884 m, 1849 m, 1801 w, 1761 m; ν(C=O, urethane) 1722 s; δ(N−H) 1517 m; ν(C−N) 1229 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.86 (br s, 8H, C_5H_4), 4.16 (br t, 4H, $CH_2OC(O)N(H)$), 3.15 (br, 4H, $OC(O)N(H)CH_2$), 2.59 (br, 4H, $C_5H_4CH_2$), 1.48 (br, 4H, $N(H)CH_2CH_2CH_2-$), 1.31−1.25 (br, 16H, $N(H)CH_2CH_2(CH_2)_4-$).

R = *trans*-1,4-cyclohexyl (**13**). Yield = 46%. IR (THF): ν(N−H) 3450 w; ν(CO) 2059 s, 2028 vs, 2004 vs, 1988 sh, 1955 m, 1928 ms, 1883 m, 1849 m, 1801 w, 1760 m; ν(C=O, urethane) 1722 s; δ(N−H) 1532 w; ν(C−N) 1290 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.87 (br s, 8H, C_5H_4), 4.15 (br, 4H, $CH_2OC(O)N(H)$), 3.42 (br, 2H, $OC(O)N(H)CH(CH_2)_4CHN(H)C(O)O$), 2.59 (br, 4H, $C_5H_4CH_2$), 1.95−1.54 (br, 8H, $OC(O)N(H)CH(CH_2)_4CHN(H)C(O)O$).

R = (C_6H_4)-4-CH_2(4-C_6H_4), MDI (**14**). Yield = 89%. IR (CH_2Cl_2): ν(N−H) 3428 w; ν(CO) 2062 s, 2033 vs, 2007 vs, 1989 sh, 1969 m, 1925 ms, 1884 m, 1848 m, 1799 w, 1771 ms; ν(C=O, urethane) 1734 s; δ(N−H) 1525 m; ν(C−N) 1213 m cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.33 (d, J = 8 Hz, 4H, $OC(O)N(H)C_6H_4CH_2$), 7.04 (d, J = 8 Hz, 4H, $OC(O)N(H)C_6H_4CH_2$), 5.13−4.99 (br m, 8H, C_5H_4), 4.22 (br t, 4H, $CH_2OC(O)N(H)$), 3.82 (br s, 2H, C_6H_4-4-CH_2-4-C_6H_4), 2.55 (br, 4H, $C_5H_4CH_2$).

Synthesis of Polyurethane (15) from Cluster Diol 4, $[-O(CH_2)_{10}C_5H_4\{Mo_2Ir_2(CO)_{10}\}C_5H_4(CH_2)_{10}OC(O)N(H)(CH_2)_6N(H)C(O)-]_n$. 1,6-Diisocyanatohexane (19.8 μL, 122 μmol) and DBTA (8 μL, 30 μmol) were added to a solution of diol cluster **4** (159 mg, 122 μmol) in 10 mL of THF, and the mixture was stirred at 40 °C for 48 h. Ethanol (ca. 0.5 mL, 9 mmol) was added and the mixture stirred for a further 30 min at 40 °C. After cooling to room temperature, the volume was reduced in vacuo to ca. 1 mL and the red mixture filtered into a vial. A layer of ethanol was carefully added to the red solution, the vial was transferred to a refrigerator, and the two layers allowed to diffuse together at 4 °C over 48 h. The mother liquor was decanted from the precipitate, and the diffusion/precipitation process was repeated with chloroform and ethanol. Removal of the liquid and drying in vacuo at room temperature yielded the polymer **15** as a deep red waxy disk (102 mg, 58%).

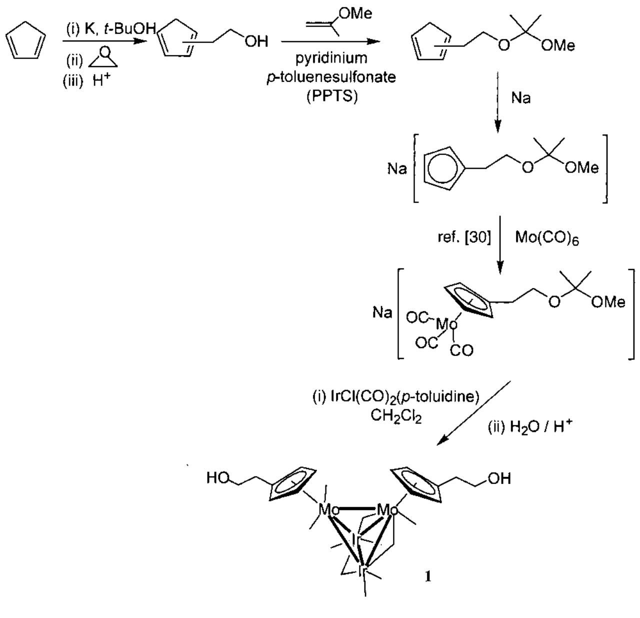
IR (CH_2Cl_2): ν(N−H) 3446 w; ν(CO) 2060 s, 2031 vs, 2005 vs, 1987 sh, 1966 m, 1924 ms, 1882 m, 1845 m, 1798 w, 1759 m; ν(C=O, urethane) 1716 s; δ(N−H) 1518 m; ν(C−N) 1239 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.82 (br s, 4H, C_5H_4), 4.78 (br s, 4H, C_5H_4), 4.00 (br t, 4H, $CH_2OC(O)N(H)$), 3.13 (br, 4H, $OC(O)N(H)CH_2$), 2.23 (br t, 4H, $C_5H_4CH_2$), 1.56 (br, 4H, $CH_2CH_2OC(O)N(H)$), 1.45 (br, 4H, $N(H)CH_2CH_2CH_2-$), 1.23 (br, 32H, $C_5H_4CH_2(CH_2)_7CH_2CH_2OC(O)N(H)CH_2CH_2CH_2-$).

Reaction of Diol Cluster 5 with 1,6-Diisocyanatohexane. To a solution of diol cluster **5** (66 mg, 65 μmol) in 15 mL of THF were added the 1,6-diisocyanatohexane (10.5 μL, 65 μmol) and DBTA (4 μL, 15 μmol), and the mixture was stirred at 40 °C for 3 days. Ethanol (ca. 0.3 mL, 5.5 mmol) was added and the mixture stirred for a further 18 h at 40 °C. After cooling to room temperature, all volatile materials were removed in vacuo, and the green residue was stirred with 5 mL of CH_2Cl_2 for 30 min. The solution was transferred to a large vial, a layer of petroleum spirit carefully added, and the two layers allowed to diffuse together at 4 °C over 48 h. The mother liquor was decanted from the precipitate, and the precipitate was dried in vacuo at room temperature. A ^{1}H NMR spectrum of the precipitate indicated that it was primarily unreacted diol cluster **5** (49 mg).

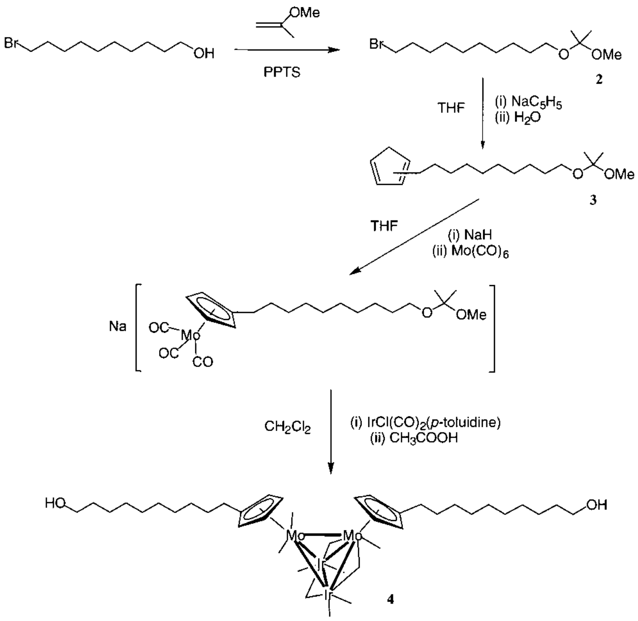
X-ray Crystal Structure Analysis of 1. Crystal data: $C_{24}H_{18}Ir_2Mo_2O_{12}$, M_r = 1074.72, monoclinic, $C2/c$ (No. 15), a = 23.413(3), b = 17.731(1), c = 15.862(2) Å, β = 124.516(5)°, V = 5426(1) Å^3, Z = 8, μ = 26.07 mm^{-1}, $F(000)$ = 3968. Crystal size: 0.40 × 0.10 × 0.10 mm^3. D_{calc} = 2.63 g cm^{-3}, θ = 3.4−60.1°. *hkl* ranges: $0 \le h \le 26$, $0 \le k \le 19$, $-17 \le l \le 14$. The unit cell parameters were obtained by least-squares refinement of 25 reflections with $20.6 \le \theta \le 24.9°$.

Intensities were collected at 296 K on a Rigaku AFC6R automated four-cycle diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) and the $\theta-2\omega$ method. An analytic absorption correction was made for a needle crystal mounted about the needle axis and a slow empirical correction (seven parameters) was further included as part of the refinement because of a large absorption coefficient. The structure was found to contain a 0.604(1):0.396 disorder of mirror-related molecules on the same general site of the spacegroup $C2/c$. The constrained refinement program RAELS[40−43] was used to refine 337 independent variables and gave a final value of R = 0.062 for 3365 independent reflections collected and that were considered to be reliably observed ($I > 3\sigma(I)$). An uncorrelated 4% error in F was included along with counting statistic error in the evaluation of weights $w = 1/[\sigma(F)^2 + (0.04F)^2]$; R_w = 0.088. A final value for the goodness of fit was 1.71 for the 3365 ($I > 3\sigma(I)$) reflections. Hydrogen atoms were included in geometrically sensible positions which were updated each refinement cycle. Their thermal parameters were

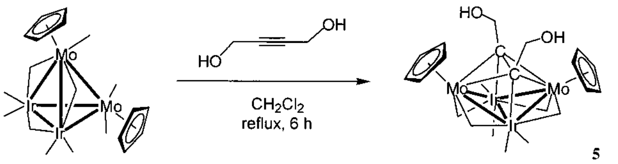
Scheme 1



Scheme 2



Scheme 3



determined by the thermal motion parameters pertaining to the atoms to which they were attached.

Further crystallographic structure solution and refinement details are available in the Supporting Information.

X-ray Crystal Structure Analysis of 6. Crystal data: $C_{34}H_{36}Ir_2N_2Mo_2O_{14}\cdot CH_2Cl_2$, $M_r = 1357.92$, monoclinic, $P2_1$ (No. 4), $a = 9.4433(1)$, $b = 14.4699(3)$, $c = 15.4939(3)$ Å, $\beta = 93.988(1)°$, $V = 2112.0(1)$ Å^3, $Z = 2$, $\mu = 7.07$ mm^{-1}, $F(000) = 1292$. Crystal size: $0.36 \times 0.17 \times 0.06$ mm^3. $D_{calc} = 2.135$, $\theta = 3.53-27.48°$. *hkl* ranges: $-12 \leq h \leq 12$, $-18 \leq k \leq 18$, $-20 \leq l \leq 20$.

The data were collected at 200 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 69 Å). The unit cell parameters were obtained by least-squares refinement[44] of 36 902 reflections with $3.40 \leq \theta \leq 27.49°$. A numerical absorption correction was applied to the data.[45,46] Of the 40 277 reflections which were collected, 5038 were unique ($R_{int} = 0.076$); equivalent reflections were merged. The structure was solved by heavy-atom Patterson methods[47] and expanded using Fourier techniques,[48] implemented within the teXsan software package.[49] The non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at idealized positions which were frequently recalculated. The three C−C bonds of each peripheral butyl group were restrained during refinement. The final cycle of full-matrix least-squares refinement was based on 8036 observed reflections ($I > 3\sigma(I)$) and 514 variable parameters, and converged with $R = 0.039$, $R_w = 0.047$ ($w = 1/[\sigma^2(F_o) + 0.0009|F_o|^2]$). A final value for the goodness of fit was 1.21 for the 8036 observed reflections.

Further crystallographic structure solution and refinement details are available in the Supporting Information.

Results and Discussion

Cluster Diol Syntheses. The preparation of polyurethanes incorporating clusters in the main chain can, in principle, proceed either from reactions between a cluster diol precursor and a diisocyanate or from reaction between a cluster diisocyanate precursor and a diol. For the present studies, the former option was chosen, the latter option requiring synthetic manipulations of hydrolytically sensitive intermediates to prepare the cluster diisocyanate precursor. The former option minimizes these synthetic difficulties and proceeds readily from the established methodology for the preparation of $[Mo(CO)_3\{\eta\text{-}C_5H_4(CH_2)_2OCMe_2(OMe)\}]^-$.[30] η-Cyclopentadienyl and μ_4-η^2-alkyne ligands are strongly bound to cluster cores and so were chosen as the mode of attachment of the alcohol groups. Synthetic procedures used to obtain the three diols utilized in the present studies are summarized in Schemes 1−3.

We have previously reported the synthesis of the unsubstituted cyclopentadienyl-containing cluster $Mo_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$[38] and the alkyne-containing cluster $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}PhC_2H)(CO)_8(\eta\text{-}C_5H_5)_2$,[50] and the present work extends these methodologies to the hydroxy-functionalized targets. Thus, reaction between the carbonylmetalate anion $Na[Mo(CO)_3\{(\eta\text{-}C_5H_4(CH_2)_2OCMe_2(OMe)\}]$ and $IrCl(CO)_2$(*p*-toluidine) in CH_2Cl_2, followed by acidic workup to deprotect the ketal to the desired hydroxy group, affords $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OH\}_2$ (**1**) in 57% yield (Scheme 1). The excess carbonylmetalate anion is protonated in acidic workup to afford $MoH(CO)_3\{\eta\text{-}C_5H_4(CH_2)_2OH\}$. We have found it preferable to convert the hydrido complex to the corresponding chloro complex $MoCl(CO)_3\{\eta\text{-}C_5H_4(CH_2)_2OH\}$ (which proceeds readily upon addition of CCl_4), as the latter is more readily separable by TLC. Synthesis of the ω-hydroxydecylcyclopentadienyl-containing cluster analogue **4** necessitated preparation of 10-bromodecanol ketal **2**, nucleophilic attack on which afforded 10-cyclopentadienyldecanol ketal **3** (Scheme 2). Reaction of the ketal **3** with sodium hydride forms the cyclopentadienide anion $[C_5H_4(CH_2)_{10}OCMe_2(OMe)_2]^-$, which reacts in situ with $Mo(CO)_6$ to give the carbonylmetalate anion $[Mo(CO)_3\{\eta\text{-}C_5H_4(CH_2)_{10}OMe_2(OMe)\}]^-$. The anion reacts with $IrCl(CO)_2$(*p*-toluidine), followed by acidic deprotection of the ketal, to give **4** after chromatographic workup. Reaction between $Mo_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$ and 2-butyne-1,4-diol affords $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}HOCH_2C_2CH_2\text{-}OH)(CO)_{10}(\eta\text{-}C_5H_5)_2$ (**5**) in moderate yield following chromatography (Scheme 3). Clusters **1**, **4**, and **5** have similar spectral properties to their non-hydroxy-func-

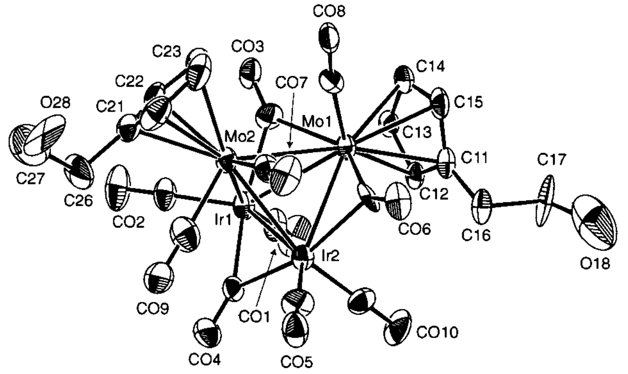


Figure 1. Molecular structure and atomic labeling scheme for $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2$ (**1**) with 30% probability ellipsoids. Selected bond lengths (Å): Ir1−Ir2 2.696(1), Ir1−Mo1 2.886(1), Ir1−Mo2 2.811(1), Ir2−Mo1 2.846(1), Ir1−Mo2 2.862(1), and Mo1−Mo2 3.110(1).

tionalized analogues. The identity of **1** was confirmed by a single-crystal X-ray diffraction study.

X-ray Study of 1. Figure 1 contains an ORTEP plot of **1** showing the molecular structure and atomic labeling scheme. Complete tables of fractional coordinates, bond distances, and bond angles are available in the Supporting Information.

The molecule has a Mo_2Ir_2 pseudotetrahedral metal cluster core with bond distances Ir−Ir [2.696(1) Å], Mo−Ir [2.811(1)−2.886(1) Å], and Mo−Mo [3.110(1) Å]. Each Mo is ligated by a η^5-(hydroxyethylcyclopentadienyl) group, while three bridging carbonyls arranged about a $MoIr_2$ face and seven terminal carbonyl ligands complete the coordination sphere. Bond lengths and angles are unexceptional and in agreement with previously studied analogues.[38,51,52] In this structural study, the OH group is located as close as 2.748 Å to the nearest metal core-bonded cyclopentadienyl ring carbon.

Syntheses of Cluster-Containing Diurethanes. To facilitate spectroscopic identification of the cluster-containing polyurethanes discussed below, a number of model diurethanes were prepared, the general procedure for which is shown in Scheme 4. Thus, reaction between **1** and alkylisocyanates in the presence of a catalytic amount of dibutyltin diacetate affords $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)NHRH\}_2$ [R = $(CH_2)_y$ (y = 4 (**6**), 6 (**7**), 12 (**8**)), *trans*-1,4-cyclohexyl (**9**)], yields for **6** − **8** (containing alkyl chains) being good (72%), in contrast to the lower-yielding cyclohexyl derivative **9** (37%). The cluster-containing diurethanes were characterized by ^1H NMR, IR, and secondary ion mass spectrometry (SIMS), with **6** being definitively identified by a single-crystal X-ray diffraction study.

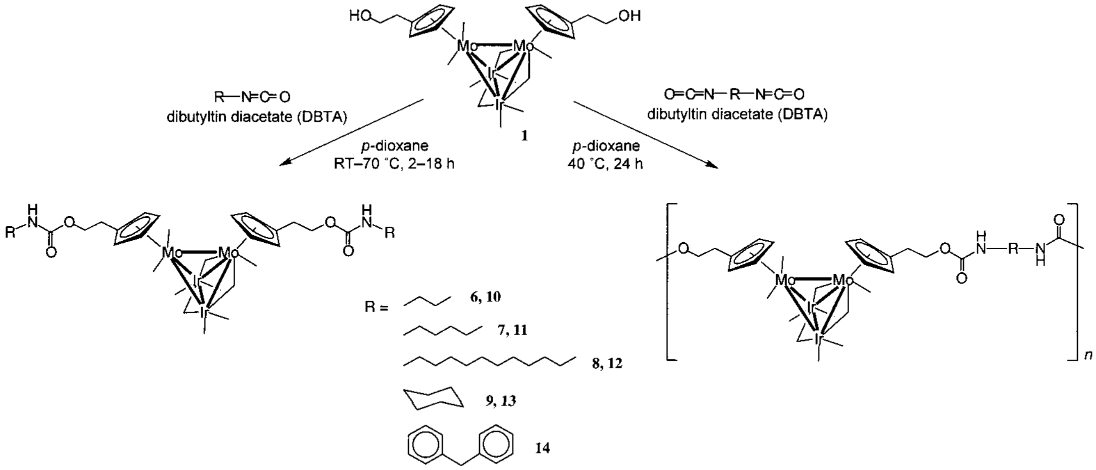
X-ray Study of 6. Figure 2 contains an ORTEP plot of **6** showing the molecular structure and atomic labeling scheme. Complete tables of fractional coordinates, bond distances, and bond angles are available in the Supporting Information.

The disposition of ligands about the pseudotetrahedral Mo_2Ir_2 core of **6** is similar to the precursor diol cluster **1** discussed above, with bond distances Ir−Ir [2.6819(4) Å], Mo−Ir [2.8311(9)−2.8617(8) Å], and Mo−Mo [3.096(1) Å]. The study confirms the presence of two *n*-butyl urethane groups, each *O*-bonded to an η^5-ethylcyclopentadienyl group. Metal core and carbonyl bond lengths and angles are in agreement with previously studied analogues.[38,51,52]

Syntheses of Cluster-Containing Oligo-Urethanes. The reactions between **1** and 1,ω-alkyl- or aryl-diisocyanates proceed to afford the corresponding oligourethanes (Scheme 4), in a fashion similar to those of the model diurethanes, affording $[\text{-}O(CH_2)_2(\eta\text{-}C_5H_4)\{Mo_2Ir_2(CO)_{10}\}(\eta\text{-}C_5H_4)(CH_2)_2OC(O)NHRNHC(O)\text{−}]_n$ [R = $(CH_2)_y$ (y = 4 (**10**), 6 (**11**), 12 (**12**)), *cyclo*-1,4-C_6H_{10} (**13**), 4-$C_6H_4CH_2$-4-C_6H_4 (**14**)] in 46−89% yield as red powders. The related reaction between **4** and 1,6-diisocyanatohexane affords $[\text{-}O(CH_2)_{10}(\eta\text{-}C_5H_4)\{Mo_2Ir_2(CO)_{10}\}(\eta\text{-}C_5H_4)(CH_2)_{10}OC(O)NH(CH_2)_6NHC(O)\text{−}]_n$ (**15**) in 58% yield, a somewhat higher yield than that of the analogue **11**; in contrast to **10**−**14**, **15** is obtained as a red waxy material. All new oligourethanes are soluble in dichloromethane, chloroform and THF, slightly soluble in acetone, toluene and diethyl ether, and insoluble in alcohols and petroleum spirit. The identities of **10**−**15** were established from a combination of IR and ^1H NMR spectra, comparison to the diurethane "model" compounds **6**−**9** revealing the only substantive difference being a broadening of ^1H NMR resonances in proceeding from model to oligomer.

The extent of polymerization was ascertained by size exclusion chromatography (calibrated vs polystyrene) and integration of ^1H NMR resonances of terminal and bridging methylene groups, the results of which are listed in Table 1. The molecular weight distributions from GPC show a tailing to low molecular weights, possibly reflecting problems in achieving 1:1 stoichiometry when using small amounts of cluster-containing

Scheme 4



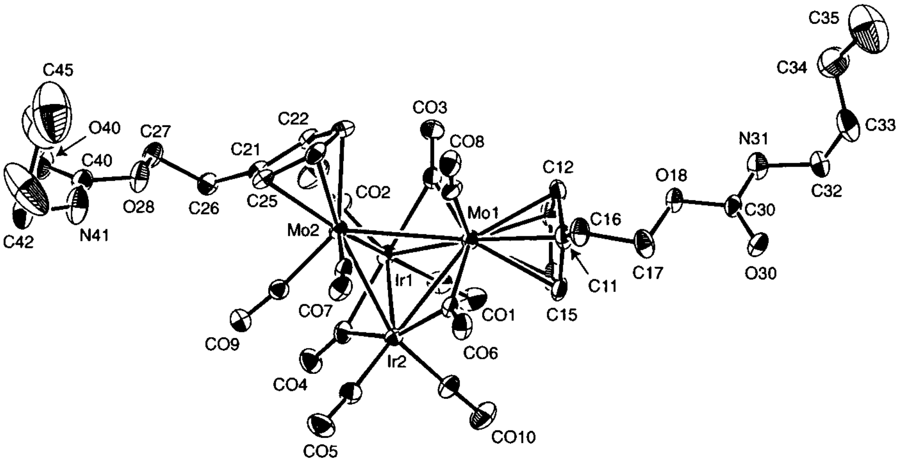


Figure 2. Molecular structure and atomic labeling scheme for $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7\{\eta^5\text{-}C_5H_4CH_2CH_2OC(O)NH(CH_2)_3CH_3\}_2$ (**6**) with 30% probability ellipsoids. Selected bond lengths (Å): Ir1−Ir2 2.6819(4), Ir1−Mo1 2.8506(8), Ir1−Mo2 2.8311(9), Ir2−Mo1 2.8617(8), Ir1−Mo2 2.8516(8), and Mo1−Mo2 3.096(1).

Table 1. Estimated Molecular Weight Averages for Cluster Oligomers 10−15,$[-O(CH_2)_xC_5H_4\{Mo_2Ir_2(CO)_{10}\}\text{-}C_5H_4(CH_2)_xOC(O)N(H)RN(H)C(O)-]_n$

	cluster oligomer	M_n[a]	n_{av}[b]	M_w/M_n[a]
10	$x = 2$, R = $(CH_2)_4$	6100	5	2.3
11	$x = 2$, R = $(CH_2)_6$	7500	6	2.8
12	$x = 2$, R = $(CH_2)_{12}$	6600	5	2.6
13	$x = 2$, R = trans−1,4-cyclohexyl	8600	7	3.1
14	$x = 2$, R = MDI	10 400	8	3.3
15	$x = 10$, R = $(CH_2)_6$	44 000	30	3.1

[a] Estimated by a combination of GPC (THF, polystyrene standards) and ^{1}H NMR analysis. [b] Average number of repeat units.

diols. The number-average molecular weights M_n of **10**−**12** do not differ significantly from each other, suggesting that the diisocyanate alkyl group chain length is not an important determinant of extent of polymerization. The cyclohexyl- and methylenediphenylene-containing oligomers **13** and **14** have marginally greater M_n, but differences with **10**−**12** are probably not significant. Replacing the ethyl spacer between cyclopentadienyl and hydroxyl groups with a decyl group in proceeding from **11** to **15** results in a significant increase in M_n, consistent with steric effects being the important determinant of extent of polymerization. The X-ray study of **1** provides evidence that the proximity of the alcohol group to the cluster coordination sphere may hinder efficient reaction at this site. In contrast to these results, attempted reactions of the sterically more hindered diol cluster **5** with 1,6-diisocyanatohexane afforded unreacted starting cluster. It seems certain that steric factors dictate the extent of polymerization.

Conclusion

Cluster-containing polymers in which the cluster is in the backbone are comparatively rare, bimetallic cluster-containing examples even more so. The present research has afforded a series of organic solvent-soluble main-chain molybdenum−iridium cluster-containing oligomers. The strategy of employing cyclopentadienyl-functionalized linkages should be applicable to many other cluster-containing systems, as the cyclopentadienyl ligand (and its various derivatives) is one of the most ubiquitous ligands in organometallic chemistry. The research detailed herein has identified the length of the cyclopentadienyl alkyl linkage as a key determinant of extent of polymerization, the ethyl linkage affording low molecular weight powders and the decyl linkage a high molecular weight waxy material. Organometallic clusters have been identified as one of the most promising materials for optical limiting applications.[53−58] The present work suggests a new procedure for obtaining processable cluster-containing materials which may have utility in such applications. Studies directed toward evaluating the optical limiting performance of mixed-metal cluster-containing monomers and polymers are currently underway.[59]

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Supporting Information Available: Text and tables giving solution and refinement details and tables of atomic coordinates, bond lengths, and bond angles for the X-ray structural studies of **1** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Part 15: Waterman, S. M.; Humphrey, M. G.; Lee, J. *J. Organomet. Chem.* **1999**, *589*, 226.
(2) Guczi, L. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; p 560.
(3) Dubois, R. A.; Garrou, P. E.; Hartwell, G. E.; Hunter, D. L. *Organometallics* **1984**, *3*, 95.
(4) Bhaduri, S.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2309.
(5) Marrakchi, H.; Haimeur, M.; Escalant, P.; Lieto, J.; Aune, J.-P. *New J. Chem.* **1986**, *10*, 159.
(6) He, B.-L.; Sun, J.-T.; Li, H.; Sang, J.-J. *J. Macromol. Sci.—Chem.* **1989**, *A26*, 417.
(7) Kaneda, K.; Fujita, K.; Takemoto, T.; Imanaka, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 602.
(8) Kaneda, K.; Mizugaki, T. *Organometallics* **1996**, *15*, 3247.
(9) Mizugaki, T.; Kanayama, Y.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **1998**, *63*, 2378.
(10) Rafalko, J. J.; Lieto, J.; Gates, B. C.; Schrader Jr, G. L. *J. Chem. Soc., Chem. Commun.* **1978**, 540.
(11) Lieto, J.; Wolf, M.; Matrana, B. A.; Prochazka, M.; Tesche, B.; Knözinger, H.; Gates, B. C. *J. Phys. Chem.* **1985**, *89*, 991.
(12) Foster, D. F.; Harrison, J.; Nicholls, B. S.; Smith, A. K. *J. Organomet. Chem.* **1985**, *295*, 99.
(13) Paetzold, E.; Pracejus, H.; Oehme, G. *J. Mol. Catal.* **1987**, *42*, 301.

(14) Lieto, J.; Prochazka, M.; Arnold, D. B.; Gates, B. C. *J. Mol. Catal.* **1985**, *31*, 89.
(15) Bhaduri, S.; Khwaja, H.; Sharma, K. R. *Indian J. Chem.* **1982**, *21A*, 155.
(16) Withers Jr, H. P.; Seyferth, D. *Inorg. Chem.* **1983**, *22*, 2931.
(17) Johnson, B. F. G.; Blake, A. J.; Brown, A. J.; Parsons, S.; Taylor, P. *J. Chem. Soc., Chem. Commun.* **1995**, 2117.
(18) Bhaduri, S.; Khwaja, H.; Narayanan, B. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2327.
(19) Lieto, J.; Rafalko, J. J.; Gates, B. C. *J. Catal.* **1980**, *62*, 149.
(20) Ley, K. D.; Schanze, K. S. *Coord. Chem. Rev.* **1998**, *171*, 287.
(21) Puddephatt, R. J. *Chem. Commun.* **1998**, 1055.
(22) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.
(23) Kaliyappan, T.; Kannan, P. *Prog. Polym. Sci.* **2000**, *25*, 343.
(24) Turner, M. L. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2000**, *96*, 491.
(25) Manners, I. *Chem. Commun.* **1999**, 857.
(26) Aime, S.; Gobetto, R.; Jannon, G.; Osella, D. *J. Organomet. Chem.* **1986**, *309*, C51.
(27) Fuchs, R.; Klüfers, P. *J. Organomet. Chem.* **1992**, *424*, 353.
(28) Bradford, A. M.; Kristof, E.; Rashidi, M.; Yang, D.-S.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1994**, *33*, 2355.
(29) Johnson, B. F. G.; Sanderson, K. M.; Shephard, D. S.; Ozkaya, D.; Zhou, W.; Ahmed, H.; Thomas, M. D. R.; Gladden, L.; Mantle, M. *Chem. Commun.* **2000**, 1317.
(30) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 473.
(31) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 1116.
(32) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1992**, *11*, 1466.
(33) Avey, A.; Tyler, D. R. *Organometallics* **1992**, *11*, 3856.
(34) Tyler, D. R.; Wolcott, J. J.; Nieckarz, G. F.; Tenhaeff, S. C. In *Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; American Chemical Society: Washington, DC, 1994; Vol. 572.
(35) Nieckarz, G. F.; Tyler, D. R. *Inorg. Chim. Acta* **1996**, *242*, 303.
(36) Nieckarz, G. F.; Litty, J. J.; Tyler, D. R. *J. Organomet. Chem.* **1998**, *554*, 19.
(37) Klabunde, U. *Inorg. Synth.* **1974**, *15*, 82.
(38) Lucas, N. T.; Humphrey, M. G.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *535*, 175.
(39) Miyashita, N.; Yashikoshi, A.; Greico, P. A. *J. Org. Chem.* **1977**, *42*, 3773.
(40) Rae, A. D. *RAELS96: A Comprehensive Constrained Least-Square Refinement Program*; Australian National University: Canberra, 1996.
(41) Rae, A. D. *Acta Crystallogr. A* **1975**, *31*, 560.
(42) Rae, A. D.; Baker, A. T. *Acta Crystallogr. A* **1984**, *40*, C428 (supplement).
(43) Haller, K. J.; Rae, A. D.; Heerdegen, A. P.; Hockless, D. C. R.; Welberry, T. R. *Acta Crystallogr.* **1995**, *B51*, 187.
(44) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, p 307.
(45) Coppens, P. In *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 255.
(46) Mackay, S.; Gilmore, C. J.; Edwards, C.; Stewart, N.; Shankland, K.: *maXus. Computer Program for the Solution and Refinement of Crystal Structures*; Nonius: Delft, The Netherlands; MacScience: Yokohama, Japan; and The University of Glasgow: Glasgow, Scotland, 1999.
(47) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATTY: The DIRDIF program system. Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1992.
(48) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M.: *The DIRDIF-94 Program System. Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands 1994.
(49) *teXsan: Single-Crystal Structure Analysis Software, 1.8*; Molecular Structure Corp.: The Woodlands, TX 77381, 1997.
(50) Lucas, N. T.; Humphrey, M. G.; Healy, P. C.; Williams, M. L. *J. Organomet. Chem.* **1997**, *545−546*, 519.
(51) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 7383.
(52) Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1359.
(53) Low, M. K. M.; Hou, H.; Zheng, H.; Wong, W.; Jin, G.; Xin, X.; Ji, W. *Chem. Commun.* **1998**, 505.
(54) Philip, R.; Kumar, G. R.; Mathur, P.; Ghosh, S. *Chem. Phys. Lett.* **1999**, *313*, 719.
(55) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.
(56) Zhang, C.; Song, Y.; Xu, Y.; Fun, H.; Fang, G.; Wang, Y.; Xin, X. *J. Chem. Soc., Dalton Trans.* **2000**, 2823.
(57) Tan, W.; Zheng, H.; Jin, Q.; Jin, G.; Ji, W.; Long, D.; Xin, X. *Polyhedron* **2000**, *19*, 1545.
(58) Song, Y.; Zhang, C.; Zhao, X.; Wang, Y.; Fang, G.; Jin, G.; Qu, S.; Wu, S.; Xin, X.; Ye, H. *Chem. Lett.* **2000**, 1076.
(59) Lucas, N. T.; Samoc, M. Unpublished results.

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