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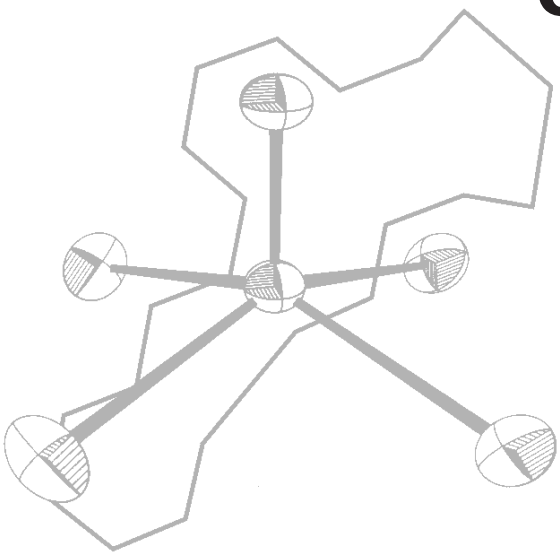

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Synthesis and Hydroboration of Lipophilic Hydroxypyridinones and Their Complexes with Molybdenum(VI)

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We have prepared four potentially lipophilic *N*-substituted hydroxypyridinones containing unsaturated hydrocarbon groups. The propyl vinyl ether derivative (3) has been characterized by an X-ray diffraction study. Complexes of the type *cis*-MoO_2L_2, where L represents the hydroxypyridinonato ligands, have also been prepared. The pyridinone ligands are bound to molybdenum in a *cis* bidentate fashion via the deprotonated hydroxy groups and the ketone moieties. Initial investigations into the hydroboration of the alkene groups in the pyridinone ligands and corresponding metal complexes is presented. Crystals of (3) are monoclinic, with *a* 10.466(1), *b* 13.388(1), *c* 15.386(2) Å, β 102.343(8)°, *Z* 8, space group $P2_1/n$.

Keywords. Molybdenum; pyridinones; hydroboration; boronic acids.

Introduction

There has been considerable recent interest in the use of 2-alkyl-3-hydroxypyridin-4-ones as bidentate chelating agents in the field of bioinorganic chemistry.[1–20] For example, hdmp (Fig. 1) has found moderate success in chelation therapy for the treatment of iron-overload in humans.[9–14] The ligand hdmp also forms complexes with trivalent metals such as aluminum, gallium, and indium, which have some application in the radioisotopic imaging of tumours.[11] However, the overall efficacy of these hydroxypyridinone compounds as medicinal agents is usually limited by poor gastrointestinal absorption. As a result, much research has focused on generating lipophilic *N*-substituted pyridinones in an attempt to increase the physiological solubilities of these compounds.

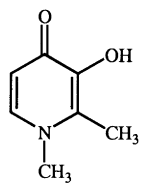

Fig. 1. 3-Hydroxy-1,2-dimethylpyridin-4(1*H*)-one (hdmp).

Our interest in this area lies in developing molybdenum complexes for the treatment of cardiac dysfunction associated with diabetes. We have found that certain molybdenum compounds help prevent depression in cardiac function in diabetic hearts.[19] In order to ascertain the effect molybdenum complexes have on heart function we have begun to synthesize numerous complexes containing pyridinone ligands with different physical and chemical properties. In this paper we report our initial efforts in generating potentially lipophilic hydroxypyridinones and their corresponding molybdenum(VI) complexes. We hypothesize that further functionalization of the pendent C=C moieties in these complexes may prove to be a facile route to making novel pyridinone compounds.

Experimental

Chemicals used were of reagent grade. Maltol and amines were obtained from Aldrich Chemicals and molybdic acid was purchased from Strem. Tetrahydrofuran, hexane, and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride and chloroform were distilled from CaH_2. N.m.r. spectra were recorded on a JEOL JNM-GSX270 Fourier-transform n.m.r. spectrometer. ^{1}H n.m.r. chemical shifts are reported in ppm and referenced to residual protons in $CDCl_3$, D_2O and $(CD_3)_2SO$ at 270 MHz. $^{13}C\{^1H\}$ n.m.r. chemical shifts are referenced to internal solvent peaks at 68 MHz. $^{11}B\{^1H\}$ n.m.r. chemical shifts are referenced to external $F_3B{\cdot}OEt_2$ at 87 MHz. Infrared spectra were obtained with Nujol on KBr/NaCl plates by using a Perkin–Elmer 710B and a Mattson Polaris spectrophotometer and are reported in cm^{-1}. Melting points were measured uncorrected with a Mel-Temp apparatus. Microanalyses for C, N, and H were carried out at Desert Analytics (Tucson, Arizona).

*Preparation of 1-Allyl-3-hydroxy-2-methylpyridin-4(1*H*)-one (Happ) (1)*[17]

Allylamine (2.05 g, 35.9 mmol) was added to maltol (2.88 g, 22.8 mmol) in water (12 cm^3) and ethanol (6 cm^3). Upon heating to reflux for

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56 h the solution changed from pale yellow to dark brown in colour. CH_2Cl_2 (25 cm^3) was added to the mixture and the organic phase was collected. Following removal of solvent under vacuum, ligand (1) was recrystallized twice from a mixture of CH_2Cl_2 (7 cm^3) and hexane (6 cm^3) to afford a brown powder. Yield: 1.39 g (37%); m.p. 136°C. ^{1}H n.m.r. (in $CDCl_3$): δ 7.24, d, *J* 8 Hz, CH; 6.43, d, *J* 8 Hz, CH; 5.98–5.88, ov m, CH; 5.33, d, *J* 11 Hz, CH; 4.99, d, *J* 16 Hz, CH; 4.50, d, *J* 5 Hz, CH_2; 4.41, br s, OH; 2.36, s, CH_3. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 169.7, 146.2, 137.0, 132.0, 129.0, 118.1, 111.5, 55.6, 11.8. I.r. (Nujol): 3338, 1630, 1585, 1561, 1453, 1377, 1347, 1288, 1227, 1037, 965, 909, 839, 732, 625.

*Preparation of 1-(2-(Cyclohex-1-enyl)ethyl)-3-hydroxy-2-methylpyridin-4(1*H*)-one (Hcpp) (2)*

2-(Cyclohex-1-enyl)ethylamine (1.59 g, 12.7 mmol) was added to maltol (1.08 g, 8.56 mmol) in water (8 cm^3) and ethanol (4 cm^3) and the mixture was heated to reflux for 56 h. CH_2Cl_2 (20 cm^3) was added to the mixture and the organic phase collected. Upon removal of solvent under vacuum, the resultant solid was recrystallized twice from CH_2Cl_2 (5 cm^3) and hexane (5 cm^3). The brown solid was collected by suction filtration and washed with hexane (3×5 cm^3). Yield: 1.39 g (70%); m.p. 173°C. ^{1}H n.m.r. (in $CDCl_3$): δ 7.17, d, *J* 8 Hz, CH; 6.38, d, *J* 8 Hz, CH; 5.50, br s; 5.39, br s; 3.94, t, *J* 5 Hz, CH_2; 2.40, s, CH_3; 2.33, t, *J* 8 Hz, CH_2; 1.92, br m; 1.65, ov m. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 169.3, 146.2, 136.8, 132.2, 128.1, 125.6, 110.9, 52.7, 39.0, 28.4, 25.1, 22.6, 21.9, 11.8. I.r. ($CHCl_3$): 3333, 3162, 2928, 1673, 1584, 1509, 1254, 822, 666.

*Preparation of 3-Hydroxy-2-methyl-1-(3-vinyloxypropyl)pyridin-4(1*H*)-one (Hvpp) (3)*

3-Vinyloxypropylamine (1.62 g, 15.9 mmol) was added to maltol (0.50 g, 3.98 mmol) in water (5 cm^3) and ethanol (5 cm^3). The initial bright yellow colour changed to brown upon heating to reflux for 16 h. CH_2Cl_2 (12 cm^3) was added to the reaction mixture and the organic phase was isolated. Solvent was removed under vacuum to give a brown oil and (3) was obtained upon recrystallization from diethyl ether (100 cm^3) and hexane (40 cm^3). Yield: 0.04 g (6%); m.p. 122°C. ^{1}H n.m.r. (in $CDCl_3$): δ 7.22, d, *J* 8 Hz, CH; 6.88, br s, CH; 6.48, dd, *J* 22, 5 Hz, CH; 6.36, d, *J* 5 Hz, CH; 4.19, d, *J* 22 Hz, CH; 4.06–3.98, ov m; 3.66, t, *J* 5 Hz, CH_2; 2.37, s, CH_2; 2.08, m, *J* 5 Hz, CH_2. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 169.4, 150.9, 146.3, 136.8, 128.3, 111.3, 87.4, 63.0, 50.3, 29.9, 11.6. I.r. (Nujol): 3155, 2921, 1627, 1573, 1509, 1465, 1379, 1193, 1027, 826.

*Preparation of 3-Hydroxy-2-methyl-1-(octadec-9-enyl)pyridin-4(1*H*)-one (Hopp) (4)*

Oleylamine (2.61 g, 9.76 mmol) was added to maltol (1.02 g, 7.93 mmol) in water (10 cm^3) and ethanol (5 cm^3). The initial colour changed from pale yellow to a dark brown upon heating to reflux for 112 h. Diethyl ether (13 cm^3) was added to the mixture and the organic phase was extracted. Solvent was removed under vacuum to afford a brown oil. Yield: 2.56 g (85%). ^{1}H n.m.r. (in $CDCl_3$): δ 7.23, d, *J* 8 Hz, CH; 6.40, d, *J* 8 Hz, CH; 5.31, br s; 4.78, br s; 3.86, t, *J* 8 Hz, CH_2; 2.36, s, CH_2; 1.97, br s, CH_2; 1.24, br s, CH_2; 0.85, t, *J* 8 Hz, CH_3. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 169.2, 146.3, 136.7, 130.1, 129.8, 129.7, 111.5, 54.3, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.3, 27.2, 26.9, 26.5, 22.8, 14.2, 11.9. I.r. (neat): 3462, 2927, 2854, 1694, 1626, 1575, 1463, 1367, 1255, 1039, 826.

Preparation of cis*-Bis(1-allyl-3-hydroxy-2-methylpyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2(app)_2$) (5)*

Compound (1) (0.11 g, 0.65 mmol) in methanol (5 cm^3) was added dropwise to molybdic acid (0.05 g, 0.15 mmol) in water (5 cm^3). The reaction was allowed to proceed for 24 h, at which point the mixture was cooled to 5°C. After 24 h, a yellow *precipitate* was collected by suction filtration and washed with cold methanol (3×2 cm^3) and dried under vacuum. Yield: 0.04 g (26%); m.p. 264°C (dec.) (Found: C, 46.7; H, 4.3; N, 6.7. $C_{18}H_{20}MoN_2O_6$ requires C, 47.4; H, 4.4; N, 6.1%). ^{1}H n.m.r. (in $CDCl_3$): δ 7.32, d, *J* 5 Hz, CH; 6.54, d, *J* 5 Hz, CH; 5.98–5.84, ov m, CH; 5.37, d, *J* 11 Hz, CH; 5.08, d, *J* 16 Hz, CH; 4.62, d, *J* 5 Hz, CH_2; 2.46, s, CH_3. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 171.2, 155.9, 136.1, 133.7, 131.1, 119.2, 110.1, 56.6, 12.5. I.r. (Nujol): 2979, 1638, 1611, 1545, 1491, 1411, 1369, 1269, 1049, 993, 921, 889, 816, 721, 650, 618, 571.

Preparation of cis*-Bis(1-[2-(cyclohex-1-enyl)ethyl]-3-hydroxy-2-methylpyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2(cpp)_2$) (6)*

Compound (2) (0.06 g, 0.26 mmol) in methanol (5 cm^3) was added to molybdic acid (0.02 g, 0.06 mmol) in methanol (5 cm^3) at room temperature. After 24 h, the dark orange solution was cooled to 5°C for 48 h. A pale yellow *precipitate* was isolated by suction filtration, washed with cold methanol (3×2 cm^3) and dried under vacuum. Yield: 0.03 g (85%); m.p. 247°C (dec.) (Found: C, 57.0; H, 6.2; N, 5.0. $C_{28}H_{36}MoN_2O_6$ requires C, 56.8; H, 6.1; N, 4.7%). ^{1}H n.m.r. (in $CDCl_3$): δ 7.24, d, *J* 8 Hz, CH; 6.51, d, *J* 8 Hz, CH; 5.43, br s; 4.03, t, *J* 5 Hz, CH_2; 2.51, s, CH_2; 2.35, t, *J* 8 Hz, CH_2; 1.97, br m; 1.60, ov m. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 171.0, 156.0, 135.8, 133.0, 132.0, 125.9, 109.8, 53.7, 39.1, 28.4, 25.2, 22.7, 22.0, 12.5. I.r. (Nujol): 2948, 1613, 1551, 1515,1493, 1407, 1376, 1265, 913, 886, 817, 743, 622, 592.

Preparation of cis*-Bis(3-hydroxy-2-methyl-1-(3-vinyloxypropyl)pyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2(vpp)_2$) (7)*

Compound (3) (crude, estimated 16 mmol) in CH_2Cl_2 (5 cm^3) was added to molybdic acid (1.36 g, 4.0 mmol) in water (10 cm^3) at room temperature. The reaction was allowed to proceed for 48 h, at which point the organic layer was collected. CH_2Cl_2 was removed under vacuum to yield a red oil which was triturated with tetrahydrofuran (10×10 cm^3) to afford an orange-yellow *solid*. Yield: 0.96 g (22%); m.p. 190°C (Found: C, 48.5; H, 5.3; N, 5.2. $C_{22}H_{28}MoN_2O_8$ requires C, 48.5; H, 5.2; N, 5.2%). ^{1}H n.m.r. (in $CDCl_3$): δ 7.35, d, *J* 8 Hz, CH, 6.48–6.41, ov m; 4.21–4.13, ov m; 4.07, d, *J* 8 Hz, CH_2; 3.70, t, *J* 8 Hz, CH_2; 2.47, s, CH_3; 2.09, br m, CH_2. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 171.0, 156.0, 151.1, 136.7, 133.5, 110.1, 87.8, 63.3, 51.7, 30.1, 12.5. I.r. (Nujol): 2926, 2856, 1642, 1612, 1553, 1490, 1467, 1374, 1268, 1184, 923, 889.

Preparation of cis*-Bis(3-hydroxy-2-methyl-1-(octadec-9-enyl)pyridin-4(1*H*)-onato)dioxomolybdenum*(VI) *($MoO_2(opp)_2$) (8)*

Compound (4) (0.59 g, 1.57 mmol) in warm methanol (20 cm^3) was added dropwise to molybdic acid (0.12 g, 0.35 mmol) in water (10 cm^3). After 4 h, CH_2Cl_2 (18 cm^3) was added to the pale yellow solution and the organic layer isolated. CH_2Cl_2 was removed under vacuum to afford a brown-yellow oil. Trituration with ether and hexane afforded a yellow *solid* which was isolated by suction filtration and dried under vacuum. Yield: 0.14 g (23%); m.p. 113°C (Found: C, 66.0; H, 9.0; N, 3.2. $C_{48}H_{80}MoN_2O_6$ requires C, 65.7; H, 9.2; N, 3.2%). ^{1}H n.m.r. (in $CDCl_3$): δ 7.32, d, *J* 5 Hz, CH; 6.48, d, *J* 5 Hz, CH; 5.35, br m; 4.01, t, *J* 8 Hz; 2.47, s, CH_3; 2.02, br d, *J* 8 Hz; 1.26, br s, CH_2; 0.88, t, *J* 8 Hz, CH_3. $^{13}C\{^1H\}$ n.m.r. (in $CDCl_3$): δ 170.7, 155.8, 136.2, 133.3, 130.1, 129.8, 109.8, 65.9, 55.1, 32.0, 31.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 27.3, 26.5, 22.8, 14.2, 12.5. I.r. (Nujol): 3507, 2966, 2901, 1650, 1613, 1551, 1520, 1461, 1413, 1377, 1268, 914, 883, 721.

Catalysed Hydroborations

In a typical experiment, compound (1) or (5) (0.01 mmol) was dissolved in 1 cm^3 of $CDCl_3$ with 7 mole % catalyst under an atmosphere of dinitrogen. Catecholborane (24 mg, 0.20 mmol) in 0.5 cm^3 of $CDCl_3$ was added dropwise to the stirred solution and the reaction was allowed to proceed for 48 h and then analysed by multinuclear magnetic resonance spectroscopy. Similar procedures were carried out for reactions with pinacolborane.

Hydroboration of (1) with 9-Borabicyclo[3.3.1]nonane

9-Borabicyclo[3.3.1]nonane dimer (0.09 g, 0.36 mmol) was dissolved in 1 cm^3 of $CDCl_3$ and then added dropwise to a 1 cm^3 $CDCl_3$ solution of (1) (0.03 g, 0.18 mmol). The reaction was allowed to proceed for 24 h at which point the mixture was analysed by multinuclear magnetic resonance spectroscopy. Selected n.m.r. spectroscopic data (in $CDCl_3$): ^{1}H δ 7.31, d, *J* 5 Hz, 1H, 6.52, d, *J* 8 Hz, 1H; 3.98, t, *J*

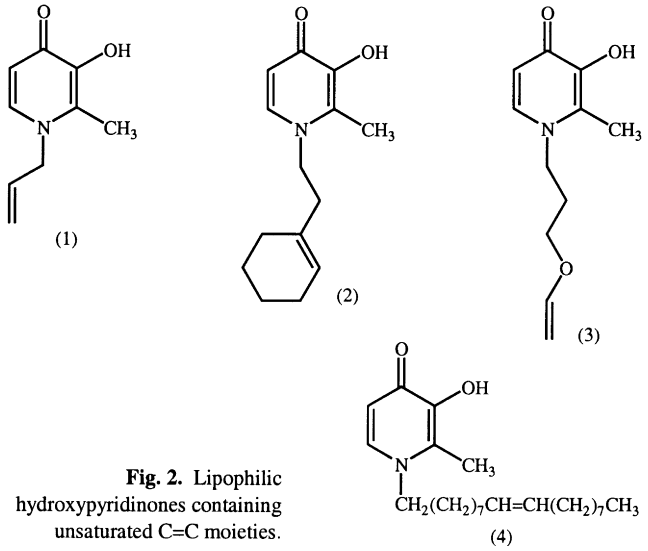


Fig. 2. Lipophilic hydroxypyridinones containing unsaturated C=C moieties.

5 Hz, 2H; 2.46, s, 3H; 1.87–1.53, ov m, 32H; $^{11}B\{^1H\}$ δ 86.1, BC_3; 59.6; 20.3.

Crystallography

Crystal Data

Compound (3). $C_{11}H_{15}NO_3$, mol. wt 209.2, monoclinic, space group $P2_1/n$, *a* 10.466(1), *b* 13.388(1), *c* 15.386(2) Å, β 102.343(8)°, *V* 2106.0(5) Å^3, *F*(000) 896, *Z* 8, D_c 1.320 g cm^{-3}, μ(Mo Kα) 0.96 cm^{-1}, temperature 180 K.

Yellow tabular prism, 0.34{110} by 0.54{001}, 2θ range 4.0–50.0°, 3913 collected reflections, 3701 unique (R_{int} 0.0140), 2634 observed ($F \geq 6\sigma(F)$), final *R* factor 0.0308, *wR* 0.0315, goodness of fit 2.15, min./max. transmission 0.9642/0.9751.

Data Collection, Structure Resolution and Refinement

Data were collected on a Nicolet LT2 equipped Siemens P4 diffractometer using the ω method ($4 \leq 2\theta \leq 50°$). The data were corrected for absorption by a faced-indexed analytical method. Three standard reflections every 100 showed no significant decay. The structures were solved by Patterson and Fourier methods, and refined by full matrix least squares (SHELXTL IRIS).[21] A weighting scheme of $w^{-1} = \sigma^2(F)$ was used in the last cycles of refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by a difference Fourier and freely refined with isotropic thermal parameters. Room-temperature cell data clearly suggest that a phase change occurs between 295 and 180 K as warming back up leads to the original cell (at 295 K, *a* 7.637(1), *b* 13.617(1), *c* 10.567(1), β 101.619(6)°, *V* 1076.4(4), indicating only one molecule per asymmetric unit). $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $Rw = [\Sigma(w(|F_o|-|F_c|)^2/\Sigma(w|F_o|)^2]^{1/2}$.

Results and Discussion

Pyridinone Ligands and Molybdenum Complexes

One method for generating *N*-substituted pyridinone ligands involves the addition of a primary amine to aqueous solutions of maltol (3-hydroxy-2-methyl-4-pyrone, Hma) at elevated temperatures.[20,22] The mechanism for this reaction is believed to involve a double Michael-type addition where initial nucleophilic attack of the amine, followed by ring opening and elimination of water with subsequent ring closure, affords the desired hydroxypyridinone compound. Four potentially lipophilic hydroxypyridinones (1)–(4) containing pendent C=C moieties have been prepared (Fig. 2) by means of this methodology.

An X-ray diffraction study was carried out on the 3-vinyloxypropylamine derivative (3) to confirm the formation of pyridinones in these reactions since Schiff-base compounds have also been reported to form under similar conditions.[20] The structure of the two independent molecules of (3) shown in Fig. 3 confirms that the amine has inserted into the ring oxygen to form the corresponding pyridinone. The two independent molecules form hydrogen-bonded pairs (Fig. 3) via OH (molecule 1) to carbonyl (molecule 2) interactions and vice versa (average 1.86(2) Å) [O(14)–H(14)···O(30), 2.639(2) Å; O–H···O, 147(2)°; O(29)–H(29)···O(15), 2.691(2) Å; O–H···O, 150(2)°]. Atomic coordinates are given in Table 1. The six-membered pyridinone ring in molecule 1 is slightly non-planar with a deviation from the mean plane of 0.017 Å towards an N(1),C(4) boat as seen previously.[4,16] Interestingly, no significant distortion towards a boat conformation is observed in molecule 2. Bond lengths and angles observed in (3) are similar to those seen in other pyridinones.[4] Atomic coordinates, thermal parameters, bond lengths and angles, and alternative views of complex (3) have been deposited as an Accessory Publication, copies of which are available (until 31 December 2005) from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.

The coordination and bioinorganic chemistry of molybdenum is an area of much interest owing to the fact that this transition metal is a trace nutrient in microorganisms, plants, and animals.[23] In this study, we have prepared molybdenum compounds (5)–(8) of the type *cis*-MoO_2L_2 (where L represents a pyridinone ligand) in low to moderate yields

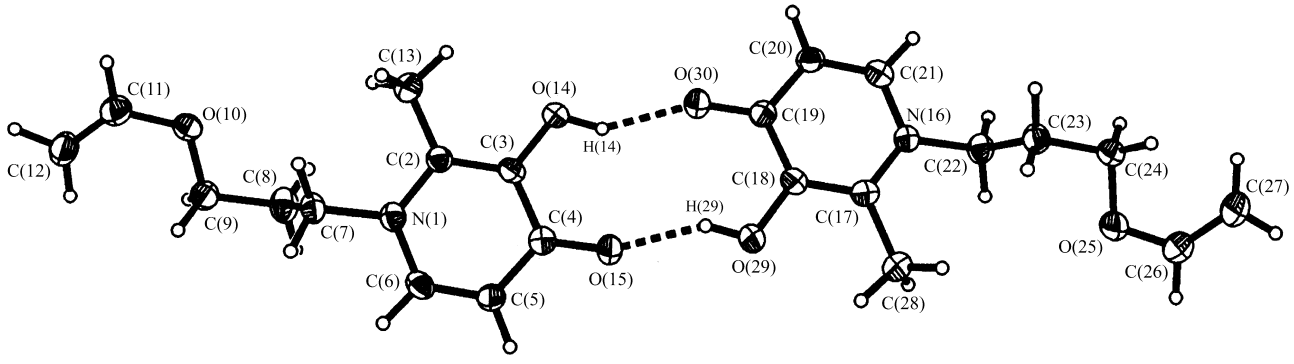
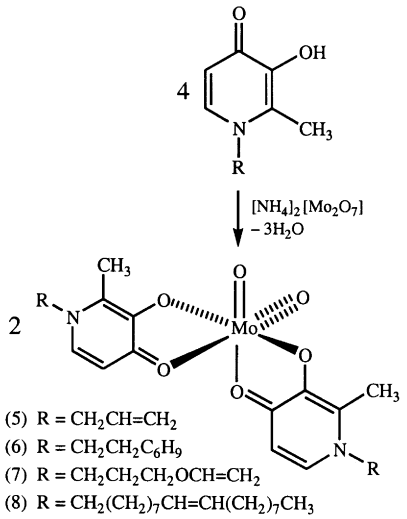


Fig. 3. The two independent molecules of (3) forming a hydrogen-bonded pair.

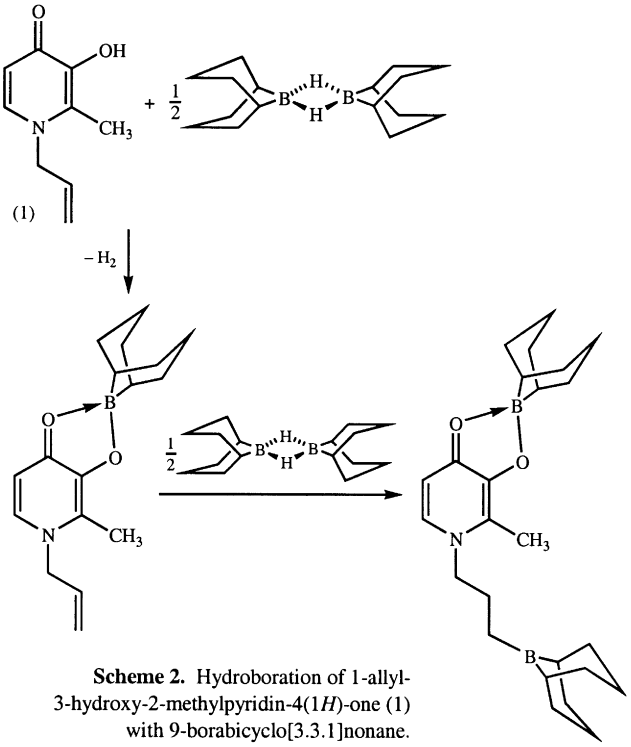
Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for (3)

Atom	Molecule 1 10^4x	10^4y	10^4z	10^4U_{eq}[A]	Atom	Molecule 2 10^4x	10^4y	10^4z	10^4U_{eq}[A]
N(1)	5752(1)	3553(1)	5522.9(9)	253(5)	N(16)	4042(1)	6258(1)	–502.6(9)	253(5)
C(2)	4730(2)	3557(1)	4788(1)	248(6)	C(17)	4944(2)	6428(1)	283(1)	246(6)
C(3)	4892(2)	4022(1)	4029(1)	252(6)	C(18)	4758(2)	5995(1)	1050(1)	247(6)
C(4)	6091(2)	4492(1)	3948(1)	245(6)	C(19)	3619(2)	5411(1)	1087(1)	252(6)
C(5)	7101(2)	4421(1)	4721(1)	279(6)	C(20)	2735(2)	5290(1)	259(1)	267(6)
C(6)	6911(2)	3976(1)	5473(1)	286(6)	C(21)	2966(2)	5695(1)	–499(1)	276(6)
C(7)	5634(2)	3078(1)	6368(1)	287(6)	C(22)	4231(2)	6658(1)	–1362(1)	304(7)
C(8)	6093(2)	1996(2)	6424(1)	355(7)	C(23)	3601(2)	7671(2)	–1578(1)	328(7)
C(9)	5956(2)	1504(2)	7278(1)	330(7)	C(24)	3866(2)	8081(2)	–2432(1)	352(7)
O(10)	4589(1)	1391(1)	7265.1(8)	341(4)	O(25)	5243(1)	8258(1)	–2304.7(8)	366(5)
C(11)	4324(2)	922(2)	7992(1)	386(7)	C(26)	5630(2)	8660(2)	–3020(1)	392(8)
C(12)	5158(2)	582(2)	8681(1)	484(9)	C(27)	4913(2)	8869(2)	–3798(2)	475(8)
C(13)	3468(2)	3067(2)	4851(1)	363(7)	C(28)	6097(2)	7082(2)	271(1)	349(7)
O(14)	3858(1)	4043(1)	3325.0(9)	382(5)	O(29)	5680(1)	6134(1)	1806.6(8)	356(5)
O(15)	6209(1)	4928(1)	3238.6(8)	329(4)	O(30)	3456(1)	5039(1)	1810.5(8)	361(4)

[A] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.



Scheme 1. Molybdenum pyridinone complexes.



Scheme 2. Hydroboration of 1-allyl-3-hydroxy-2-methylpyridin-4(1*H*)-one (1) with 9-borabicyclo[3.3.1]nonane.

(22–42%) by the direct addition of the hydroxypyridinones to molybdic acid (Scheme 1). Molybdenum pyridinone complexes have been reported previously for examples containing simple alkyl or aryl groups attached to the ring carbon.[19,24] The four-band infrared spectral pattern between 1400 and 1610 cm^{-1}, characteristic of pyridinone ligands,[25,26] is observed upon complexation with molybdenum. These four bands are assigned collectively as ν(C=C) and ν(C=O). As expected for a d^0 metal, no significant shift for the pyridinone alkene protons is observed in the ^1H n.m.r. spectra upon complexation.

Hydroboration Reactions

Hydroboration constitutes the formal addition of B–H bonds to unsaturated organic fragments to give the corresponding organoboranes and is one of the most important reactions in synthetic organic chemistry.[27] Hydroboration of the alkene groups in pyridinones (1)–(4) would allow for further functionalization of these novel ligands. In order to test this hypothesis, we have examined the addition of a number of hydroborating agents to allylamine-derived pyridinone (1).

Addition of 9-borabicyclo[3.3.1]nonane to (1) gave initial formation of a borinic ester intermediate (R_2BOR), along with concomitant generation of dihydrogen, by reaction with the active hydroxy site. Similar intermediates have been reported recently when substituted quinones are treated with trialkylboranes.[27] In our study, a second equivalent of 9-borobicyclo[3.3.1]nonane was required to effect the hydroboration of the alkene group in (1) (Scheme 2). The diagnostic peak at 86 ppm in the $^{11}B\{^1H\}$ n.m.r. spectrum suggests the formation of a BR_3 (R = alkyl) species.[28] Further evidence that the alkene is being reduced is found by the absence of the vinylic peaks in the ^1H n.m.r. spectrum. Interestingly, attempts to catalyse the hydroboration of (1) with either catecholborane or pinacolborane,[29] using a number of transition metal complexes, led to a number of unidentified products arising from the nucleophilic degradation of the corresponding borane. Not surprisingly, addition of B–H bonds to the corresponding molybdenum

complexes also resulted in numerous degradation compounds including decomplexation of the pyridinone ligand.

Conclusions

A series of lipophilic hydroxypyridinones, and their corresponding dioxomolybdenum(VI) complexes, have been prepared and characterized by a number of physical methods, including X-ray diffraction studies for (3). The resulting metal complexes, like the hydroxypyridinone ligands, have appreciable solubility in common organic solvents. Initial results into the hydroboration of the alkene moieties in these pyridinones have been successful using 9-borabicyclo[3.3.1]nonane. We are currently investigating these hydroboration reactions and the corresponding workups in more detail, the results of which will be published in due course.

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