

η^2 -Iminoacyl and η^2 -Acyl Monocyclopentadienyl Tantalum Complexes Bearing Oxo and Oxo-Borane Ligands

Javier Sánchez-Nieves,^[a] Pascual Royo,^{*[a]} and Marta E. G. Mosquera^{[a][‡]}

Dedicated to J. Antonio Abad, an excellent scientist and friend

Keywords: Tantalum / Oxo ligands / Insertion reactions / Isocyanide / Carbon monoxide

Alkyl-chloro ligand exchange by the reaction of $[\text{TaCp}^*\text{R}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{R} = \text{CH}_2\text{Ph}$, Me) with Ph_3CCl gave the monoalkyl compounds $[\text{TaCp}^*\text{RCl}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{R} = \text{CH}_2\text{Ph}$, Me). Insertion of CNAr ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) and CO into a Ta–C bond of the mono- and dialkyl complexes gave the iminoacyl compounds $[\text{TaCp}^*\text{X}\{\eta^2\text{-C}(\text{R})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{X} = \text{R} = \text{CH}_2\text{Ph}$, Me; $\text{X} = \text{Cl}$, $\text{R} = \text{CH}_2\text{Ph}$) and the acyl compounds $[\text{TaCp}^*\text{X}\{\eta^2\text{-C}(\text{R})=\text{O}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{X} = \text{R} = \text{CH}_2\text{Ph}$, Me; $\text{X} = \text{Cl}$, $\text{R} = \text{CH}_2\text{Ph}$), respectively. The related chloro compound $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ was isolated from the reaction of the oxo derivative

$[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Addition of CNAr or pyridine to $[\text{TaCp}^*(\text{CH}_2\text{Ph})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ afforded the borane-free complex $[\text{TaCp}^*(\text{CH}_2\text{Ph})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}(\text{O})]$ and the acid-base adduct $\text{L}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{L} = \text{py}$, CNAr). The molecular structures of $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ and $[\text{TaCp}^*(\text{CH}_2\text{Ph})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{O}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ were obtained from X-ray diffraction studies.

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Introduction

The formation of C–C bonds through insertion of isocyanides (CNR) and carbon monoxide (CO) into M–C bonds is well-documented, and this reaction initially affords iminoacyl and acyl complexes, respectively.^[1] For a given metal atom, the stability and further evolution of these compounds are determined by the nature of the ancillary ligands. Many reaction pathways may follow to give a broad variety of products:^[1] (a) migratory insertion of a second alkyl or aryl group to give η^2 -imine or η^2 -ketene complexes;^[2–5] (b) intra- or intermolecular coupling of iminoacyl or acyl units affording diaza- or dioxobutene complexes;^[6,7] (c) transfer of the NR or O moieties to the metal centre;^[8–11] (d) insertion of a second CNR^[12–16] or CO^[17] molecule into the new M–C bond formed after the first insertion process and (e) hydrogen migration.^[18,19]

We reported the results of our studies on the insertion reactions of CNR into the Ta–C(methyl) bond of monocyclopentadienyl complexes of the type $[\text{TaCp}^*\text{Cl}_x\text{Me}_{4-x}]$ ^[8–10] for which processes (a) and (c) were observed. Similar reactions with imido compounds of the type $[\text{TaCp}^*\text{MeX}(\text{NR})]$ ($\text{X} = \text{Cl}$, Me, OR, $\text{NH}t\text{Bu}$) gave

the imine- η^2 -iminoacyl derivatives $[\text{TaCp}^*(\text{N}t\text{Bu})\text{X}\{\eta^2\text{-C}(\text{Me})=\text{NR}\}=\text{NR}]$.^[20] With regard to the CO insertion reactions, double migration of the alkyl group [process (a)] was observed for $[\text{TaCp}^*\text{Cl}_2\text{Me}_2]$,^[10] whereas the coupling of the acyl groups [process (b)] occurred for $[\text{TaCp}^*\text{Me}_2(\text{NR})]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) to give the dinuclear compound $[\text{TaCp}^*(\text{NR})\text{Me}_2\{\mu\text{-}\eta^2\text{-OC}(\text{Me})=\text{C}(\text{Me})\text{O}\}]$,^[10] and ligand exchange [process (c)] for complexes $[\text{TaCp}^*\text{ClMe}(\text{NR})]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $t\text{Bu}$)^[11] led to the oxo compounds $[\text{TaCp}^*\text{Cl}(\text{O})\{\eta^2\text{-C}(\text{Me})=\text{NR}\}]$. Furthermore, the η^2 -(methyl)acyl complexes remained elusive and were only detected as intermediates by NMR spectroscopy, whereas the related η^2 -iminoacyl complexes are stable.

It was observed that for monocyclopentadienyl imido tantalum derivatives addition of a second CNR molecule into the iminoacyl compounds $[\text{TaCp}^*(\text{NR})\text{X}\{\eta^2\text{-C}(\text{Me})=\text{NR}\}]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $t\text{Bu}$; $\text{X} = \text{Cl}$, Me) resulted in differing behaviours depending on the R group of the imido ligand. No reaction was found for $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$,^[10] whereas a second insertion occurred for $\text{R} = t\text{Bu}$.^[20] Conversely, the imido complexes $[\text{TaCp}^*\text{MeX}(\text{NR})]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $t\text{Bu}$; $\text{X} = \text{Cl}$, Me) reacted with CO to give the dinuclear compound $[\text{TaCp}^*(\text{NR})\text{Me}_2\{\mu\text{-}\eta^2\text{-OC}(\text{Me})=\text{C}(\text{Me})\text{O}\}]$ for $\text{X} = \text{Me}$ ^[10] and one of the few mononuclear derivatives $[\text{TaCp}^*\text{Cl}(\text{O})\{\eta^2\text{-C}(\text{Me})=\text{NR}\}]$ containing a terminal tantalum-oxo double bond for $\text{X} = \text{Cl}$.^[10,11]

The versatility and potential applications of all these results determined by the R and X substituents of the imido

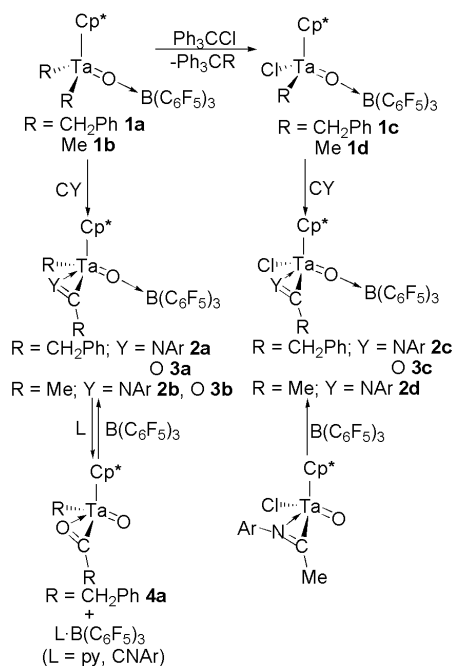
[a] Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Madrid, Spain
Fax: +34-91-885-4683
E-mail: pascual.royo@uah.es

[‡] X-ray diffraction studies.

complexes $[\text{TaCp}^*\text{MeX}(\text{NR})]$ led us to extend our studies to similar insertion reactions of CNR and CO into the Ta–alkyl bonds of the related oxo-borane compounds $[\text{TaCp}^*\text{X}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ that have recently been isolated.^[21]

Results and Discussion

The monoalkyl oxo-borane compounds $[\text{TaCp}^*\text{RCl}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{R} = \text{CH}_2\text{Ph}$ **1c**, **Me 1d**) were synthesised by an alkyl-chloro metathesis reaction of $[\text{TaCp}^*\text{R}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{R} = \text{CH}_2\text{Ph}$ **1a**, **Me 1b**) with one equiv. of Ph_3CCl as chlorinating agent (Scheme 1). The reaction for **1c** proceeded smoothly at room temperature to give a pale yellow solid in good yield, whereas complex **1d** could not be isolated in the solid state. The formation of **1d** was demonstrated on a small scale by ^1H NMR spectroscopy with a C_6D_6 solution of **1b** that was treated with Ph_3CCl and heated to 40°C . All attempts made to obtain the monomethyl complex through alkylation of $[\text{TaCp}^*\text{Cl}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ and redistribution reactions between $[\text{TaCp}^*\text{Cl}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ and $[\text{TaCp}^*\text{Me}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ failed. The ^{11}B and ^{19}F NMR spectra of complexes **1c** and **1d** are consistent with the presence of a tetra-coordinate boron atom,^[21–31] and the ^1H NMR spectra with the monosubstitution of only one of the alkyl ligands.



Scheme 1.

The alkyl complexes $[\text{TaCp}^*\text{R}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{R} = \text{CH}_2\text{Ph}$ **1a**, **Me 1b**) and $[\text{TaCp}^*(\text{CH}_2\text{Ph})\text{Cl}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ (**1c**) immediately reacted at room temperature with one equiv. of the isocyanide CNAr ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) to give the corresponding η^2 -iminoacyl compounds $[\text{TaCp}^*\text{X}\{\eta^2\text{-C}(\text{R})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{X} = \text{R} = \text{CH}_2\text{Ph}$ **2a**, **Me 2b**; $\text{X} = \text{Cl}$, $\text{R} = \text{CH}_2\text{Ph}$ **2c**) in high yields by insertion of the isocyanide ligand into a Ta–C bond (Scheme 1).

These pale yellow complexes are air and thermally stable in solution. The ^{13}C NMR resonance at ca. $\delta = 240$ ppm is the most apparent spectroscopic feature and confirms the presence of the η^2 -iminoacyl ligand in complexes **2**.

We previously reported^[10] on the isolation of the related oxo complex $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ from the reaction of the monomethyl compound $[\text{TaCp}^*\text{ClMe}(\text{NAr})]$ with CO through a process that involved insertion of CO into the Ta–Me bond and further rearrangement of the η^2 -acyl intermediate with intramolecular oxo-imido exchange. Since the starting oxo-borane chloro-methyl complex could not be isolated, thus preventing access to the oxo-borane compound $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ (**2d**) by insertion of CNAr into the Ta–C bond of the corresponding alkyl-chloro compound, we tried to obtain this compound by an alternative route. With this aim, we investigated the reaction of the oxo iminoacyl compound $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ with $\text{B}(\text{C}_6\text{F}_5)_3$, which afforded **2d** in high yield. The formation of **2d** was confirmed by ^{13}C and ^{19}F NMR spectroscopy. The ^{13}C NMR spectrum shows the resonance corresponding to the C_{sp^2} atom of the η^2 -iminoacyl ligand ($\delta = 240.1$ ppm) to be slightly low-field shifted with respect to that of the starting compound $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ ($\delta = 236.8$ ppm). An analogous behaviour was observed in the ^1H NMR spectrum for the methyl-iminoacyl group, which was shifted from $\delta = 2.65$ ppm in $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ to $\delta = 2.94$ ppm in **2d**.

The molecular structure of compound $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) (**2d**) was obtained by X-ray diffraction studies. Figure 1 depicts an ORTEP drawing of **2d** with selected bond lengths and angles. Compound **2d** exhibits the typical geometry known for group 5 half-sandwich iminoacyl compounds with a tetrahedral coordination environment around the tantalum atom. Considering the centroid of the Cp^* ring and the midpoint of the $\text{C}(10)\text{--N}$ bond as coordination sites, the other two positions are occupied by the chloro and oxo ligands. The N atom of the η^2 -iminoacyl group is located in a *trans* position with respect to the oxo ligand, as in analogous half-sandwich imido complexes and in $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$. Furthermore, the oxygen atom is attached to the boron atom of the $\text{B}(\text{C}_6\text{F}_5)_3$ group.

All the values of the bond lengths and angles of compound **2d** are very close to the corresponding bond lengths and angles found for the parent compound $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ ^[10] except for the Ta–O bond, which is longer in $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ [$1.731(7)$ Å] than in **2d** [$1.809(5)$ Å] as a consequence of the coordination of the oxygen atom to the $\text{B}(\text{C}_6\text{F}_5)_3$ ligand.^[21,23–28,30,31] The linear Ta–O–B angle [$174.4(6)^\circ$] and the B–O bond length [$1.52(1)$ Å] are typical of oxo-borane compounds.^[21–31] The Ta–O bond in **2d** is longer than that in the oxo-borane compound $[\text{TaCp}^*\text{Cl}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ^[21] [$1.784(2)$ Å]. This bond length is similar to the lower end of the range of Ta–O bond lengths for compounds with Ta–O–Ta bridges ($1.82\text{--}2.10$ Å)^[32–35] and with terminal Ta–OH bonds ($1.85\text{--}1.97$ Å).^[36–38] However, the single bond Ta–O distances are ca. 2.18 Å,

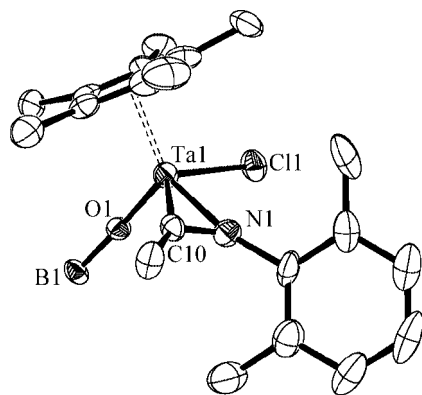


Figure 1. ORTEP diagram of the X-ray structure of compound **2d**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms and C_6F_5 groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta–O 1.809(5), Ta–N 2.127(7), Ta–C(10) 2.120(9), Ta–Cl 2.392(2), B–O 1.525(11), N–C(10) 1.26(1), N–Ta–C(10) 34.5(3), C(10)–N–Ta 72.4(5), N–C(10)–Ta 73.1(5), B–O–Ta 174.4(6).

and thus a bond order of two should be considered for the Ta–O bond in **2d**.

The reaction of the dialkyl $[\text{TaCp}^*\text{R}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{R} = \text{CH}_2\text{Ph}$ **1a**, Me **1b**) and the monobenzyl $[\text{TaCp}^*(\text{CH}_2\text{Ph})\text{Cl}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ (**1c**) complexes with CO in toluene gave the η^2 -acyl compounds $[\text{TaCp}^*\text{X}\{\eta^2\text{-C}(\text{R})=\text{O}\}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($\text{X} = \text{R} = \text{CH}_2\text{Ph}$ **3a**, Me **3b**; $\text{X} = \text{Cl}$, $\text{R} = \text{CH}_2\text{Ph}$ **3c**) after ca. 24 h at room temperature in moderate yields (Scheme 1). These pale yellow compounds were air and thermally stable below 120 °C for several hours. The ^{13}C NMR spectra showed a resonance at ca. $\delta = 305$ ppm corresponding to the C_{sp^2} atom of the η^2 -acyl fragment. The slowness of the insertion reactions of CO is in contrast with the rapid transformations observed for complexes **1** with isocyanide and the behaviour observed^[10,11] for the reactions of the imido compounds $[\text{TaCp}^*\text{MeX}(\text{NR})]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $t\text{Bu}$; $\text{X} = \text{Cl}$, Me) with CO. This difference may be attributed to the lower oxophilicity of the tantalum atom in compounds **1** that is caused by the presence of the oxo ligand.

The X-ray structure of compound **3a** is shown in Figure 2. The environment around the Ta atom is analogous to that described for compound **2d** (see above) with the oxygen atom of the acyl group located *trans* to the oxo-borane ligand, as expected. The Ta–O(1) bond length of 1.816(2) Å is similar to that observed for compound **2d**, and the O(1)–B bond length [1.512(4) Å] and Ta–O(1)–B angle [173.0(2)°] have values that are normally seen for these types of compounds.^[21–31]

The whole set of angles and bond lengths of the $[\text{Ta}(\eta^2\text{-acyl})]$ group is in line with compounds of this type^[1] and is similar to those found in the other two tantalum-acyl complexes for which X-ray structures are known, $[\text{TaCp}^*\text{Me}\{\eta^2\text{-C}(\text{CH}_2\text{CMe}_2\text{Ph})=\text{O}\}\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ ^[39] and $[\text{TaCp}^*\text{Cl}_3\{\eta^2\text{-C}(\text{CH}_2\text{CMe}_2\text{Ph})=\text{O}\}]$.^[40] However, in the particular case of the isostructural imido derivative $[\text{TaCp}^*\text{Me}\{\eta^2\text{-C}(\text{CH}_2\text{CMe}_2\text{Ph})=\text{O}\}\{\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$, the Ta–O bond [2.21(1) Å] is slightly longer than the corre-

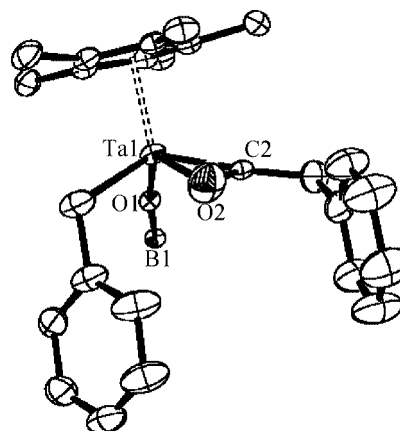


Figure 2. ORTEP diagram of the X-ray structure of compound **3a**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms and C_6F_5 groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta–O(1) 1.816(2), Ta–O(2) 2.110(3), Ta–C(1) 2.229(4), Ta–C(2) 2.011(3), B–O(1) 1.512(4), O(2)–C(2) 1.209(4), O(2)–Ta–C(2) 34.02(12), C(2)–O(2)–Ta 68.5(2), O(2)–C(2)–Ta 77.5(2), B–O(1)–Ta 173.02(19).

sponding bond in compound **3a** [2.110(3) Å], because of the different *trans* effect and higher donor capacity of the imido ligand.

The insertion of a second CNAr or CO molecule into these new acyl and iminoacyl oxo-borane complexes was not observed, in contrast with the behaviour observed for the analogous *tert*-butyl imido complexes.^[20] Rather, all complexes **2–3** released the acid-base adduct $\text{L}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{L} = \text{py}$, CNAr) in the presence of donor ligands such as isocyanide or pyridine.^[41] Only in the case of compound **2a** were we able to isolate the borane-free 18-electron compound $[\text{TaCp}^*(\text{CH}_2\text{Ph})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}(\text{O})]$ (**4a**), with a terminal oxo-tantalum bond. The remaining oxo-borane complexes decomposed under similar conditions. The ^{13}C NMR spectrum of the new oxo iminoacyl compound **4a** showed the η^2 -iminoacyl C_{sp^2} resonance at $\delta = 240.3$ ppm. A comparison of this ^{13}C resonance and that assigned to the CH_2 -iminoacyl group in the ^1H NMR spectrum with the corresponding resonances in the parent compound **2a**, showed a behaviour that is opposite to that observed for **2d** and $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$.

Conclusions

The dialkyl oxo-borane compounds $[\text{TaCp}^*\text{R}_2\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ can be transformed into the monoalkyl derivatives $[\text{TaCp}^*\text{RX}\{\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]$ by alkyl-chloro exchange with Ph_3CCl . All of these complexes reacted with one molecule of isocyanide or carbon monoxide to give the η^2 -iminoacyl or η^2 -acyl compounds, respectively. No further insertion processes have been observed. This behaviour is analogous to that observed for the imido compounds $[\text{TaCp}^*\text{MeX}(\text{NR})]$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; $\text{X} = \text{Cl}$, Me), although in the oxo-borane compounds the insertion of CO gave stable η^2 -acyl derivatives because of the presence of a Ta–O multiple bond, which prevents further rearrangement.

Experimental Section

All manipulations were carried out under argon, and solvents were distilled from appropriate drying agents. NMR spectra were recorded at 300.13 (^1H NMR), 188.31 (^{19}F NMR), 75.47 (^{13}C NMR) and 128.38 Hz (^{11}B NMR) at room temperature with a Varian Unity 300 (^1H , ^{13}C , ^{19}F) or Bruker Advance 400 (^{11}B NMR) instrument. Chemical shifts (δ , CDCl_3) are given in ppm, relative to internal TMS (^1H and ^{13}C NMR), and external CFCl_3 (^{19}F NMR) and $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B NMR). Elemental analyses were performed with a Perkin–Elmer 240C instrument. Compounds $[\text{TaCp}^*\text{Me}_4]$,^[42] $[\text{TaCp}^*(\text{CH}_2\text{Ph})_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$,^[21] $[\text{TaCp}^*\text{Me}_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$,^[21] $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ ^[40] and $\text{B}(\text{C}_6\text{F}_5)_3$ ^[43] were prepared by literature methods, and $\text{H}_2\text{O-B}(\text{C}_6\text{F}_5)_3$ ^[44] was prepared from H_2O and $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at room temperature and used in situ without further purification.

$[\text{TaCp}^*\text{Cl}(\text{CH}_2\text{Ph})\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1c): A suspension of Ph_3CCl (0.14 g, 0.50 mmol) and $[\text{TaCp}^*(\text{CH}_2\text{Ph})_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1a) (0.50 g, 0.49 mmol) in toluene (5 mL) was stirred overnight at room temperature, with a colour change from yellow to brown. Later, all volatile components were removed under vacuum until the volume was ca. 1 mL, leaving a dark oil that was washed with hexane (2×10 mL) to yield **1c** as a brownish solid (0.36 g, 76%). $\text{C}_{35}\text{H}_{22}\text{BClF}_{15}\text{OTa}$ (970.75): calcd. C 43.31, H 2.28; found C 42.99, H 2.25. ^1H NMR: δ = 2.14 (s, 15 H, C_5Me_5), 2.52 (d, $^2J_{\text{H,H}} = 14.0$ Hz, 1 H, CH_2Ph), 2.80 (d, $^2J_{\text{H,H}} = 14.0$ Hz, 1 H, CH_2Ph), 6.74 (m, 2 H, C_6H_5), 7.02 (m, 3 H, C_6H_5) ppm. ^{11}B NMR: δ = 0.10 [$\text{O-B}(\text{C}_6\text{F}_5)_3$] ppm; ^{13}C NMR (^1H): δ = 11.5 (C_5Me_5), 82.3 (CH_2Ph), 125.7 (C_5Me_5), 127.1 (C_6H_5), 128.2 (C_6H_5), 128.3 (C_6H_5), 131.4 (C_6H_5), 135.0 (C_6F_5), 138.3 (C_6F_5), 145.9 (C_6F_5), 149.1 (C_6F_5) ppm; ^{19}F NMR: δ = -132.9 ($o\text{-C}_6\text{F}_5$), -157.7 ($p\text{-C}_6\text{F}_5$), -163.3 ($m\text{-C}_6\text{F}_5$) ppm.

$[\text{TaCp}^*\text{ClMe}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1d): A solution of Ph_3CCl (0.080 g, 0.028 mmol) and $[\text{TaCp}^*\text{Me}_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1d) (0.025 g, 0.028 mmol) in C_6D_6 was heated at 45 °C for 18 h. Total transformation of **1b** to **1d** was then observed. ^1H NMR (C_6D_6): δ = 1.26 (s, 3 H, Ta-Me), 2.13 (s, 15 H, C_5Me_5) ppm. ^{11}B NMR (C_6D_6): δ = 0.05 [$\text{O-B}(\text{C}_6\text{F}_5)_3$] ppm. ^{19}F NMR (C_6D_6): δ = -133.0 ($o\text{-C}_6\text{F}_5$), -157.2 ($p\text{-C}_6\text{F}_5$), -163.3 ($m\text{-C}_6\text{F}_5$) ppm.

$[\text{TaCp}^*(\text{CH}_2\text{Ph})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) (2a): A solution of $[\text{TaCp}^*(\text{CH}_2\text{Ph})_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1a) (0.50 g, 0.49 mmol) in toluene (5 mL) was treated with CNAr (0.065 g, 0.50 mmol), and the mixture was stirred for 1 h at room temperature. All volatile components were removed under vacuum, and the remaining solid was washed with hexane (2×10 mL) to give **2a** as a white solid (0.49 g, 87%). $\text{C}_{51}\text{H}_{38}\text{BF}_{15}\text{NOTa}$ (1157.59): calcd. C 52.91, H 3.31, N 1.21; found C 52.67, H 3.21, N 1.09. ^1H NMR: δ = 1.34 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 1.41 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 1.93 (s, 15 H, C_5Me_5), 2.78 (d, $^2J_{\text{H,H}} = 12.5$ Hz, 1 H, $\text{Ta-CH}_2\text{Ph}$), 2.93 (d, $^2J_{\text{H,H}} = 12.5$ Hz, 1 H, $\text{Ta-CH}_2\text{Ph}$), 4.46 (d, $^2J_{\text{H,H}} = 17.4$ Hz, 1 H, $\text{C-CH}_2\text{Ph}$), 4.56 (d, $^2J_{\text{H,H}} = 17.4$ Hz, 1 H, $\text{C-CH}_2\text{Ph}$), 6.47–7.03 (m, 13 H, C_6H_5 and C_6H_5) ppm. ^{13}C NMR (^1H): δ = 11.1 (C_5Me_5), 17.6 ($\text{Me}_2\text{C}_6\text{H}_3$), 18.8 ($\text{Me}_2\text{C}_6\text{H}_3$), 42.2 ($\text{C-CH}_2\text{Ph}$), 54.8 ($\text{Ta-CH}_2\text{Ph}$), 120.1 (C_5Me_5), 123.5–149.2 (C_6H_5 , $\text{Me}_2\text{C}_6\text{H}_3$ and C_6F_5), 237.7 (Ta-C=N) ppm. ^{19}F NMR: δ = -130.7 ($o\text{-C}_6\text{F}_5$), -158.3 ($p\text{-C}_6\text{F}_5$), -163.8 ($m\text{-C}_6\text{F}_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1601 (C=N) cm^{-1} .

$[\text{TaCp}^*\text{Me}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) (2b): The procedure used for **2a**, but starting from $[\text{TaCp}^*\text{Me}_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1b) (0.50 g, 0.57 mmol) and CNAr (0.079 g, 0.060 mmol), gave **2b** (0.52 g, 91%). $\text{C}_{39}\text{H}_{30}\text{BF}_{15}\text{NOTa}$ (1005.41): calcd. C 46.59, H 3.09, N 1.39; found C 46.40, H 3.00,

N 1.28. ^1H NMR: δ = 0.79 (s, 3 H, Ta-Me), 1.48 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 1.69 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 1.95 (s, 15 H, C_5Me_5), 2.72 (s, 3 H, C-Me), 7.06 (m, 2 H, $\text{Me}_2\text{C}_6\text{H}_3$), 7.13 (m, 1 H, $\text{Me}_2\text{C}_6\text{H}_3$) ppm. ^{13}C NMR (^1H): δ = 11.0 (C_5Me_5), 17.2 ($\text{Me}_2\text{C}_6\text{H}_3$), 18.6 ($\text{Me}_2\text{C}_6\text{H}_3$), 20.0 (Ta-Me), 31.6 (C-Me), 118.7 (C_5Me_5), 127.6–148.8 ($\text{Me}_2\text{C}_6\text{H}_3$ and C_6F_5), 238.3 (Ta-C=N) ppm. ^{19}F NMR: δ = -131.7 ($o\text{-C}_6\text{F}_5$), -158.4 ($p\text{-C}_6\text{F}_5$), -163.8 ($m\text{-C}_6\text{F}_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1629 (C=N) cm^{-1} .

$[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{NAr}\}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) (2c): The procedure used for **2a**, but starting from $[\text{TaCp}^*\text{Cl}(\text{CH}_2\text{Ph})\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1c) (0.50 g, 0.52 mmol) and CNAr (0.072 g, 0.55 mmol), gave **2c** (0.51 g, 89%). $\text{C}_{44}\text{H}_{31}\text{BClF}_{15}\text{NOTa}$ (1101.91): calcd. C 47.96, H 2.84, N 1.27; found C 47.00, H 2.75, N 1.24. ^1H NMR: δ = 1.55 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 1.64 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 2.09 (s, 15 H, C_5Me_5), 4.59 (d, $^2J_{\text{H,H}} = 18.5$ Hz, 1 H, $\text{C-CH}_2\text{Ph}$), 4.72 (d, $^2J_{\text{H,H}} = 18.5$ Hz, 1 H, $\text{C-CH}_2\text{Ph}$), 6.76–7.06 (m, 8 H, C_6H_5 and C_6H_5) ppm. ^{13}C NMR (^1H): δ = 11.4 (C_5Me_5), 17.8 ($\text{Me}_2\text{C}_6\text{H}_3$), 21.4 ($\text{Me}_2\text{C}_6\text{H}_3$), 43.3 ($\text{C-CH}_2\text{Ph}$), 123.2 (C_5Me_5), 125.3–149.2 (C_6H_5 , $\text{Me}_2\text{C}_6\text{H}_3$ and C_6F_5), 236.7 (Ta-C=N) ppm. ^{19}F NMR: δ = -130.6 ($o\text{-C}_6\text{F}_5$), -157.9 ($p\text{-C}_6\text{F}_5$), -163.4 ($m\text{-C}_6\text{F}_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1644 (C=N) cm^{-1} .

$[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) (2d): A solution of $[\text{TaCp}^*\text{Cl}\{\eta^2\text{-C}(\text{Me})=\text{NAr}\}(\text{O})]$ (0.25 g, 0.49 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.28 g, 0.51 mmol) in toluene (5 mL) was stirred at room temperature for 1 h. Later, the solution was filtered, layered with hexane (5 mL) and cooled to -10 °C, obtaining **2d** as yellow crystals (0.40 g, 74%). $\text{C}_{38}\text{H}_{27}\text{BClF}_{15}\text{NOTa}(\text{C}_7\text{H}_8)_2$ (1210.09): calcd. C 51.61, H 3.58, N 1.16; found C 51.01, H 3.22, N 1.19. ^1H NMR: δ = 1.62 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 1.91 (s, 3 H, $\text{Me}_2\text{C}_6\text{H}_3$), 2.18 (s, 15 H, C_5Me_5), 2.94 (s, 3 H, C-Me), 7.13 (m, 2 H, $\text{Me}_2\text{C}_6\text{H}_3$), 7.20 (m, 1 H, $\text{Me}_2\text{C}_6\text{H}_3$) ppm. ^{13}C NMR (^1H): δ = 11.5 (C_5Me_5), 17.6 ($\text{Me}_2\text{C}_6\text{H}_3$), 19.2 (C-Me), 21.1 ($\text{Me}_2\text{C}_6\text{H}_3$), 113.3 (C_5Me_5), 128.7–149.4 ($\text{Me}_2\text{C}_6\text{H}_3$ and C_6F_5), 240.1 (Ta-C=N) ppm. ^{19}F NMR: δ = -131.5 ($o\text{-C}_6\text{F}_5$), -158.4 ($p\text{-C}_6\text{F}_5$), -164.0 ($m\text{-C}_6\text{F}_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1638 (C=N) cm^{-1} .

$[\text{TaCp}^*(\text{CH}_2\text{Ph})\{\eta^2\text{-C}(\text{CH}_2\text{Ph})=\text{O}\}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (3a): A flask containing a solution of $[\text{TaCp}^*(\text{CH}_2\text{Ph})_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1a) (0.50 g, 0.49 mmol) in toluene (10 mL) was charged with CO, and the mixture was stirred for 24 h at room temperature. The solution was then filtered, all volatile components were removed under vacuum to leave ca. 4 mL of solution and the solution was layered with hexane (4 mL) and cooled to -10 °C to give **3a** as yellow crystals (0.39 g, 70%). $\text{C}_{43}\text{H}_{29}\text{BF}_{15}\text{O}_2\text{Ta}(\text{C}_7\text{H}_8)$ (1146.56): calcd. C 52.38, H 3.25; found C 52.43, H 3.17. ^1H NMR: δ = 1.88 (s, 15 H, C_5Me_5), 2.54 (d, $^2J_{\text{H,H}} = 12.1$ Hz, 1 H, $\text{Ta-CH}_2\text{Ph}$), 2.70 (d, $^2J_{\text{H,H}} = 12.1$ Hz, 1 H, $\text{Ta-CH}_2\text{Ph}$), 4.59 (d, $^2J_{\text{H,H}} = 19.4$ Hz, 1 H, $\text{C-CH}_2\text{Ph}$), 4.88 (d, $^2J_{\text{H,H}} = 19.4$ Hz, 1 H, $\text{C-CH}_2\text{Ph}$), 6.70–6.90 (m, 6 H, C_6H_5), 7.20–7.45 (m, 4 H, C_6H_5) ppm. ^{13}C NMR (^1H): δ = 10.8 (C_5Me_5), 49.2 ($\text{C-CH}_2\text{Ph}$), 60.0 ($\text{Ta-CH}_2\text{Ph}$), 120.0 (C_5Me_5), 123.5–148.9 (C_6H_5 and C_6F_5), 306.9 (Ta-C=O) ppm. ^{19}F NMR: δ = -133.0 ($o\text{-C}_6\text{F}_5$), -157.7 ($p\text{-C}_6\text{F}_5$), -163.4 ($m\text{-C}_6\text{F}_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1643 (C=O) cm^{-1} .

$[\text{TaCp}^*\text{Me}\{\eta^2\text{-C}(\text{Me})=\text{O}\}\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (3b): The procedure used for **3a**, but starting from $[\text{TaCp}^*\text{Me}_2\{\text{O-B}(\text{C}_6\text{F}_5)_3\}]$ (1b) (0.50 g, 0.57 mmol) and CO, gave **3b** as a white solid (0.41 g, 80%). $\text{C}_{31}\text{H}_{21}\text{BF}_{15}\text{O}_2\text{Ta}$ (902.23): calcd. C 41.27, H 2.35; found C 40.87, H 2.30. ^1H NMR: δ = 0.81 (s, 3 H, Ta-Me), 1.90 (s, 15 H, C_5Me_5), 3.23 (s, 3 H, C-Me) ppm. ^{13}C NMR (^1H): δ = 10.6 (C_5Me_5), 28.7 (Ta-Me), 37.6 (C-Me), 119.4 (C_5Me_5), 134.3–149.8 (C_6F_5), 313.8 (Ta-C=O) ppm. ^{19}F NMR: δ = -133.2 ($o\text{-C}_6\text{F}_5$), -157.7 ($p\text{-C}_6\text{F}_5$), -163.4 ($m\text{-C}_6\text{F}_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1644 (C=O) cm^{-1} .

[TaCp*Cl(η^2 -C(CH₂Ph)=O){O·B(C₆F₅)₃}] (3c): The procedure used for **3a**, but starting from [TaCp*Cl(CH₂Ph){O·B(C₆F₅)₃}] (**1c**) (0.50 g, 0.52 mmol) and CO, gave **3c** as a yellowish solid (0.40 g, 78%). C₃₆H₂₂BClF₁₅O₂Ta (998.76): calcd. C 43.29, H 2.22; found C 43.17, H 2.24. ¹H NMR: δ = 2.05 (s, 15 H, C₅Me₅), 4.41 (d, ²J_{H,H} = 19.0 Hz, 1 H, C–CH₂Ph), 4.91 (d, ²J_{H,H} = 19.0 Hz, 1 H, C–CH₂Ph), 7.05–7.40 (m, 5 H, C₆H₅) ppm. ¹³C NMR [¹H]: δ = 10.5 (C₅Me₅), 49.2 (C–CH₂Ph), 123.7 (C₅Me₅), 127.8–130.0 (C₆H₅), 135.8, 138.3, 139.2, 141.7, 146.8 and 150.1 (C₆F₅), 310.5 (Ta–C=O) ppm. ¹⁹F NMR: δ = –132.5 (*o*-C₆F₅), –156.9 (*p*-C₆F₅), –162.9 (*m*-C₆F₅) ppm. IR (KBr): $\tilde{\nu}$ = 1658 (C=O) cm^{–1}.

[TaCp*(CH₂Ph){ η^2 -C(CH₂Ph)=NAr}(O)] (Ar = 2,6-Me₂C₆H₃) (4a): A solution of [TaCp*(CH₂Ph){ η^2 -C(CH₂Ph)=NAr}{O·B(C₆F₅)₃}] (**2a**) (0.25 g, 0.22 mmol) in toluene (5 mL) was treated with pyridine (0.026 g, 0.33 mmol), and the mixture was stirred for 2 h at room temperature. All volatile components were removed under vacuum until ca. 1 mL remained, and hexane (10 mL) was added to precipitate a white solid that was washed with a hexane/toluene mixture (2 × 10 mL, 9:1) to give **4a** (0.10 g, 72%). C₃₃H₃₈NOTa (645.62): calcd. C 61.39, H 5.93, N 2.17; found C 61.00, H 5.83, N 2.21. ¹H NMR: δ = 1.25 (s, 3 H, Me₂C₆H₃), 1.72 (d, ²J_{H,H} = 11.9 Hz, 1 H, Ta–CH₂Ph), 1.80 (s, 3 H, Me₂C₆H₃), 1.99 (s, 15 H, C₅Me₅), 2.77 (d, ²J_{H,H} = 11.9 Hz, 1 H, Ta–CH₂Ph), 3.75 (d, ²J_{H,H} = 17.6 Hz, 1 H, C–CH₂Ph), 4.25 (d, ²J_{H,H} = 17.6 Hz, 1 H, C–CH₂Ph), 6.50–7.26 (m, 13 H, C₆H₃ and C₆H₅) ppm. ¹³C NMR [¹H]: δ = 10.9 (C₅Me₅), 17.2 (Me₂C₆H₃), 18.4 (Me₂C₆H₃), 39.3 (C–CH₂Ph), 48.8 (Ta–CH₂Ph), 121.1 (C₅Me₅), 126.1–149.8 (C₆H₅ and Me₂C₆H₃), 240.3 (Ta–C=N) ppm. IR (KBr): $\tilde{\nu}$ = 1631 (C=N) cm^{–1}.

Crystal Structure Determination for 2d and 3a: Selected crystals were covered with perfluoropolyether oil and mounted on a Nonius KAPPA-CCD single crystal diffractometer. The crystal structure was solved by direct methods and refined using full-matrix least-squares on *F*² (SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. Two molecules of toluene crystal-

lised with every molecule of **2d**; both solvent molecules were found in the difference Fourier map but one of them was very disordered and it was not possible to get a chemically sensible model for it, so the Squeeze procedure^[45] was used to remove its contribution to the structural factors. In **3a** some restraints on the solvent molecule were applied. Crystal data for both compounds are given in Table 1. CCDC-272817 (for **2d**) and CCDC-272818 (for **3a**) contain the supplementary 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.

Acknowledgments

We gratefully acknowledge the Ministerio de Educación y Ciencia (project MAT2004-02614) and DGUI-Comunidad de Madrid (project GR/MAT/0622/2004) (Spain) for financial support.

Table 1. Crystallographic data for compounds **2d** and **3a**.

Compound	2d	3a
Empirical formula	C ₅₂ H ₄₃ BClF ₁₅ NOTa	C ₅₀ H ₃₇ BF ₁₅ O ₂ Ta
Formula mass	1210.08	1146.56
λ [Å]	0.71069	0.71069
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>T</i> [K]	200(2)	150(2)
<i>a</i> [Å]	9.565(1)	12.739(2)
<i>b</i> [Å]	13.7547(3)	13.171(2)
<i>c</i> [Å]	19.545(3)	15.104(2)
α [°]	77.483(7)	88.20(1)
β [°]	79.50(1)	82.58(2)
γ [°]	71.389(4)	63.20(1)
<i>V</i> [Å ³]	2361.1(5)	2242.1(6)
<i>Z</i>	2	2
Calcd. density [mgm ^{–3}]	1.572	1.698
Absorption coefficient [mm ^{–1}]	2.478	2.555
θ range [°]	3.52–27.50	3.61–27.50
Reflections collected/unique reflections	13375/8067	19150/10201
<i>R</i> (int.)	0.0863	0.0228
Data/restraints/parameters	8067/3/586	10201/239/622
GOF	1.101	1.042
Final <i>R</i> indices	<i>R</i> ₁ = 0.0575	<i>R</i> ₁ = 0.0292
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> ₂ = 0.1211	<i>wR</i> ₂ = 0.0678
Largest diff. peak/hole [e Å ^{–3}]	1.596/–1.899	1.303/–1.364

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Received: July 19, 2005

Published Online: November 11, 2005