Synthesis and Reactivity of Oxametallacyclic Niobium Compounds by Using α,β-Unsaturated Carbonyl Ligands

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Dedicated to Prof. Dr. W. Herrmann on the occasion of his 60th birthday

Keywords: Niobium / Cyclopentadienyl ligands / Diene ligands / Metallacycles / Acrylate ligands

Reduction of mono(cyclopentadienyl)niobium complexes [NbCpRCl4] [CpR = C5Me4H (1), C5H4SiMe2Cl (2), C5H4SiMe3 (3)] with Na/Hg in the presence of methyl methacrylate [MMA, CH2=C(Me)C(O)OMe (a)], methyl acrylate [MA, CH2=CHC(O)OMe (b)] and mesityl oxide [MO, CMe2=CHC(O)Me (c)] afforded the corresponding derivatives [NbCpRCl2(LL)] [CpR = C5Me4H, LL = MMA (1a); CpR = C5H4SiMe2Cl, LL = MMA (2a), MA (2b), MO (2c); CpR = C5H4SiMe3, LL = MMA (3a), MA (3b)] in variable yields depending on both the cyclopentadienyl and the α,β-unsaturated carbonyl compounds. The reactivity of these complexes was studied toward protic and Lewis acids. Addition of triflic acid TfOH (Tf = CF3SO2) to 3b gave the triflate complex [NbCpRCl2{(CH2)2C(O)OMe}(OTf)] [CpR = C5H4SiMe3 (4)].

The Lewis acids E(C6F5)3 (E = B, Al) reacted with complexes 2a and 3b to give the three-membered metallacyclic (or η2-enone) compounds [NbCpRCl2{η2-CH2=CHC(OMe){O·E(C6F5)3}}] [CpR = C5H4SiMe2Cl, E = B (5), Al (6); CpR = C5H4SiMe3, E = B (7), Al (8)], which decomposed to the corresponding adducts MA·E(C6F5)3. The same reaction with the 2a and 3a derivatives only allowed the observation of the corresponding adducts MMA·E(C6F5)3. Complexes 2a, b and 3a, b reacted with CO with elimination of the acrylate compounds, MA and MMA, respectively, to give the carbonylniobium(III) compounds [NbCpRCl2(CO)2]2 [CpR = C5H4SiMe2Cl (9), C5H4SiMe3 (10)]. Analogous reactions with CNAr showed the elimination of the free MA and MMA compounds.

Introduction

The bonding interaction of a butadiene ligand with a metal center is clearly dependent on the metal atom and may be formulated as a system containing a dianionic ligand for early high-valent transition metals or as a neutral ligand for low-valent late transition metals. However, the stability of the formal oxidation state of the metal atom and the nature of the ancillary substituents of both the complex and the diene ligand could play an important role in defining this interaction. Hence, complexes with this type of ligand are better represented with contributions from two main canonical forms, σ2,π-metallacyclic or π2-butadiene (Figure 1).[1–5]

Replacement of at least one of the terminal CR2 moieties by an isolobal fragment such as NR, O, S, etc. induces an important modification on the butadiene ligand.[6–11] Functionalization with one oxygen atom provides an oxametallacyclic system, which consists of a cyclic enolate ligand. The study of enolate derivatives has attracted attention because they have been proposed as the active species for polymerization of polar monomers.[11–16] Another feature of these compounds is that coordination of the asymmetric α,β-unsaturated carbonyl ligands will create two new reactive points in the molecule at the M–C and M–O bonds.

We describe herein the synthesis of mono(cyclopentadienyl)niobium compounds by using different α,β-unsaturated carbonyl ligands and their reactivity with Brönsted...
and Lewis acids and with strong π-acceptor ligands such as CO and CNAr.

Results and Discussion

Synthesis of Metallacyclic Compounds

The reduction of the niobium compound [NbCp*Cl4] in toluene with Na/Hg amalgam in the presence of MMA has been reported previously,[7] and we have applied this method using the α,β-unsaturated carbonyl compounds CH2=C(Me)C(O)OMe (MMA), CH2=CHC(O)OMe (MA), and CMe2=CHC(O)Me (MO) to isolate the new derivatives [NbCpRCl2(LL)] [CpR = C5Me4H, LL = MMA (1a); CpR = C5H4SiMe2Cl, LL = MMA (2a), MA (2b), MO (2c); CpR = C5H4SiMe3, LL = MMA (3a), MA (3b)] (Scheme 1). The whole process can be considered as a reduction of the metal center followed by the oxidative coupling of the α,β-unsaturated carbonyl ligand. These compounds were obtained in good yields for the MMA and MA derivatives, whereas the unique isolated mesityl oxide MO complex was obtained in rather poor yield, probably because of the steric hindrance of the terminal Me2C group. A similar low yield was reported for the related [TaCp*Cl2(MO)] complex which was obtained from a CO/MO exchange reaction.[17] It is remarkable that reduction proceeded selectively at the niobium atom even in the case of the (chlorosilyl)cyclopentadienyl-functionalized derivatives.

The presence of the enolate ligand endows asymmetry to all of the complexes for which the 1H NMR spectra showed an ABCD spin system for the cyclopentadienyl ring protons and methyl groups. The formation of the metallacyclic compounds 1a–3a and 2b and 3b was supported by the low-field signals observed in the 1H NMR spectra for the Nb–CH2 group, shifted to δ = 1.00 and 1.70 ppm from δ = 5–6 ppm in the starting free acrylate ligands, and also observed in the 13C NMR spectra shifted to δ = 70 ppm with respect to the free acrylate compounds (δ = 130 ppm). Moreover, for the MA complexes 2b and 3b the signal of the internal C–H proton was observed at δ = 5.0 ppm. The coupling constant J1C,H for the CH2 group of compounds 1a–3a showed a slight decrease consistent with the lower s character of this carbon atom (J ≈ 150 Hz in 1a–3a, J = 159 Hz for free MMA), which was corroborated with the geminal J2H,H coupling constant of this group (J = 7 Hz in 1a–3a, J = 2 Hz for free MMA). However, in compounds 2b–3b the J1C,H coupling constant for the CH2 group remained unchanged, although the increase of J1C,H for the internal carbon atom suggested higher s character (J ≈ 180 Hz in 2b and 3b, J = 162 Hz for free MMA), consistent with the metallacyclic disposition of the MA ligands. The poor yield and the lack of purity of the mesityl oxide compound 2c made its characterization by NMR and IR spectroscopy difficult, although its molecular structure was determined by X-ray diffraction studies (vide infra) on a single crystal.

The metallacyclic configuration was also supported by the two absorption bands observed in the IR spectrum at about 1515 and 750 cm−1 corresponding to ν(C=C) and ν(Nb–O) bands, respectively.

X-ray Structure of 1a, 2a, and 2c

The X-ray structures of complexes 1a, 2a, and 2c (Figure 2, Table 1) were similar to those reported for other related complexes.[7,11,17] The MMA and MO ligands presented a supine coordination as expected for the disposition of the five-membered metallacycle folded through the O–C(1) vector, with a dihedral angle of about 103°, as in related oxametallacyclic tantalum compounds.

![Diagram of complexes [NbCp^RCl_2(LL)] [Cp^R = C_5Me_4H, LL = MMA (1a); Cp^R = C_5H_4SiMe_2Cl, LL = MMA (2a), MO (2c)]. Hydrogen atoms have been omitted and thermal ellipsoids are shown at the 50% level.](image-url)
A comparison of the O–C and C–C bond lengths of the coordinated MMA and MO ligands in complexes 1a, 2a, and 2c with the corresponding average bond lengths of vinyl ether and α,β-unsaturated carbonyl compounds (Table 1)\(^{[18]}\) showed that the O–C and the internal C–C bond values are closer to a vinyl ether disposition (metallicity), mainly for derivatives 1a and 2c, whereas the C(1)–C(2) bond lengths present values intermediate between these two situations. These parameter sets for complexes 1a and 2c are very similar to those observed for related compounds [TaCp*Cl2(MMA)]\(^{[11]}\) and [TaCpCl2(MO)].\(^{[17]}\)

The Nb–O bonds are longer than those found for (alkoxido)niobium compounds, although they are in the range observed for five-membered alkoxido-metalacyclic derivatives.\(^{[19]}\) The distortion due to the formation of the metallacycle makes the Nb–O–C angles (about 88°) clearly more acute than in alkoxido compounds (over 120°) preventing the π-bonding contribution in the oxygen–niobium bond. The Nb–C(terminal) bonds are slightly shorter than in activated solvents giving a mixture of unidentifiable compounds.

The presence of the ester moiety coordinated to the metal atom favors stabilization of complex 4 increasing the electron count and preventing possible side-reactions due to the β-hydrogen atoms of the new alkyl chain.\(^{[25–29]}\) This proposal was supported by NMR spectroscopy (see below) and by comparison with the reported analogous tantalum derivative, which was isolated by transmetalation with a zinc enolate compound.\(^{[29]}\) Complex 4 was unstable in chlorinated solvents giving a mixture of unidentifiable compounds.

The higher nucleophilicity of alkoxido compared with methyl and chlorido ligands may justify the preferential protonolysis of the Nb–O bond. The formation of the five-membered ring may prevent the π-bonding contribution to the Nb–O bond due to the close Nb–O–C angle, which would increase the nucleophilicity of this alkoxido group that is sterically less protected with respect to the more linear M–O–C bond angle in related alkoxido complexes.

Formation of the C\(_5\)-symmetric compound 4 was in agreement with the AA'BB' pattern observed in the \(^1H\) NMR spectrum for the cyclopentadienyl ligand. The new alkyl chain bonded to the Nb center was confirmed by the \(^1H\) NMR spectrum that shows two multiplets at \(\delta = 1.90\) and 3.39 ppm corresponding to the Nb–CH\(_2\) group and the new internal CH\(_2\) group. Also, the generation of this new CH\(_2\) group was supported by a 2-D HSQC-NMR experiment. Finally, the presence of the ester moiety coordinated to the metal atom was confirmed by a resonance observed at \(\delta = 194.8\) ppm in the \(^{13}C\) NMR spectrum, which was shifted downfield with respect to this carbon signal in organic esters (\(\delta = 170\) ppm). This formulation was confirmed.
by comparison with the related tantalum compound [TaCp*Cl2(CH2CH2C(O)OMe)], for which the X-ray molecular structure has been reported.[29]

The same reaction with compounds 2a, 2b, and 3a and related reactions employing HCl as the Brønsted acid led to decomposition of the starting materials, whereas none of these compounds reacted with the related Lewis acids [Me3O][BF4] and (Me3Si)OTf.[30]

Reaction with the Lewis Acids E(C6F5)3 (E = B, Al)

The reaction of B(C6F5)3 with butadiene compounds has been reported to give betaine derivatives by rupture of the M–C bond.[4,8,31] We have investigated the reactivity of complexes 2a·b and 3a·b with the Lewis acids E(C6F5)3 (E = B, Al) with the aim of abstracting the alkyl ligand to generate a cationic enolate compound, considering that early transition-metal derivatives of this type have been used as precursors for the catalytic polymerization of acrylates.[12–16] Although the nucleophilicity of the oxygen atom bonded to the niobium atom could compete with that of the carbon atom, we have previously observed that alkoxido complexes of the type [CpTaMe2(OR)] reacted with these Lewis acids E(C6F5)3 at the Ta–C bond.[132] Furthermore, Mashima and co-workers also reported that reaction of the MMA complex [TaCp*([DAD](MMA)] [DAD = N(R) CH=CHN(R)] with AlMe3 produced the activation of the Ta–C bond of the coordinated MMA ligand.[11]

Addition of 1 equiv. of E(C6F5)3 (E = B, Al) to compounds 2b and 3b gave the three-membered metallacyclic compounds [NB(Cp)(CO)2]2 (Cp = C5H4SiMe3, E = B, 3a·b, H (E(C6F5)3). The 19F NMR spectra were also in agreement with the formation of adducts of the type R2CO·E(C6F5)3. The generation of the carbonyl group was confirmed by the absorption band observed at 1640 cm⁻¹ in the IR spectra.

Reaction with CO and CNAr (Ar = 2,6-Me2C6H3)

Following from our study on the chemical behavior of the oxametallacyclic system, we carried out the reaction of the starting complexes 2a, 2b, 3a, and 3b with CO and CNAr, for which the ability to be inserted into σ–M–C bonds is well documented.[36–40] However, the insertion reaction was not observed, rather displacement of the coordinated MMA and MA ligands (Scheme 4) gave the carbonyl derivatives [NB(Cp)(CO)2]2 [CpR = C5H4SiMe3Cl (9), CpR = C5H4SiMe3 (10)] for the reaction with CO, although we could not characterize the corresponding organometallic species resulting from the reaction with CNAr (Scheme 4).
Therefore, the formally NbV starting compounds 2–3 undergo a reductive decoupling to the NbIII derivatives. This process is the reverse of the procedure used for their synthesis. This behavior is a demonstration of the weak Nb–O interaction of the coordinated ligands, highlighting the tendency of Nb to reduce its oxidation state in the presence of strong π-acceptor ligands. This type of complex has been previously synthesized by reduction of [NbCpRCl4] into the complexes[41–43] and the molecular structure of complex 10 was confirmed by X-ray diffraction studies on an appropriate single crystal (Figure 3).

The molecular structure of complex 10 corresponds to a dimetallocyclic system with both niobium atoms hexacoordinate, assuming that the cyclopentadienyl ligand occupies only one coordination position. The carbonyl ligands are located in equatorial positions, one chlorido ligand in an apical position trans to the cyclopentadienyl group, and the other two positions correspond with two bridging chlorido substituents. The substituents on one metal atom present a trans disposition with respect to the substituents on the other niobium atom. The Nb–Cl(bridge) bonds are about 0.1 Å longer than the Nb–Cl(terminals). The terminal carbonyl ligands are linear with Nb–C–O bond angles of 178.6(2)° and 178.8(2)°. All these bond lengths and angles are similar to those reported in the literature.[41–43]

Figure 3. ORTEP diagram of [NbCpRCl2(CO)2] (CpR = C5H4SiMe3) (10). Hydrogen atoms have been omitted and thermal ellipsoids are shown at the 50% level. Selected bond lengths [Å] and angles [°]: Nb(1)–Cl(1) 2.6266(7), Nb(1)–Cl(2) 2.5103(7), Nb(1)–C(7) 2.132(2), C(7)–O(7) 1.141(4); Nb(1)–C(6)–O(6) 176.9(2), Nb(1)–C(7)–O(7) 178.8(2), Nb(1)–O(1)–Nb(2) 101.92(2).

Conclusions

Compounds of the type [NbCpRCl2(LL)] (CpR = C5Me4H, LL = MMA (1a); CpR = C5H4SiMe3Cl, LL = MMA (2a), MA (2b), MO (2c); CpR = C5H4SiMe3, LL = MMA (3a), MA (3b)) were obtained by reactions based on the oxidative addition of the α,β-unsaturated carbonyl ligands LL to the NbIII species generated in situ by reduction of the NbV halides [NbCpRCl3] with Na/Hg. The NMR and crystallographic data supported the formulation of these complexes as alkyl-alcohol-metallacyclic rather than as butadiene species.

The reactivity of these complexes with Brønsted and Lewis acids is controlled by the higher nucleophilicity of the oxygen atom compared with that of the metallacyclic carbon atom, because of the closely bent Nb–O–C angle, which probably does not allow strong π-bonding of the oxygen atom free pairs with the metal atom and also makes this oxygen atom easily accessible. However, the different nature of both types of acid employed showed two different transformations. Thus, whereas protonation of the Nb–O bond with TFOH gives an enol intermediate which evolves to give an alkyl ester derivative, addition of the Lewis acids E(C6F5)3 (E = B, Al) generated a new three-membered metallacyclic system by reforming the α,β-unsaturated carbonyl ligands which remained coordinated by the terminal C=C double bond. This interaction was not stable enough, and their evolution to give the adducts MMA-E(C6F5)3 and MA-E(C6F5)3 was observed, implying a reduction of the metal center.

Finally, addition of CO and CNAr produced the reductive decoupling and displacement of the coordinated α,β-unsaturated carbonyl ligands to give the NbIII complexes demonstrating the important contribution of the butadiene-like canonical form.

Experimental Section

General Considerations: All manipulations were carried out under argon, and solvents were purified from appropriate drying agents. NMR spectra were recorded at 400.13 (1H), 376.70 (19F), and 100.60 (13C) MHz with a Bruker AV400 spectrometer. Chemical shifts (δ) are given in ppm using CDCl3 as solvent, unless otherwise stated. 1H and 13C resonances were measured relative to solvent peaks considering δ(TMS) = 0 ppm, whereas 19F resonances were measured relative to external CFC12. Assignment of resonances was made from HMBC and HMBC NMR experiments. Elemental analyses were performed with a Perkin–Elmer 240C spectrometer. Compounds C5Me4H(SiMe3),[44] [NbCpRCl4] (CpR = C5H4SiMe3) (21), C5H4SiMe-coordinated, Al(C6F5)3[46] and 0.5(toluene)-were prepared according to literature methods. The α,β-unsaturated carbonyl compounds C(R3)2=C(R2)C(O)R1 were purchased from Aldrich, dried with CaH2, distilled under vacuum, and stored under an inert gas prior to use. HOTf (Tf = CF3SO2) from Aldrich was used without further purification.

Conclusion
[\text{Nb}(\eta^5-C_5H_5)\text{SiMe}_2\text{Cl}] (1) (1.00 g, 2.81 mmol) and \text{CH}_2=\text{C(}\text{Me})\text{O} \text{(OMe) (MMA) (0.30 g, 3.0 mmol) in tolue}n (30 mL) was added to 10% Na/Hg amalgam (0.13 g, 5.62 mmol), and the mixture was stirred overnight. The solution was filtered, concentrated to ca. 15 mL and cooled to –40 °C to yield 1a as green crystals (0.52 g, 48%). 1H NMR: \( \delta = 0.80 \) (d, \( J = 6.3 \) Hz, 1 H, Nb-CH\(_2\)), 1.58 (d, \( J = 6.3 \) Hz, 1 H, Nb-CH\(_2\)), 1.76 (s, 3 H, C\(_5\)H\(_4\), C\(_5\)Me\(_2\)H), 1.80 (s, 3 H, C\(_5\)H\(_4\), C\(_5\)Me\(_2\)H), 2.05 (s, 3 H, C\(_5\)H\(_4\), C\(_5\)Me\(_2\)H), 2.40 (s, 3 H, CH\(_2\)=C\(_2\)), 3.40 (s, 3 H, O\(_{Me}\)), 5.68 (s, 1 H, C\(_5\)H\(_4\)), 5.79 (s, 1 H, C\(_5\)Me\(_2\)H) ppm. 13C{1H} NMR: \( \delta = 116.1 \) (C\(_5\)H\(_4\)), 13.2 (C\(_5\)H\(_4\), C\(_5\)Me\(_2\)H), 13.9 (C\(_5\)Me\(_2\)H) ppm. 19F NMR: \( \delta = –0.7 \) (3 F, 6 F5), 146.4 (C\(_5\)Me\(_2\)H), 149.6 (C\(_5\)Me\(_2\)H) ppm. 1H NMR: \( \delta = 0.26 \) (s, 9 H, SiMe\(_3\)), 1.99 (m, 1 H, Nb-CH\(_2\)), 1.97 (m, 1 H, Nb-CH\(_2\)), 3.35 (s, 3 H, O\(_{Me}\)), 5.05 (m, 1 H, CH\(_2\)=C\(_2\)), 5.80 (m, 1 H, CH\(_2\)=C\(_2\)), 6.27 (m, 1 H, CH\(_2\)=C\(_2\)), 6.55 (m, 1 H, CH\(_2\)=C\(_2\)), 6.70 (m, 1 H, CH\(_2\)=C\(_2\)) ppm. 13C{1H} NMR: \( \delta = –0.5 \) (SiMe\(_3\)), 54.7 (O\(_{Me}\)), 68.3 (Nb-CH\(_2\)), 76.2 (C\(_5\)H\(_4\)), 119.3 (C\(_5\)H\(_4\)), 121.5 (C\(_5\)H\(_4\)), 125.3 (C\(_5\)H\(_4\)), 125.6 (C\(_5\)H\(_4\)), 160.0 (MeOC) ppm. C\(_{13}\)H\(_{21}\)Cl\(_2\)NbO\(_2\)Si (401.20) ppm: C 38.72, H 4.06 ppm. 13C{1H} NMR: C\(_{13}\)H\(_{21}\)Cl\(_2\)NbO\(_2\)Si (401.20) ppm: C 38.72, H 4.06 ppm. 13C{1H} NMR: C\(_{13}\)H\(_{21}\)Cl\(_2\)NbO\(_2\)Si (401.20) ppm: C 38.72, H 4.06 ppm. 13C{1H} NMR: C\(_{13}\)H\(_{21}\)Cl\(_2\)NbO\(_2\)Si (401.20) ppm: C 38.72, H 4.06 ppm.
CH₂), 119.2 (C₂H₅), 119.5 (C₃H₇), 121.4 (C₄H₉), 125.7 (C₅H₉), Cipso of C₅H₄ not observed, 135.5 (C₆F₅), 138.8 (C₇F₇), 148.9 (C₈F₈), 152.1 (C₉F₉), 184.2 (MeOOC ppm). ³¹P NMR: δ = 123.8 (m, 6 F, o-C₅F₅), –153.1 (m, 3 F, p-C₅F₅), –161.7 (m, 6 F, m-C₅F₅) ppm. IR (C(1D₅)): 2v = 1638 [v(CO)] cm⁻¹. ⁷'H NMR: δ = 0.02 (s, 9 H, SiMe₅), 2.45 (m, 1 H, Nb-CH₂), 2.62 (m, 1 H, Nb-CH₂), 3.09 (m, 1 H, CH₂-CCH₂), 3.51 (s, 3 H, OMe), 4.66 (m, 1 H, CH₄), 4.77 (m, 1 H, C=H₄), 5.43 (m, 1 H, C=H₄), 5.48 (m, 1 H, C=H₄) ppm. ¹³C{¹H} NMR: δ = –1.1 (SiMe₅), 55.1 (OMe), 56.0 (CH₂-CCH₂), 67.1 (Nb-CH₂), 116.5 (C₆H₄), 117.1 (C₆H₄), 118.6 (C₆H₄), 119.5 (C₆H₄), Cipso of C₆H₄ not observed, 135.7 (C₆H₄), 139.1 (C₆H₄), 146.7 (C₆H₄), 149.9 (C₆H₄), 186.4 (MeOOC ppm). ¹⁹F NMR: δ = –123.3 (m, 6 F, o-C₅F₅), –156.7 (m, 3 F, p-C₅F₅), –164.1 (m, 6 F, m-C₅F₅) ppm. IR (C(1D₅)): 2v = 1640 [v(CO)] cm⁻¹. ⁸¹³NMR: δ = 0.01 (s, 12 H, SiMe₃), δ = 0.00 (s, 12 H, Me), δ = 0.05 (s, 18 H, SiMe₃). ¹³C{¹H} NMR: δ = –0.7 (SiMe₅), 102.6 (C₆H₄), 108.7 (C₆H₄), Cipso of C₆H₄ not observed, 185.0 (CO) ppm. IR (nujol): δ = 2030, 1953 [v(CO)] cm⁻¹. C₁₂H₁₅Cl₂Nb₂O₈Si₂ (714.22): calc. C 33.66, H 3.67; found C 33.99, H 3.57.

Table 2. Crystallographic data for 1a, 2a, 2c, and 10.[a]

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<tr>
<td>No. of independent reflections (Rint)</td>
<td>7206/0.1301</td>
<td>3671/0.0761</td>
<td>4107/0.1047</td>
<td>3218/0.0260</td>
</tr>
<tr>
<td>No. of observed reflections [I &gt; 2σ(I)]</td>
<td>4507</td>
<td>3102</td>
<td>2613</td>
<td>2721</td>
</tr>
<tr>
<td>No. of data/restraints/parameters</td>
<td>7206/0.355</td>
<td>3671/0.177</td>
<td>4107/0.176</td>
<td>3218/0.145</td>
</tr>
<tr>
<td>R₁/wR₂ [I &gt; 2σ(I)][a]</td>
<td>0.0722/0.1222</td>
<td>0.0376/0.0700</td>
<td>0.0470/0.0962</td>
<td>0.0298/0.0379</td>
</tr>
<tr>
<td>R₁/wR₂ (all data)[a]</td>
<td>0.1305/0.1338</td>
<td>0.0528/0.0743</td>
<td>0.0991/0.1076</td>
<td>0.0384/0.0770</td>
</tr>
<tr>
<td>GOF (on F²)[a]</td>
<td>1.161</td>
<td>1.023</td>
<td>0.987</td>
<td>1.052</td>
</tr>
<tr>
<td>Largest difference peak/hole [e·Å⁻³]</td>
<td>+0.818/–0.864</td>
<td>+0.568/–0.529</td>
<td>0.563/–0.807</td>
<td>+0.7021/–0.938</td>
</tr>
</tbody>
</table>

[a] R₁ = Σ(|Fo| – |Fc|)²/Σ|Fo|²; wR₂ = Σ[w(Fo² – Fc²)²]²/Σ[w(Fo²)²]⁻¹; GOF = Σ[w(Fo² – Fc²)²]/(n – p)⁻¹/².
crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected NMR spectra.

Acknowledgments

We gratefully acknowledge the Ministerio de Educación y Ciencia (MEC) (project MAT2007-60997) and the Dirección General de Universidades e Investigación (DGUI) – Comunidad de Madrid (programme S-0505/PPQ-0328 COMAL-CM) (Spain) for financial support. R. A. A.-M. acknowledges MEC for a fellowship.


Received: January 18, 2008
Published Online: April 4, 2008