Organometallics **2006,** *25,* 2331−2336

Synthesis of the Cation Complex $[TaCp^*Me_3]^+$ and a Comparison of Its Reactivity with That of $[TaCp^*Me_4]$[†]

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

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario,
E-28871 Alcalá de Henares, Madrid, Spain

Received January 10, 2006

The new ionic compound $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) was obtained by reaction of $[TaCp^*Me_4]$ with $B(C_6F_5)_3$. Addition of pyridine to the strongly acidic cation of **1** gave the new pyridine-coordinated cation $[TaCp^*Me_3(py)]^+$ (**2**). Hydrolysis of **1** in wet dichloromethane yielded the ionic compound $[(TaCp^*Me_2)_2(\mu\text{-}O)][MeB(C_6F_5)_3]_2$ (**3**), containing a dinuclear dication identified by X-ray diffraction. Similar hydrolysis of cation **1** as well as its pyridine adduct **2** with $H_2O\cdot B(C_6F_5)_3$ afforded the neutral oxoborane compound $[TaCp^*Me_2\{O\cdot B(C_6F_5)_3\}]$ with elimination of $B(C_6F_5)_3$ and $py\cdot B(C_6F_5)_3$, respectively. Cation **1** inserted 1 equiv of PhC(O)H at room temperature to give the cationic alkoxo complex $[TaCp^*Me_2(OCHMePh)]^+$ (**4**), which reacted further with an additional 1 equiv of PhC(O)H to give a mixture of the *rac* and *meso* diastereoisomers of $[TaCp^*Me(OCHMePh)_2]^+$ (**5**), whereas only the neutral alkoxo compound $[TaCp^*Me_3(OCHMePh)]$ (**6**) was formed from the reaction of $[TaCp^*Me_4]$ with PhC(O)H upon heating. Cation **1** also reacted with 1 and 2 equiv of PhNCO to give $[TaCp^*Me_2\{OC(Me)NPh\}]^+$ (**7**) and $[TaCp^*Me\{OC(Me)NPh\}_2]^+$ (**8**) by insertion of isocyanate into one or two Ta−C bonds, respectively. However, heating $[TaCp^*Me_4]$ with PhNCO gave the dinuclear μ-oxo compound $[(TaCp^*Me_3)_2(\mu\text{-}O)]$ (**9**). Compound **1** showed rather low activity when tested as an ethylene polymerization catalyst.

Introduction

The synthesis of stable alkyl cationic complexes of the early transition metals is an objective of prime importance in organometallic chemistry, as these compounds are active in many catalytic processes. The isolation and structural characterization of these types of thermally stable compounds provide a further insight into the mechanism of the catalytic reactions and also improves their catalytic efficiency. Monocyclopentadienyl trialkyl group 4[1−10] and tetraalkyl Nb[11] and Ta[12−14] compounds are well-known, although the presence of bulky alkyl groups in the Nb and Ta compounds causes the formation of alkylidene ligands through α-hydrogen elimination.[13,15] We described previously[16] the versatile products resulting from the insertion of isocyanides into the tantalum−methyl bonds of the tantalum derivative $[TaCp^*Me_4]$,[12,14] for which related insertion reactions of carbon monoxide[12] and ketones[17] have also been reported.

The cationic derivatives from these group 4 parent compounds are not thermally stable,[18,19] due to their electron deficiency and the coordinative unsaturation of their metal centers, which can be alleviated by coordinating different ligands.[20−23] Although related cationic derivatives of group 5 metals would be expected to be more stable, these types of species has not been reported and, in addition, few examples of monocyclopentadienyl tantalum compounds suitable for ethylene polymerization have been described,[24−27] principally due to the expected lower acidity of the cationic intermediates compared with that of the corre-

---

* To whom correspondence should be addressed. Fax: 00 34 91 885 4683. E-mail: pascual.royo@uah.es.

[†] This paper is dedicated to Professor Víctor Riera on the occasion of his 70th birthday.

[‡] X-ray diffraction studies.

(1) Giannini, U.; Cesca, S. *Tetrahedron Lett.* **1960**, 19.

(2) Cannell, L. G. *J. Am. Chem. Soc.* **1972**, *94*, 6867.

(3) Chivers, T.; Ibrahim, E. D. *J. Organomet. Chem.* **1974**, *77*, 241.

(4) Green, M. L. H.; Lucas, C. R. *J. Organomet. Chem.* **1974**, *73*, 259.

(5) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.

(6) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

(7) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118.

(8) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(9) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476.

(10) Cano, A. M.; Cano, J.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Inorg. Chim. Acta* **1998**, *280*, 1.

(11) Alcalde, M. I.; de la Mata, J.; Gómez, M.; Royo, P.; Sánchez, F. *J. Organomet. Chem.* **1995**, *492*, 151.

(12) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

(13) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.

(14) Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157.

(15) de Castro, I.; de la Mata, J.; Gómez, M.; Gómez-Sal, P.; Royo, P.; Selas, J. M. *Polyhedron* **1992**, *11*, 1023.

(16) Galakhov, M. V.; Gómez, M.; Jiménez, G.; Pellinghelli, M. A.; Royo, P.; Tiripicchio, A. *Organometallics* **1994**, *13*, 1564.

(17) Fandos, R.; Hernández, C.; Otero, A.; Rodríguez, A.; Ruiz, M. J.; Terreros, P. *Dalton Trans.* **2000**, 2990.

(18) Gillis, D. J.; Tudoret, M. J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543.

(19) Wang, Q. Y.; Gillis, D. J.; Quyoum, R.; Jeremic, D.; Tudoret, M. J.; Baird, M. C. *J. Organomet. Chem.* **1997**, *527*, 7.

(20) Amor, J. I.; Cuenca, T.; Galakhov, M.; Royo, P. *J. Organomet. Chem.* **1995**, *497*, 127.

(21) Amor, J. I.; Cuenca, T.; Galakhov, M.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *J. Organomet. Chem.* **1997**, *535*, 155.

(22) Deckers, P. J. W.; van der Linden, A. J.; Meetsma, A.; Hessen, B. *Eur. J. Inorg. Chem.* **2000**, 929.

(23) Deckers, P. J. W.; Hessen, B. *Organometallics* **2002**, *21*, 5564.

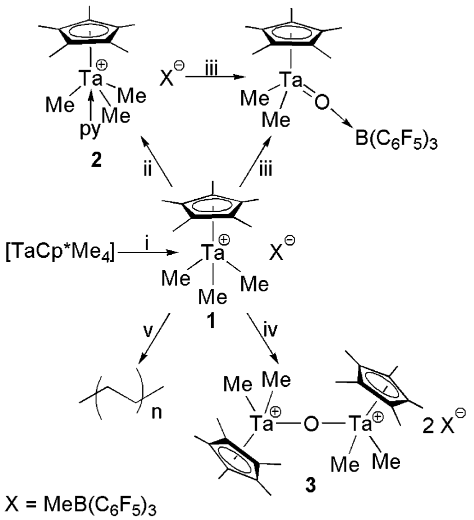
(24) Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990.

(25) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633.

(26) Antonelli, D. M.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500.

10.1021/om060027c CCC: $33.50

Scheme 1[a]



[a] Legend: (i) $B(C_6F_5)_3$; (ii) pyridine; (iii) $H_2O{\cdot}B(C_6F_5)_3$; (iv) H_2O; (v) C_2H_4.

sponding group 4 catalysts. However, the related cationic dialkyltantalocene complexes $[TaCp_2Me_2]^+$ were easily prepared by reaction of the trimethyl derivative with Ph_3CBF_4[28,29] or oxidation of neutral dialkyltantalocene with $AgBF_4$.[30] More recently it has been reported that activation of $[TaCp_2Me_3]$ with $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ gave a stable dimethyltantalocene cation, characterized by X-ray diffraction, which could not coordinate the $[MeM(C_6F_5)_3]^-$ counteranion.[31]

Herein we report the synthesis and chemical behavior of the cationic compound $[TaCp^*Me_3]^+$ obtained by reaction of the tetramethyl derivative $[TaCp^*Me_4]$ with $B(C_6F_5)_3$. We also report the comparative reactivities of both neutral and cationic complexes in the insertion reactions of C═O-containing compounds such as benzaldehyde (PhC(O)H) and phenyl isocyanate (PhNCO) and the structural characterization of the resulting alkoxo and amidate derivatives. Furthermore, we describe the catalytic activity observed when the new permethylated cationic complex was used as an ethylene polymerization catalyst.

Results and Discussion

Synthesis and Reactivity of Cationic Compounds. Addition of 1 equiv of the Lewis acid $B(C_6F_5)_3$ to a toluene solution of the peralkylated monocyclopentadienyl tantalum compound $[TaCp^*Me_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) afforded high yields of an insoluble brownish oil characterized as the ionic derivative $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**) (Scheme 1). Compound **1** was soluble in dichloromethane, its ^1H and ^{13}C NMR spectra in CD_2Cl_2 showed one resonance for the three equivalent Ta−Me groups of a pseudo-tetrahedral cation, and one broad signal for the methyl group of the borate anion was also observed in the ^1H NMR spectrum. Furthermore, the resonances in the ^{19}F NMR spectrum were in agreement with the formation of the $[MeB(C_6F_5)_3]$ anion, the difference between the *m*- and *p*-C_6F_5 values ($\Delta\delta = 2.6$) being consistent with the presence of separate cationic and anionic $[MeB(C_6F_5)_3]^-$ moieties.[32]

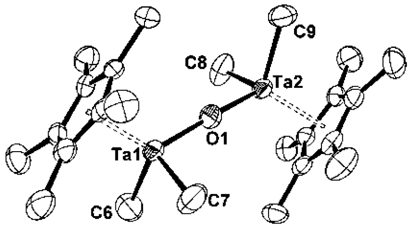


Figure 1. ORTEP diagram of the cation of $[(TaCp^*Me_2)_2(\mu\text{-}O)][MeB(C_6F_5)_3]_2$ (**3**). Hydrogen atoms have been omitted, and thermal ellipsoids are shown at the 50% level. Selected bond distances (Å) and angles (deg): Ta(1)−O = 1.914(3), Ta(2)−O = 1.910(3), Ta(1)−C(6) = 2.120(5), Ta(1)−C(7) = 2.125(5), Ta(2)−C(8) = 2.135(5), Ta(2)−C(9) = 2.118(5); Ta(1)−O−Ta(2) = 173.7(2).

Compound **1** was thermally stable under an inert atmosphere for long periods even in halogenated solvents. We believe that the remarkable thermal stability of its CH_2Cl_2 solution is due to the reduced Lewis acidity of the metal center imposed by the strongly donating pentamethylcyclopentadienyl ligand and the inductive effect of the three tantalum-bonded methyl groups, as was confirmed by the X-ray structure of one of the ionic complexes obtained in this work (vide infra). Nevertheless, compound **1** was still a strong Lewis acid that reacted with pyridine to give the cationic adduct $[TaCp^*Me_3(py)][MeB(C_6F_5)_3]$ (**2**) (Scheme 1), with no evidence of methyl or C_6F_5 transfer from the $[MeB(C_6F_5)_3]^-$ anion, as usually observed for compounds in which bonding interactions between such anion and cation pairs are present. The ^1H and ^{13}C NMR spectra of compound **2** showed one narrow signal due to the three equivalent Ta−Me groups and the signals expected for a symmetric pyridine ligand. This behavior is consistent with a triangular-bipyramidal geometry, with the pyridine ligand located in an axial position trans to the Cp* ligand and the three methyl groups occupying the equatorial coordination sites. The ^{19}F NMR spectrum of **2** showed resonances very similar to those described for **1** and for the remaining ionic complexes described in this paper that will not be discussed further.

The cation of compound **1** was very air sensitive and highly unstable in the presence of traces of water. Hence, in our attempt to crystallize compound **1** from CH_2Cl_2 solutions, yellow crystals suitable for X-ray diffraction studies of the dinuclear complex $[(TaCp^*Me_2)_2(\mu\text{-}O)][MeB(C_6F_5)_3]_2$ (**3**) were obtained, as a consequence of hydrolysis of one Ta−Me bond and formation of an oxo bridge. However, we were unable to isolate pure complex **3** by hydrolysis reactions of **1** to allow spectroscopic characterization. The molecular structure of cation **3** (Figure 1) presents a distorted-tetrahedral environment about the Ta atom with an almost linear Ta−O−Ta bridge (173.7(2)°), indicating the high contribution of the dπ−pπ interaction to the Ta−O bond. This feature is similar to that found in the related neutral μ-oxo compound $[(TaCp^*Me_3)_2(\mu\text{-}O)]$, which presents an exactly linear Ta−O−Ta bridge (180°).[33] Both Ta−O bond distances (1.910(3) and 1.914(3) Å) are in the middle of the range of Ta−O bond values of complexes containing Ta−O−Ta bridges (1.82−2.10 Å) and are very close to those found in the neutral μ-oxo compound $[(TaCp^*Me_3)_2(\mu\text{-}O)]$ (1.909(7) Å).[33] This Ta−O bond in compound **3** is surprisingly longer than expected, due to the higher electrophilicity of the 14-electron Ta atom, with respect to the 16-electron Ta atom in the neutral complex $[(TaCp^*Me_3)_2(\mu\text{-}O)]$, assuming

---

[27] Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4417.

[28] Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577.

[29] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[30] Lappert, M. F.; Milne, C. R. C. *J. Chem. Soc., Chem. Commun.* **1978**, 925.

[31] Feng, S. G.; Roof, G. R.; Chen, E. Y. X. *Organometallics* **2002**, *21*, 832.

[32] Horton, A. D.; de With, J.; van der Linden, A. J.; van der Weg, H. *Organometallics* **1996**, *15*, 2672.

[33] Jernakoff, P.; de Bellefon, C. D.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362.

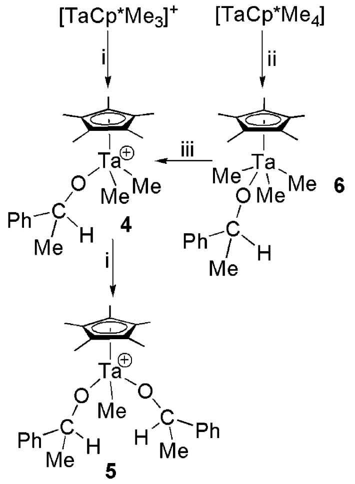
that the bridging oxygen atom is a 3-electron donor for each metal center. On the other hand, the Ta−Me bond distances were mainly affected in compound **3** in comparison with [(TaCp*Me$_3$)$_2$(μ-O)], decreasing from the range 2.223−2.259 Å to the range 2.118−2.135 Å, indicating the higher inductive donor capacity of the methyl groups. This increased inductive effect of the methyl groups together with the π-bonding donation observed for the μ-oxo bridging system compensates the electron deficiency of the metal center enough to stabilize the dinuclear dication, keeping the free methylborate anion without any interionic pairing. Therefore, the free cationic species is stable and can be isolated not only when three methyl groups are coordinated to the metal, as in the cation of compound **1**, but also when one methyl group is substituted by the less donating μ-oxo ligand, leaving only two additional methyl groups.

In the view of this result, we tried to hydrolyze compound **1** with the oxo transfer reagent $H_2O{\cdot}B(C_6F_5)_3$. Hence, the reaction of **1** with 0.5 mol of the water adduct in CD_2Cl_2 was monitored by ^{1}H NMR spectroscopy; the only reaction products observed were the neutral oxo−borane derivative [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}][34] and the free borane compound $B(C_6F_5)_3$, together with the starting compound **1** (Scheme 1). This process is consistent with the protonolysis of two Ta−Me bonds on the same metal center to form the undetectable, electron-deficient, and coordinatively unsaturated cation [TaCp*Me{O·B(C$_6$F$_5$)$_3$}]$^+$, which is immediately stabilized by transfer of the methyl group from the [MeB(C$_6$F$_5$)$_3$]$^-$ anion, making evident that the Lewis acidity of the intermediate (oxoborane)methyltantalum cation is stronger than that known for the borane $B(C_6F_5)_3$. This proposal is supported by the lack of reactivity of [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}] toward the Lewis acid $B(C_6F_5)_3$. The same behavior was observed when the pyridine cationic adduct **2** was treated with the water adduct $H_2O{\cdot}B(C_6F_5)_3$, this process also being consistent with the transfer of the methyl group from the [MeB(C$_6$F$_5$)$_3$]$^-$ anion to the intermediate undetected (oxoborane)methyl cation to give the neutral compound [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}] and the pyridine adduct py·B(C$_6$F$_5$)$_3$.

Insertion Reactions of Benzaldehyde and Phenyl Isocyanate. We have discussed above that the more electrophilic metal center of cationic compounds is responsible for the increased inductive effect of the remaining methyl groups, for which shorter Ta−Me bond distances are observed. It should be expected that insertion reactions would be favored by a higher positive charge at the Ta atom that would increase the electrophilic character of the atom at the coordinated ligand, which is attacked by the migrating alkyl group. However, it could be also expected that migration should be hindered for the more stable metal−alkyl bonds. To find the right answer to this matter, we decided to develop a comparative study of insertion reactions of benzaldehyde and phenyl isocyanate into the Ta−Me bonds of the 12-electron cationic trimethyl compound **1** [TaCp*Me$_3$]$^+$ and the 14-electron neutral tetramethyl complex [TaCp*Me$_4$].

Complex **1** reacted with benzaldehyde (PhC(O)H) to form the alkoxo compound [TaCp*Me$_2$(OCHMePh)][MeB(C$_6$F$_5$)$_3$] (**4**) at room temperature in 1 h (Scheme 2), after a process that involved coordination of the oxygen atom to the metal center and further migration of one methyl group to the sp^2 C atom. The main spectroscopic ^{1}H NMR data that confirmed the formation of **4** were the doublet at δ 1.90 and the quartet at δ 5.86 for the methyl group and the hydrogen atom of the alkoxo OCHMePh fragment, respectively. Moreover, the ^{13}C NMR spectrum showed one resonance at δ 89.2 for the alkoxo carbon atom. The chirality at the carbon atom of this OCHMePh ligand is consistent with the presence of two resonances for the diastereotopic Ta−Me groups in both ^{1}H and ^{13}C NMR spectra.

Scheme 2[a]



[a] Legend: (i) PhC(O)H, 20 °C; (ii) PhC(O)H, 70 °C; (iii) $B(C_6F_5)_3$.

The same reactivity was observed for compound **4** in the presence of a second equivalent of PhC(O)H, which after 6 h at room temperature gave a mixture in an approximately 3:2.5 molar ratio of the *rac* and *meso* diastereoisomers of the complex [TaCp*Me(OCHMePh)$_2$][MeB(C$_6$F$_5$)$_3$] (**5**) (Scheme 2). This is as expected for the presence of two stereogenic carbon atoms, one for each OCHMePh ligand. This mixture could not be separated, although the small difference in the proportion of the two components helped us to distinguish some ^{1}H and ^{13}C NMR resonances for each diastereoisomer. Hence, the C_s symmetry of each molecule of the *meso* diastereoisomer (*SR*/*RS*, **5a**) gave rise to one doublet for the methyl group (^{1}H NMR) and only one resonance for the carbon atom (^{13}C NMR) of the alkoxo group. In contrast, the lack of any symmetry of the *rac* diastereoisomer (*RR*/*SS*, **5b**) was reflected by the presence of two doublets for the methyl group in the ^{1}H NMR and of two resonances for the carbon atoms of the OCHMePh groups in the ^{13}C NMR.

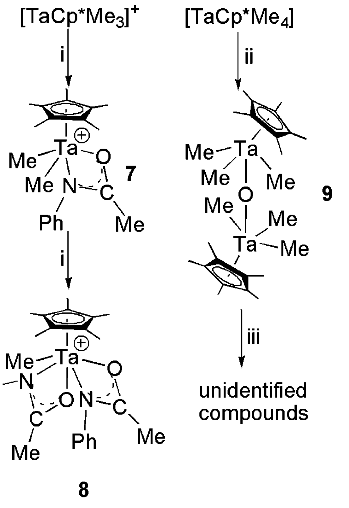
Comparatively much less reactive was the neutral compound [TaCp*Me$_4$], which reacted with 1 equiv of benzaldehyde upon heating at 70 °C for 24 h, leading to [TaCp*Me$_3$(OCHMePh)] (**6**) (Scheme 2). No further insertion of a second molecule of PhC(O)H was observed, and heating **6** over 100 °C caused decomposition. Compound **6** was also a precursor for the cationic complex **4** upon addition of 1 equiv of the Lewis acid $B(C_6F_5)_3$. It seems clear that the higher electron density at the tantalum atom of [TaCp*Me$_4$] hindered the insertion reaction, and once the 16-electron alkoxo compound **6** was formed (considering a 3-electron-donor oxygen atom) the electronic and steric saturation at the metal center blocked the possible insertion of PhC(O)H. The ^{1}H and ^{13}C NMR spectra of **6** showed signals corresponding to the formation of the new alkoxo OCHMePh ligand, as was the case for **4** and **5** (vide supra).

Similar studies were carried out for insertion reactions of PhN=C=O. Reaction of the cationic complex **1** with 1 equiv of phenyl isocyanate at room temperature gave the dimethyl amidate complex [TaCp*Me$_2${η^2-OC(Me)NPh}][MeB(C$_6$F$_5$)$_3$] (**7**) (Scheme 3), as a result of the insertion of the C=O group into one Ta−Me bond. This reaction was not selective but was followed by a second insertion into another Ta−Me bond, affording the monomethyl derivative [TaCp*Me{η^2-OC(Me)-

---

[34] Sánchez-Nieves, J.; Frutos, L. M.; Royo, P.; Castaño, O.; Herdtweck, E. *Organometallics* **2005**, *24*, 2004.

Scheme 3[a]



[a] Legend: (i) PhNCO, 20 °C; (ii) PhNCO, 90 °C; (iii) $B(C_6F_5)_3$.

$NPh\}_2][MeB(C_6F_5)_3]$ (**8**) (Scheme 3), leaving part of the unreacted starting complex **1**. However, the 16-electron compound **8** was isolated as the unique reaction product when **1** was treated with 2 equiv of isocyanate for 3 h in dichloromethane. The most significant NMR feature for compounds **7** and **8** was the resonance in the ^{13}C NMR spectrum at about δ 185 corresponding to the C−O carbon atom and the high-field shift (δ 18.6 for **7** and δ 20.2 for **8**) of the migrated C-bonded methyl group, which is observed in the ^1H NMR spectrum as a singlet shifted to low field (δ 2.23 for **7** and δ 1.98 for **8**), in comparison with that observed for the starting complex **1**. The acidity of the metal center and the length of the Ta−O−C−N chain should favor a chelate disposition of the amidate ligand, as previously observed for early-transition-metal complexes with this type of ligand.[35]

Surprisingly, a similar reaction of the tetramethyl complex $[TaCp^*Me_4]$ with 1 equiv of PhNCO did not give the expected insertion product; instead, the dinuclear oxo-bridged complex $[(TaCp^*Me_3)_2(\mu\text{-}O)]$ (**9**) was isolated in moderate yield upon heating in toluene at 90 °C (Scheme 3). Compound **9** was the only tantalum-containing product of the reaction, even in the presence of excess PhNCO. When the experiment was carried out into a sealed NMR tube and the reaction was monitored by ^1H NMR spectroscopy, broadening of signals corresponding to the phenyl ring was observed and the resonances belonging to the starting PhNCO disappeared. Unfortunately we could not identify the organic byproduct. It is important to note that this process required the addition of an equimolecular amount of PhNCO to complete the reaction, because in the presence of a smaller amount of PhNCO the corresponding remnant of starting $[TaCp^*Me_4]$ was recovered. Unexpectedly, complex **9** could not be used as a precursor to isolate the dicationic dinuclear compound **3** by reaction with 2 equiv of $B(C_6F_5)_3$, which only led to an unidentified mixture of reaction products.

Ethylene Polymerization. The ionic compound **1** generated in situ was studied as an ethylene polymerization catalyst. It exhibited rather poor activity (1.6 g of PE (mmol of Ta)$^{-1}$ h^{-1} atm^{-1} at 50 °C and 5 atm over 1 h), yielding HDPE ($T_m = 135$ °C) with a molecular mass of ca. 45×10^3 g mol^{-1} and a narrow polydispersity ($M_w/M_n = 2.5$). Lower catalytic activity was observed when lower temperature and ethylene pressure were used. This behavior is not surprising, in comparison with that reported for related monocyclopentadienyl group 4 compounds, taking into account the lower acidity of the 12-electron cationic tantalum complex $[TaCp^*Me_3]^+$ in relation to the 10-electron group 4 metal species $[MCpR_2]^+$. The activity of complex **1** is clearly lower than that reported for other nonmetallocene tantalum compounds such as $[TaCl_3(\text{aminopyridinato})_2]$ (1000 g of PE (mmol of Ta)$^{-1}$ h^{-1} atm^{-1}; MAO, 60 °C, 1 atm),[36] $[TaCp^*Cl_3\{MeC(N\textit{i}Pr)_2\}]$ (470 g of PE (mmol of Ta)$^{-1}$ h^{-1} atm^{-1}; MAO, 60 °C, 8 atm),[27] and $[TaCp^*Cl_2(NSi\textit{t}Bu_3)]$ (60 g of PE (mmol of Ta)$^{-1}$ h^{-1} atm^{-1}; MAO, 25 °C, 5 atm)[26] but close to that reported for $[TaCp^*X_2(\eta^4\text{-diene})]$ (X = Cl, Me; 1−7 g of PE (mmol of Ta)$^{-1}$ h^{-1} atm^{-1}; MAO, −60 to −20 °C, 1 atm),[24,25] although in this case the polydispersity was ca. 1.0. On the other hand, the alkyl derivatives $[TaCp^*Me_3\{MeC(N\textit{i}Pr)_2\}]$[27] and $[TaCp^*(CH_2Ph)_2(N\textit{t}Bu)]$[37] showed no activity; meanwhile, the allyl compound $[TaCp^*(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)(NAr)]$ (Ar = 2,6-$\textit{i}Pr_2C_6H_3$) was scarcely active for ethylene polymerization (38 g of PE (mmol of Ta)$^{-1}$ h^{-1} atm^{-1}; $[Ph_3C][B(C_6F_5)_4]$; 25 °C, 1 atm).[26]

Conclusions

Methyl abstraction from $[TaCp^*Me_4]$ with the strong Lewis acid $B(C_6F_5)_3$ gave the thermally stable ionic compound $[TaCp^*Me_3][MeB(C_6F_5)_3]$, which remained unchanged in CH_2Cl_2. The 12-electron cation $[TaCp^*Me_3]^+$ was more reactive than its 14-electron neutral precursor $[TaCp^*Me_4]$. It was shown to be a strong Lewis acid that coordinated pyridine to give the 14-electron cation $[TaCp^*Me_3(py)]^+$ and was extremely unstable in the presence of traces of water to give the dinuclear cation $[(TaCp^*Me_2)_2(\mu\text{-}O)]^{2+}$. However, hydrolysis of $[TaCp^*Me_3]^+$ and $[TaCp^*Me_3(py)]^+$ with the oxo transfer reagent $H_2O\cdot B(C_6F_5)_3$ afforded the neutral compound $[TaCp^*Me_2\{O\cdot B(C_6F_5)_3\}]$ by methyl transfer from the borate anion to the unstable cationic intermediate, which was a stronger Lewis acid. The tantalum atom of the cationic complex $[TaCp^*Me_3]^+$ was highly electrophilic, and insertion at room temperature of 1 and 2 equiv of the C=O-containing compounds PhC(O)H and PhNCO into one and two Ta−Me bonds was observed, giving the alkoxo and amidate cations $[TaCp^*Me_2(OCHMePh)]^+$ and $[TaCp^*Me_2\{\eta^2\text{-}OC(Me)NPh\}]^+$ in a first step and the dialkoxo and diamidate cations $[TaCp^*Me(OCHMePh)_2]^+$ and $[TaCp^*Me\{\eta^2\text{-}OC(Me)NPh\}_2]^+$ after the second insertion, respectively. In contrast, only one molecule of PhC(O)H and PhNCO was inserted into one Ta−Me bond upon heating of the less electrophilic compound $[TaCp^*Me_4]$, forming the corresponding alkoxo derivative $[TaCp^*Me_3(OCHMePh)]$ and the dinuclear compound $[(TaCp^*Me_3)_2(\mu\text{-}O)]$, respectively.

All of the ionic complexes reported in this paper showed $\delta(F_{meta}) - \delta(F_{para})$ differences in the ^{19}F NMR spectra lower than 2.8 ppm, demonstrating the presence of separated ion pairs.[32] Furthermore, this difference was almost the same for all of the complexes, whatever the electron density at the metal center, which changed from 12 electrons in cation **1** to 14 electrons in **2** and **4** (considering the alkoxo group as a 3-electron-donor ligand) and in **7** and to 16 electrons in **5** and **8**. Also, cation **8**, with two bidentate amidate ligands, one methyl group, and one cyclopentadienyl ring, was coordinatively saturated, preventing any possible ion-pairing interaction.

---

(35) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927.

(36) Hakala, K.; Lofgren, B.; Polamo, M.; Leskela, M. *Macromol. Rapid Commun.* **1997**, *18*, 635.

(37) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Little, I. R.; Marshall, E. L.; da Costa, M. H. R.; Mastroianni, S. *J. Organomet. Chem.* **1999**, *591*, 78.

Finally, the cation complex $[TaCp^*Me_3]^+$ was active for ethylene polymerization, although it showed rather low catalytic activity.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere, and solvents were distilled from appropriate drying agents. NMR spectra were recorded at 300.13 (^{1}H), 188.31 (^{19}F), and 75.47 (^{13}C) MHz at room temperature on a Varian Unity 300. The ^{13}C NMR data for the methyl group of the $[MeB(C_6F_5)_3]$ anion was observed by gHMQC experiments. Chemical shifts (δ) are given in ppm relative to internal TMS (^{1}H and ^{13}C) or external $CFCl_3$ (^{19}F). Elemental analyses were performed on a Perkin-Elmer 240C. The compounds $[TaCp^*Me_4]$,[14] $B(C_6F_5)_3$,[38] and $[H_2O{\cdot}B(C_6F_5)_3]$[39] were prepared by literature methods. PhC(O)H and PhNCO were distilled from CaH_2 and P_2O_5, respectively, under vacuum and stored under argon.

$[TaCp^*Me_3][MeB(C_6F_5)_3]$ (1). $[TaCp^*Me_4]$ (0.100 g, 0.26 mmol) and $B(C_6F_5)_3$ (0.150 g, 0.29 mmol) were stirred in toluene (5 mL) for 5 min. The solution was then filtered off, leaving an oil that was washed with hexane (5 mL), to give **1** as a brownish oil (0.20 g, 85%). Data for **1**: ^{1}H NMR (CD_2Cl_2) 0.47 (bs, 3 H, *Me*−B), 1.36 (s, 9 H, *Me*−Ta), 2.26 (s, 15 H, C_5*Me*$_5$); ^{13}C NMR (CD_2Cl_2) 10.4 (*Me*$B(C_6F_5)_3$), 12.2 (C_5*Me*$_5$), 86.8 (*Me*−Ta), 125.3 (*C*$_5$Me$_5$), 136.4 (m, *C*$_6$F$_5$), 137.9 (m, *C*$_6$F$_5$), 148.7 (m, *C*$_6$F$_5$); ^{19}F NMR (CD_2Cl_2) −130.0 (*o*-C_6F_5), −162.1 (*p*-C_6F_5), −164.7 (*m*-C_6F_5). Anal. Calcd for $C_{32}H_{27}BF_{15}Ta$ (888.29): C, 43.27; H, 3.06. Found: C, 43.63; H, 3.14.

$[TaCp^*Me_3(py)][MeB(C_6F_5)_3]$ (2). Pyridine (0.021 g, 0.26 mmol) was added to a suspension of $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**; 0.26 mmol) in toluene (5 mL), prepared in situ. After the mixture was stirred for 10 min, the solution was filtered off and the remaining oil was washed with hexane (5 mL) to give **2** (0.21 g, 83%). Data for **2**: ^{1}H NMR (CD_2Cl_2) 0.47 (s, 3 H, *Me*−B), 0.50 (s, 9 H, *Me*−Ta), 2.26 (s, 15 H, C_5*Me*$_5$), 7.52 (m, 2 H, *m*-C_5*H*$_5$N), 7.91 (m, 1 H, *p*-C_5*H*$_5$N), 8.77 (m, 2 H, *o*-C_5*H*$_5$N); ^{13}C NMR (CD_2Cl_2) 10.7 (*Me*$B(C_6F_5)_3$), 11.7 (C_5*Me*$_5$), 76.5 (*Me*−Ta), 121.5 (*C*$_5$Me$_5$), 125.8 (*p*-*C*$_5$H$_5$N), 135.7 (m, *C*$_6$F$_5$), 139.0 (m, *C*$_6$F$_5$), 139.3 (*m*-*C*$_5$H$_5$N), 148.2 (m, *C*$_6$F$_5$), 149.4 (*o*-*C*$_5$H$_5$N); ^{19}F NMR (CD_2Cl_2) −130.0 (*o*-C_6F_5), −162.1 (*p*-C_6F_5), −164.7 (*m*-C_6F_5). Anal. Calcd for $C_{37}H_{32}BF_{15}NTa$ (967.39): C, 45.94; H, 3.33; N, 1.45. Found: C, 45.38; H, 3.10; N, 1.29.

Reaction of $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (1) with $H_2O{\cdot}B(C_6F_5)_3$. A Teflon-valved NMR tube was charged with a solution of **1** (0.018 g, 0.020 mmol) and $H_2O{\cdot}B(C_6F_5)_3$ (0.005 g, 0.010 mmol) in CD_2Cl_2. After 3 h, the ^{1}H NMR spectrum revealed that the reactants had been transformed into $[TaCp^*Me_2\{O{\cdot}B(C_6F_5)_3\}]$[34] and $B(C_6F_5)_3$, with minor amounts of other unidentified products.

$[TaCp^*Me_2(OCHMePh)][MeB(C_6F_5)_3]$ (4). PhC(O)H (0.028 g, 0.26 mmol) was added to a solution of $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**; 0.26 mmol) in CH_2Cl_2 (5 mL), prepared in situ. After the mixture was stirred for 1 h, the volatiles were removed under vacuum and the remaining oil was washed first with toluene (5 mL) and then with hexane (5 mL) to give **4** (0.23 g, 87%). Data for **4**: ^{1}H NMR (CD_2Cl_2) 0.47 (bs, 3 H, *Me*−B), 0.93 (s, 3 H, *Me*−Ta), 1.02 (s, 3 H, *Me*−Ta), 1.90 (d, 3 H, ^3J(H−H) = 6.5 Hz, *Me*−C−O), 2.09 (s, 15 H, C_5*Me*$_5$), 5.87 (q, 1 H, ^3J(H−H) = 6.5 Hz, *H*−C−O), 7.38 (m, 2 H, *m*-C_6*H*$_5$), 7.46 (m, 3 H, *p*-C_6*H*$_5$ and *o*-C_6*H*$_5$); ^{13}C NMR (CD_2Cl_2) 10.5 (*Me*$B(C_6F_5)_3$), 11.2 (C_5*Me*$_5$), 24.7 (*Me*−C−O), 67.1 (*Me*−Ta), 67.2 (*Me*−Ta), 89.2 (*C*−O), 125.3, 126.1, 129.8, 130.3 (*C*$_6$H$_5$ and *C*$_5$Me$_5$), 135.7 (m, *C*$_6$F$_5$), 139.0 (m, *C*$_6$F$_5$), 140.5 (*o*-*C*$_6$H$_5$), 148.2 (m, *C*$_6$F$_5$); ^{19}F NMR (CD_2Cl_2) −131.3 (*o*-C_6F_5), −162.0 (*p*-C_6F_5), −164.7 (*m*-C_6F_5). Anal. Calcd for $C_{39}H_{33}BF_{15}OTa$ (994.41): C, 47.10; H, 3.34. Found: C, 47.20; H, 3.48.

$[TaCp^*Me(OCHMePh)_2][MeB(C_6F_5)_3]$ (5). PhC(O)H (0.058 g, 0.54 mmol) was added to a solution of $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**; 0.26 mmol) in CH_2Cl_2 (5 mL), prepared in situ. After the mixture was stirred for 6 h, the volatiles were removed under vacuum and the remaining oil was washed first with toluene and then with hexane to give **5** (0.26 g, 89%). Data for **5**: ^{1}H NMR (CD_2Cl_2) 0.50 (bs, 6 H, *Me*−B, **5a** and **5b**), 1.07 (s, 3 H, *Me*−Ta, **5a**), 1.17 (s, 3 H, *Me*−Ta, **5b**), 1.56 (d, 3 H, ^3J(H−H) = 6.5 Hz, *Me*−C−O, **5b**), 1.67 (d, 3 H, ^3J(H−H) = 6.5 Hz, *Me*−C−O, **5b**), 1.72 (d, 6 H, ^3J(H−H) = 6.5 Hz, *Me*−C−O, **5a**), 2.02 (s, 15 H, C_5*Me*$_5$, **5a**), 2.05 (s, 15 H, C_5*Me*$_5$, **5b**), 5.60−5.79 (m, 4 H, *H*-C−O), 7.15−7.50 (m, 10 H, C_6*H*$_5$); ^{13}C NMR (CD_2Cl_2) 10.6 (*Me*$B(C_6F_5)_3$), 10.9 (C_5*Me*$_5$), 24.6 (*Me*−C−O, **5b**), 25.0 (*Me*−C−O, **5b**), 25.1 (*Me*−C−O, **5a**), 43.1 (*Me*−Ta), 43.7 (*Me*−Ta), 87.2 (*C*−O), 87.3 (*C*−O), 87.4 (*C*−O), 124.6, 124.7, 126.0, 129.5, 129.6, 129.7, 129.8, 141.1, 141.2 (*C*$_6$H$_5$ and *C*$_5$Me$_5$), 136.8 (m, *C*$_6$F$_5$), 137.9 (m, *C*$_6$F$_5$), 148.2 (m, *C*$_6$F$_5$); ^{19}F NMR (CD_2Cl_2) −131.3 (*o*-C_6F_5), −162.0 (*p*-C_6F_5), −164.7 (*m*-C_6F_5). Anal. Calcd for $C_{46}H_{39}BF_{15}O_2Ta$ (1100.54): C, 50.20; H, 3.57. Found: C, 49.95; H, 3.48.

$[TaCp^*Me_3(OCHMePh)]$ (6). A solution of $[TaCp^*Me_4]$ (0.300 g, 0.78 mmol) and PhC(O)H (0.120 g, 1.20 mmol) in toluene (5 mL) was heated at 70 °C for 24 h. Afterward, the volatiles were removed under vacuum and hexane was added (15 mL). The solution was filtered and the filtrate was concentrated to a volume of ca. 4 mL and cooled to −40 °C, yielding **6** as yellow crystals (0.25 g, 65%). Data for **6**: ^{1}H NMR ($CDCl_3$) 0.06 (s, 6 H, *Me*−Ta), 0.17 (s, 3 H, *Me*−Ta), 1.55 (d, 3 H, ^3J(H−H) = 6.4 Hz, *Me*−C−O), 1.86 (s, 15 H, C_5*Me*$_5$), 5.40 (q, 1 H, ^3J(H−H) = 6.4 Hz, *H*-C−O), 7.30 (m, 5 H, C_6*H*$_5$); ^{13}C NMR ($CDCl_3$) 11.0 (C_5*Me*$_5$), 25.4 (*Me*−C−O), 50.5 (*Me*−Ta), 50.8 (*Me*−Ta), 53.2 (*Me*−Ta), 81.4 (*C*−O), 115.9 (*C*$_5$Me$_5$), 125.9, 127.1, 128.1, and 145.3 (*C*$_6$H$_5$). Anal. Calcd for $C_{21}H_{33}OTa$ (482.43): C, 52.28; H, 6.89. Found: C, 52.10; H, 6.70.

$[TaCp^*Me_2\{OC(Me)NPh\}][MeB(C_6F_5)_3]$ (7). PhNCO (0.040 mmol) was added to a solution of $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**; 0.040 mmol) in CD_2Cl_2, prepared in situ. The reaction was monitored by NMR until it was finished after 30 min, showing the remaining unreacted **1** and the formation of **7** and **8**. Data for **7**: ^{1}H NMR (CD_2Cl_2) 0.47 (bs, 3 H, *Me*−B), 0.95 (s, 6 H, *Me*−Ta), 2.18 (s, 15 H, C_5*Me*$_5$), 2.23 (s, 3 H, *Me*−C−O), 7.24−7.60 (C_6*H*$_5$, underneath with those corresponding with compound **8**); ^{13}C NMR (CD_2Cl_2) 10.5 (*Me*$B(C_6F_5)_3$), 11.0 (C_5*Me*$_5$), 18.6 (*Me*−C−O), 77.1 (*Me*−Ta), 124.9, 125.4, 128.5, 130.5 and 139.3 (*C*$_6$H$_5$ and *C*$_5$Me$_5$), 135.7 (m, *C*$_6$F$_5$), 138.9 (m, *C*$_6$F$_5$), 148.5 (m, *C*$_6$F$_5$), 187.7 (*C*−O); ^{19}F NMR (CD_2Cl_2) −130.5 (*o*-C_6F_5), −162.5 (*p*-C_6F_5), −165.1 (*m*-C_6F_5).

$[TaCp^*Me\{OC(Me)NPh\}_2][MeB(C_6F_5)_3]$ (8). PhNCO (0.056 g, 0.56 mmol) was added to a solution of $[TaCp^*Me_3][MeB(C_6F_5)_3]$ (**1**; 0.26 mmol) in CH_2Cl_2 (5 mL), prepared in situ. After the mixture was stirred for 3 h, the volatiles were removed under vacuum and the remaining oil was washed first with toluene and then with hexane to give **8** (0.27 g, 89%). Data for **8**: ^{1}H NMR (CD_2Cl_2) 0.47 (bs, 3 H, *Me*−B), 1.05 (s, 3 H, *Me*−Ta), 1.98 (s, 6 H, *Me*−C−O), 2.27 (s, 15 H, C_5*Me*$_5$), 6.66 (bs, 2 H, C_6*H*$_5$), 7.34 (m, 8 H, C_6*H*$_5$); ^{13}C NMR (CD_2Cl_2) 10.5 (*Me*$B(C_6F_5)_3$), 11.1 (C_5*Me*$_5$), 20.2 (*Me*−C−O), 67.3 (*Me*−Ta), 124.7 (*C*$_5$Me$_5$), 127.3, 128.3, 130.1, and 139.9 (*C*$_6$H$_5$), 135.5, 139.9, and 148.7 (m, *C*$_6$F$_5$), 184.5 (*C*−O); ^{19}F NMR (CD_2Cl_2) −130.4 (*o*-C_6F_5), −162.5 (*p*-C_6F_5), −165.1 (*m*-C_6F_5). Anal. Calcd for $C_{46}H_{37}BF_{15}N_2O_2Ta$ (1126.53): C, 49.04; H, 3.31; N, 2.49. Found: C, 49.35; H, 3.48; N, 2.27.

$[(TaCp^*Me_3)_2(\mu\text{-}O)]$ (9). A solution of $[TaCp^*Me_4]$ (0.300 g, 0.78 mmol) and PhNCO (0.095 g, 0.78 mmol) in toluene (5 mL) was heated at 90 °C for 24 h. Afterward, the volatiles were removed under vacuum and hexane was added (10 mL). The solution was filtered off, leaving a pale orange solid that was identified as **9**[33] (0.24 g, 80%). Data for **9**: ^{1}H NMR ($CDCl_3$) 0.36 (s, 3 H, *Me*−

---

(38) Lancaster, S. In www.syntheticpages.org **2003**, 215.

(39) Doerrer, L. H.; Green, M. L. H. *Dalton Trans.* **1999**, 4325.

Ta), 0.39 (s, 6 H, *Me*−Ta), 2.07 (s, 15 H, C_5Me_5). Anal. Calcd for $C_{26}H_{48}OTa_2$ (482.43): C, 42.28; H, 6.55. Found: C, 42.10; H, 6.70.

Polymerization of C_2H_4 with [TaCp*Me_3][MeB$(C_6F_5)_3$] (1). A sealed glass ampule containing a solid mixture of [TaCp*Me_4] (0.030 g, 0.08 mmol) and $B(C_6F_5)_3$ (0.042 g, 0.08 mmol) was introduced into a Büchi reactor, and 60 mL of toluene containing 10 × 0.08 mmol of Al^iBu_3 was added to the reactor. The system was purged with argon for 30 min and then ethylene for 10 min at the required temperature and pressure, and then the ampule was broken and the suspension stirred for 60 min. Afterward the polymerization was terminated by closing the ethylene supply and venting the autoclave to the atmosphere. The isolated polymer was washed first with MeOH/HCl (dilute) and then with MeOH/water and dried overnight in vacuo at 80 °C. Melting and crystallization temperatures of polymers were measured by differential scanning calorimetry (DSC, Perkin-Elmer DSC6). High-temperature gel permeation chromatography (GPC) analyses of polymer samples were carried out in 1,2,4-trichlorobenzene at 135 °C (Waters GPCV-2000).

X-ray Structure Determination of 3·C_6H_6. Yellow crystals suitable for X-ray diffraction studies were obtained by cooling a dichloromethane/C_6H_6 solution of **1** at 0 °C. Crystal data for **3**·C_6H_6: $C_{68}H_{54}B_2F_{30}OTa_2$, $M_r = 1840.63$, triclinic, space group $P\bar{1}$, $a = 13.5223(12)$ Å, $b = 15.006(3)$ Å, $c = 17.416(4)$ Å, $\alpha = 81.144(18)°$, $\beta = 88.494(9)°$, $\gamma = 79.818(15)°$, $V = 3436.8(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.779$ g cm^{-3}, $F(000) = 1792$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $\mu = 3.306$ mm^{-1}. Data collection was performed at 200(2) K on a Nonius KappaCCD single-crystal diffractometer. The crystal structure was solved by direct methods and refined using full-matrix least squares on F^2. All non-hydrogen atoms were anisotropically refined, except for a disordered benzene molecule. Hydrogen atoms were geometrically placed and left riding on their parent atoms. The final cycle of full-matrix least-squares refinement based on 15 731 reflections and 922 parameters converged to final values of $R1(F^2 > 2\sigma(F^2)) = 0.0404$, $wR2(F^2 > 2\sigma(F^2)) = 0.0673$, $R1(F^2) = 0.0968$, and $wR2(F^2) = 0.0782$. Final difference Fourier maps showed no peaks higher than 1.135 or deeper than −0.820 e Å^{-3}.

Acknowledgment. We gratefully acknowledge the Ministerio de Educación y Ciencia (Project No. MAT2004-02614) and DGUI-Comunidad de Madrid (Programme S-0505/PPQ-0328, COMAL-CM) (Spain) for financial support.

Supporting Information Available: Crystallographic data for **3** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060027C