New Monocyclopentadienyl Complexes of Tantalum with Dithiolate Ligands. Crystal and Molecular Structures of $Cp^*TaCl_2(SCH_2CH_2)_2S$, $Cp^*TaMe_2(SCH_2CH_2)_2O$, $Cp^*TaMe_2(SCH_2CH_2)_2S$, and $Cp^*Ta(xylylNC(Me)_2C{=}Nxylyl)(SCH_2CH_2)_2O$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

Rosa Fandos,*,[†] Carolina Hernández,[†] Isabel López-Solera,[‡] Antonio Otero,*,[‡]
Ana Rodríguez,[§] and Maria José Ruiz[†]

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, Avd. Carlos III, s/n 45071 Toledo, Spain, Facultad de Químicas, Universidad de Castilla-La Mancha, Campus de Ciudad Real, 13071 Ciudad Real, Spain, and ETS Ingenieros Industriales, Avd. Camilo José Cela, 3, 13071 Ciudad Real, Spain

Pilar Terreros

Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

Received July 19, 2000

Cp^*TaCl_4 reacts with $X(CH_2CH_2SH)_2$ in the presence of NEt_3 to yield the corresponding thiolate complexes $Cp^*TaCl_2(SCH_2CH_2)_2X$ (X = O (**1**), S (**2**)). The crystal structure of complex **2** has been determined by X-ray diffraction. The tantalum methyl complex Cp^*TaMe_4 reacts with $X(CH_2CH_2SH)_2$, rendering $Cp^*TaMe_2(SCH_2CH_2)_2X$ (X = O (**3**), S (**4**)). They have both been characterized by X-ray diffraction methods. Complex **3** reacts with xylylisocyanide to yield the imine complex $Cp^*Ta(\eta^2\text{-xylylNCMe}_2)(SCH_2CH_2)_2O$ (**6**), which undergoes insertion of a second isocyanide molecule to yield an η^1-iminoacyl-containing azatantalacyclobutane compound $Cp^*Ta(xylylNC(Me)_2C{=}N(xylyl)(SCH_2CH_2)_2O$ (**5**), whose structure has been also determined by X-ray diffraction.

Introduction

Thiolate derivatives of the early transition metals, mainly metallocene complexes, have received considerable attention in recent years. In contrast, comparatively little is known about analogous monocyclopentadienyl species.[1] In this field a systematic study of the chemistry of monocyclopentadienyl titanium and zirconium complexes with alkylthiolate and dithiolate ligands has been carried out.[2] For group 5 transition metals a relatively small number of simple monocyclopentadienyl polythiolates have been reported.[3,4] This interest in complexes that incorporate thiolate ligands is prompted by several motivating facts. Among these are the important role that such compounds are believed to play as intermediates in different reactions such as desulfurization of organosulfur compounds,[5,6] metal-catalyzed synthetic reactions involving C−S bond cleavage and formation.[7]

On the other hand, the propensity of sulfur to form M(μ-SR)M′ bridges has led to the widespread use of sulfur-containing complexes as synthons for multinuclear transition metal complexes, and so a number of zirconocene thiolate complexes have been prepared.[1]

[†] Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha.

[‡] Facultad de Químicas, Universidad de Castilla-La Mancha.

[§] ETS Ingenieros Industriales.

(1) Stephan, D. W.; Nadasdi, T. T. *Coord. Chem. Rev.* **1996**, *147*, 147, and references therein.

(2) (a) Firth, A. V.; Stephan, D. W. *Organometallics* **1997**, *16*, 2183. (b) Huang, Y.; Etkin, N.; Heyn, R. R.; Stephan, D. W.; Nadasdi, T. T. *Organometallics* **1996**, *15*, 2320. (c) Heyn, R. R.; Stephan, D. W. *Inorg. Chem.* **1995**, *34*, 2804.

(3) (a) Spence, M. A.; Rosair, G. M.; Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1998**, 1581**.** (b) Spence, M. A.; Rosair, G. M.; Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1998**, 3281. (c) Tatsumi, K.; Takeda, J.; Inoue, Y.; Sekiguchi, Y.; Kosaka, M.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24,* 332. (d) Tatsumi, K.; Inoue, Y. M.; Nakamura, A. *J. Organomet. Chem.* **1993**, *444*, C25. (e) Curnow, O. J.; Curtis, M. D.; Rheingold, A.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 4043. (f) Tatsumi, K.; Tahara, A.; Nakamura, A. *J. Organomet. Chem.* **1994**, *471*, 111.

(4) (a) Kawaguchi, H.; Tatsumi, K. *Organometallics* **1997**, *16*, 307. (b) Tatsumi, K.; Kawaguchi, H.; Tani, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 591. (c) Tatsumi, K.; Kawaguchi, H.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; Golen, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 763. (d) Tatsumi, K.; Inoue, Y.; Kawaguchi, H.; Kohsaka, M.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Taogishi, G. J.; Richman, P. N. *Organometallics* **1993**, *12*, 352.

(5) (a) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (b) Nishikota, M. *Energy Fuels* **1988**, *2*, 214. (c) Orr, W. L. *Oil Sand and Oil Shale Chemistry*; Verlag Chemie: Weinheim, 1978; p 223. (d) Cyr, T. D.; Payzant, J. D.; Montgomery, D. S.; Srausz, O. P. *Org. Geochem.* **1986**, *9*, 139. (e) Nishikota, M. *Energy Fuels* **1988**, *2*, 214.

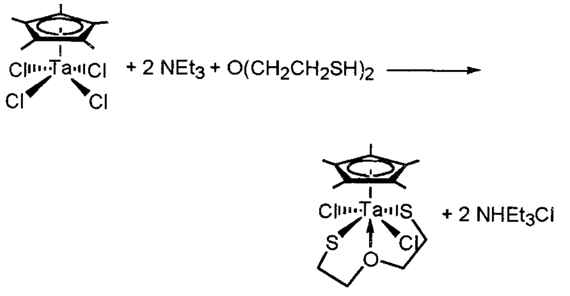
(6) (a) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (b) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (c) Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1987**, *184*, 75. (d) Eisch, J. J.; Hallenbeck, L. E.; Han, K. L. *J. Org. Chem.* **1983**, *48*, 2963. (e) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (f) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (g) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61. (h) Chen, J.; Angelici, R. J. *Organometallics* **1992**, *11*, 992. (i) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

10.1021/om000626y CCC: $19.00
Publication on Web 11/04/2000

In the last years we have developed studies based on the synthesis of several families of cyclopentadienyl-containing early transition metal complexes with different classes of assisted ligands, namely, mercapto–amide,[8] and pyrimidine–thiolate.[9] Now we are interested in the study of the reactivity of monocyclopentadienyltantalum derivatives toward dithiolate ligands, and herein we report the synthesis and characterization of some assisted dithiolate monocyclopentadienyltantalum complexes as well as an interesting insertion reactions to yield both η^2-imine and azatantalacyclobutane species.

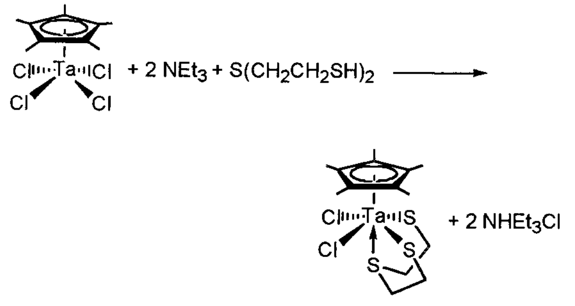
Results and Discussion

The reaction of Cp^*TaCl_4 with $X(CH_2CH_2SH)_2$ (X = O, S) in the presence of 2 equiv of triethylamine proceeds at 80 °C in toluene to yield complexes $Cp^*TaCl_2(SCH_2CH_2)_2X$ (X = O (**1**), S (**2**)) (eqs 1 and 2).



(1)

1



(2)

2

Complexes **1** and **2** are isolated as air-sensitive solids after appropriate workup, and they are soluble in toluene and THF and less soluble in pentane or Et_2O. They and the subsequent complexes described in this work have been characterized by ^1H and ^{13}C NMR and IR spectroscopic techniques as well as by elemental analysis (see Experimental Section). The ^1H NMR spectrum of **1** exhibits resonances at 2.27 (s), 3.50 (t, $^3J_{CH}$ = 5.62 Hz), and 4.08 (t, $^3J_{CH}$ = 5.62 Hz) ppm attributable to the Cp* ring and the methylene groups bonded to the sulfur and the oxygen atoms, respectively. No change of the spectra took place upon lowering the temperature from room temperature to −80 °C. The ratio of the integrals is consistent with the proposed stoichiometry. The multiplicity and number of the methylene proton signals point to a trans disposition of the sulfur atoms of the dithiolate ligand (see eq 1). The ^{13}C NMR spectrum is in agreement with the proposed disposition. In contrast, complex **2** shows, in the ^1H NMR spectrum, the Cp* methyl resonance at 2.20 ppm, while at 3.16, 3.37, and 3.73 ppm appear two complex signals due to the methylene groups. It can be inferred from these results that in complex **2** the sulfur atoms of the dithiolate ligand are in cis position (see eq 2).

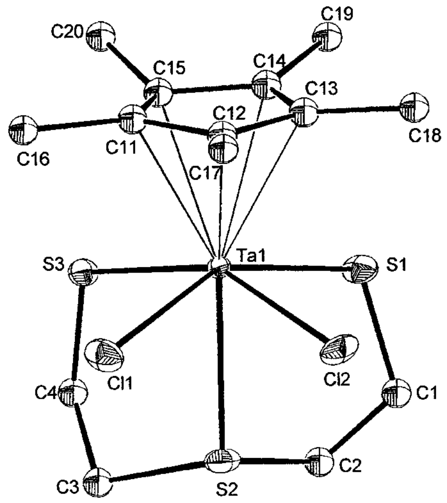


Figure 1. Perspective ORTEP drawing of the molecular structure of complex **2**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Ta(1)–Cl(1)	2.483(8)	Cl(1)–Ta(1)–Cl(2)	77.5(3)
Ta(1)–Cl(2)	2.475(7)	Cl(1)–Ta(1)–S(2)	73.7(3)
Ta(1)–S(1)	2.427(8)	Cl(1)–Ta(1)–S(3)	87.7(3)
Ta(1)–S(2)	2.641(7)	Cl(2)–Ta(1)–S(1)	84.7(3)
Ta(1)–S(3)	2.425(7)	Cl(2)–Ta(1)–S(2)	74.1(3)
S(1)–C(1)	1.72(4)	S(1)–Ta(1)–S(2)	79.3(3)
S(3)–C(4)	1.76(3)	S(1)–Ta(1)–S(3)	97.9(3)
S(2)–C(3)	1.88(4)	S(2)–Ta(1)–S(3)	79.2(3)
S(2)–C(2)	1.79(5)	C(4)–S(3)–Ta(1)	112(1)
		C(1)–S(1)–Ta(1)	107(1)
		C(3)–S(2)–Ta(1)	104(1)
		C(2)–S(2)–Ta(1)	101(2)
		C(3)–S(2)–C(2)	107(2)

To confirm the proposed structure, the solid-state structure of **2** has been determined by an X-ray diffraction study. An ORTEP drawing of **2** is shown in Figure 1, and selected bond distances and angles are summarized in Table 1.

The structure consists of discrete molecules separated by van der Waals distances. The tantalum atom is bonded to the cyclopentadienyl ring in an η^5 mode and to two chlorine atoms and to the thiolate ligand through all three sulfur atoms with the central one occupying the trans position to the Cp* group, while those placed in the equatorial plane are in cis disposition to each other. The coordination around the metal is best described as pseudo-octahedral geometry, with the tantalum atom 0.560(4) Å out of the plane defined by Cl(1), Cl(2), S(1), and S(3) atoms. The Ta(1)–S(1) and Ta(1)–

---

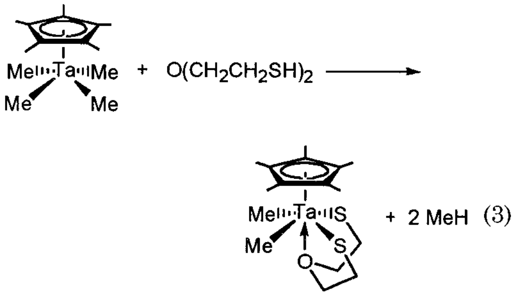
(7) (a) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, 43. (b) Okamura, H.; Takei, H. *Tetrahedron Lett.* **1979**, 3425. (c) Murahashi, S.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408. (d) Kosugi, M.; Shimizu, T.; Migita, T. *Chem. Lett.* **1978**, 13. (e) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *48*, 4380. (f) Wenkert, E.; Hanna, J. M., Jr.; Leftin, M. H.; Michelotti, E. L.; Potts, K. T.; Usifer, D. *J. Org. Chem.* **1985**, *50*, 1125. (g) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, P.; Wenkert, E. *Tetrahedron Lett.* **1982**, *23*, 4629. (h) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1987**, *27*, 6321.

(8) Fandos, R.; Martínez-Ripoll, M.; Otero, A.; Ruiz, M. J.; Rodríguez, A.; Terreros, P. *Organometallics* **1998**, *17*, 1465.

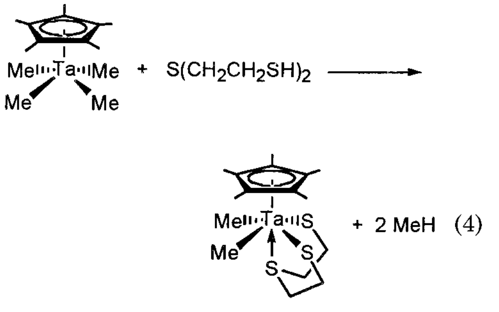
(9) Fandos, R.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A.; Ruiz, M. J.; Terreros, P. *Organometallics* **1996**, *15*, 4725.

S(3) bond distances (2.427(8) and 2.425(7) Å, respectively) are normal for tantalum thiolate complexes[10] but slightly shorter than that found for the rest of the complexes reported in this paper (vide infra).

Another general way to synthesize thiolate complexes is to carry out the protonolysis of metal−alkyl bonds with the corresponding thiol. In this way, the reaction of Cp*TaMe$_4$ with the thiol derivatives X(CH$_2$CH$_2$SH)$_2$ (X = O, S) yields complexes **3** and **4**, respectively (eqs 3 and 4).



3



4

Complexes **3** and **4** are isolated as air-sensitive compounds after appropriate workup, and they are very soluble in toluene or THF and less soluble in pentane or Et$_2$O. The ^{1}H NMR spectrum of complex **3** shows a singlet signal at 0.15 ppm assigned to the methyl groups bonded to the tantalum center, at 1.97 appear the signal due to the Cp* group, and the resonances of the methylene protons appear at 2.81, 2.88, 3.31, and 4.07 ppm as multiplet signals. The ^{13}C{^{1}H} NMR spectrum shows a singlet signal, at 12.2 ppm, assigned to the methyls of the Cp* ligand, at 30.6 ppm appear the resonance of the carbon atom bonded to the sulfur atom, while at 42.1 ppm resonates the methyl group bonded to the tantalum center and at 79.3 ppm the carbon atom bonded to the oxygen. Cp* ring carbon atoms give rise to a singlet at 117.6 ppm. Analogous spectroscopic data were found for complex **4** (see Experimental Section). In accordance with these data the coordination mode of the ligand is proposed to be analogous to that found in complex **2** with a cis disposition of the sulfur atoms of the dithiolate ligand. To confirm this proposal X-ray crystal structure determinations for complexes **3** and **4** were carried out.

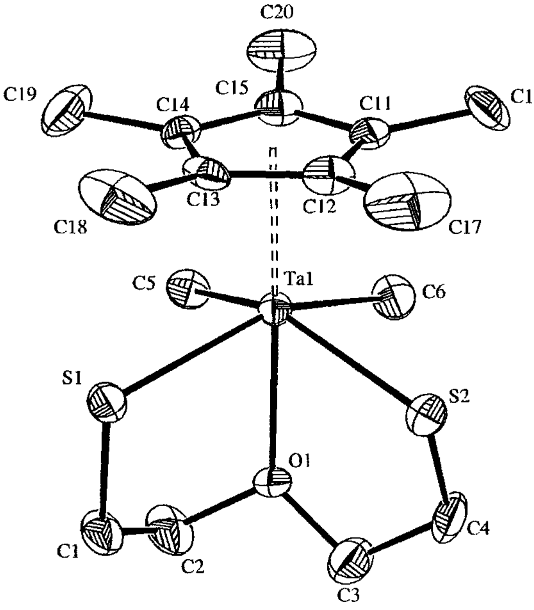


Figure 2. Perspective ORTEP drawing of the molecular structure of complex **3**.

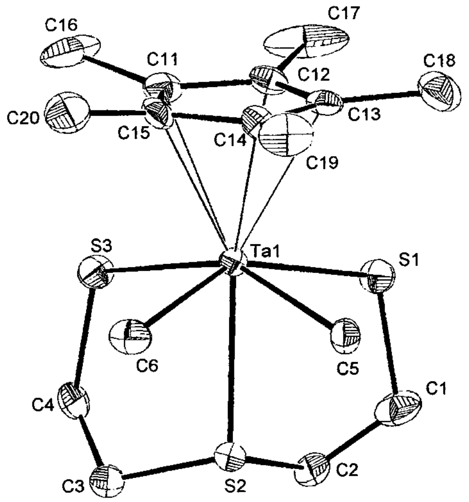


Figure 3. Perspective ORTEP drawing of the molecular structure of complex **4** (Molecule A).

Crystals of **3** and **4** were obtained by slow diffusion of pentane into a saturated solution of the appropriate complex in toluene. Figure 2 and Figure 3 represent the ORTEP diagrams of the structures of complex **3** and one of the two independent molecules found in compound **4** (molecule A), respectively, while selected bond distances and angles are listed in Table 2 (complex **3**) and Table 3 (complex **4**). In both cases the structure shows a distorted octahedral geometry around the tantalum atom with the terminal sulfur atom placed in cis position at the equatorial plane. The central oxygen (**3**) or sulfur (**4**) atoms of the dithiolate ligand are coordinated in trans position to the Cp* group. The tantalum atom is out of the ecuatorial plane (0.5909(3) Å in complex **3**; 0.570(6) and 0.575(7) Å in complex **4** A and B, respectively).

Coordination parameters around the tantalum atom are rather similar for both complexes. In complex **3** the Ta(1)−S(1) and Ta(1)−S(2) bond distances (2.455(3) and 2.458(3) Å) are analogous to that found in complex **4** Ta(1)−S(1) (2.470(4) and 2.462(5) Å in molecules A and

---

[10] (a) Tatsumi, K.; Matsubara, I.; Inoue, Y.; Nakamura, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1989**, *111*, 7766. (b) Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844. (c) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050. (d) Martin, J. L.; Takats, J. *Inorg. Chem.* **1975**, *14*, 1358.

Scheme 1

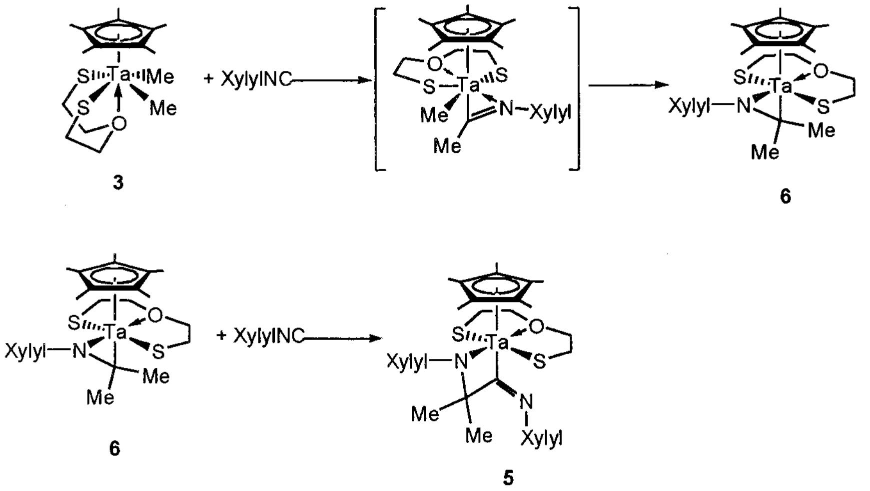


Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Ta(1)–S(1)	2.455(3)	S(1)–Ta(1)–S(2)	99.50(10)
Ta(1)–S(2)	2.458(3)	C(5)–Ta(1)–C(6)	73.9(5)
Ta(1)–O(1)	2.375(6)	C(5)–Ta(1)–S(1)	88.3(3)
Ta(1)–C(5)	2.241(11)	C(6)–Ta(1)–S(2)	83.7(4)
Ta(1)–C(6)	2.233(12)	O(1)–Ta(1)–S(1)	73.92(18)
S(1)–C(1)	1.799(12)	O(1)–Ta(1)–S(2)	74.27(19)
S(2)–C(4)	1.805(14)	O(1)–Ta(1)–C(5)	76.6(3)
O(1)–C(2)	1.455(14)	O(1)–Ta(1)–C(6)	78.0(4)
O(1)–C(3)	1.412(13)	C(1)–S(1)–Ta(1)	106.9(4)
C(1)–C(2)	1.433(17)	C(4)–S(2)–Ta(1)	101.4(5)
C(3)–C(4)	1.441(17)	C(3)–O(1)–C(2)	110.7(9)
		C(3)–O(1)–Ta(1)	121.3(7)
		C(2)–O(1)–Ta(1)	116.3(7)
		C(2)–C(1)–S(1)	113.2(9)
		C(1)–C(2)–O(1)	111.8(10)
		O(1)–C(3)–C(4)	112.7(11)
		C(3)–C(4)–S(2)	112.7(9)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

	molecule A	molecule B
Ta(1)–S(1)	2.470(4)	2.462(5)
Ta(1)–S(2)	2.629(4)	2.612(4)
Ta(1)–S(3)	2.468(4)	2.475(5)
Ta(1)–C(5)	2.28(2)	2.27(2)
Ta(1)–C(6)	2.25(2)	2.26(2)
S(1)–Ta(1)–S(2)	77.7(1)	77.2(2)
S(1)–Ta(1)–S(3)	97.9(2)	97.8(2)
S(2)–Ta(1)–S(3)	77.3(1)	78.2(2)
S(1)–Ta(1)–C(5)	82.5(5)	83.2(6)
S(2)–Ta(1)–C(5)	75.0(5)	73.6(5)
S(2)–Ta(1)–C(6)	73.8(5)	74.0(5)
S(3)–Ta(1)–C(6)	88.7(6)	87.9(6)
C(5)–Ta(1)–C(6)	77.6(8)	77.5(9)

B, respectively) and Ta(1)–S(3) (2.468(4) and 2.475(5) Å, in molecules A and B, respectively). All of them are in the range of typical tantalum(V)–thiolate distances (2.35–2.47 Å).[10] Ta–S–C angles are small probably to allow coordination of the central donor atom. Bond distances from the tantalum atom to the carbon of the methyl groups are also similar in both complexes (Ta(1)–C(5) 2.24(1) Å, Ta(1)–C(6) 2.23 (2) Å for complex **3** and in complex **4** Ta(1)–C(5) 2.28(2) and 2.27(2) Å and Ta(1)–C(6) 2.25(2) and 2.26(2) Å for molecules A and B, respectively) and comparable to those found in other tantalum–alkyl complexes.[11] Ta(1)–O(1) bond distance in complex **3** (2.375(6) Å) is rather long,[12] pointing to a weak interaction between the metal and the oxygen atom.

Reactivity studies on the insertion process of 2,6-$Me_2C_6H_3NC$ into the Ta–Me bond for complexes **3** and **4** were carried out. Different results were found: while complex **3** shows an interesting reactivity, complex **4** does not react under the same experimental conditions. First, we have carried out the reaction of **3** in toluene in the presence of an excess of xylylisocyanide to yield an air-sensitive orange solid, which was identified as an azatantalacyclobutane containing an η^1-iminoacyl complex **5** (see Experimental Section). The ^1H NMR spectrum shows a singlet signal at 1.64 ppm which is assigned to the Cp* ligand protons and three singlet signals at 1.28, 2.18, and 2.52 ppm with a relative integral of six protons each which correspond to methyl groups. In addition, the spectrum shows four multiplet signals attributable to the methylene protons of the thiolate moiety and several multiplet signals due to the aromatic protons. Furthermore, ^{13}C NMR shows, among others, two singlet signals at 240.1 and 81.3 ppm, which we tentatively assign to an iminoacyl carbon atom and to the quaternary carbon of the Ta–N–C–C metallacycle.[13] All those data suggest that complex **3** has reacted with 2 molar equiv of xylylisocyanide to yield a rather symmetric compound (see Scheme 1). Presumably, the formation of **5** arises via a pathway involving initial insertion of xylylisocyanide into one Ta–Me bond to form the corresponding mono(η^2-iminoacyl) complex. A second methyl migration would then occur, forming an η^2-imine-containing complex **6**. Finally, insertion of a second isocyanide into the newly formed Ta–C bond would lead to **5**. An analogous mechanism has been described[14] for the reaction of xylylisocyanide with $Cp^*TaCl_2Me_2$, in which the formation of an azatantalacyclobutane complex was proposed as an intermediate

The solid-state structure of complex **5** was also determined by an X-ray diffraction study. Figure 4

---

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

[12] Meyer, T. Y.; Garner, L. R.; Baenziger, N. C.; Messerle, L. *Inorg. Chem.* **1990**, *29*, 4045.

[13] Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857.

[14] Galakhov, M. V.; Gómez, M.; Jiménez, G.; Royo, P. *Organometallics* **1995**, *14*, 2843.

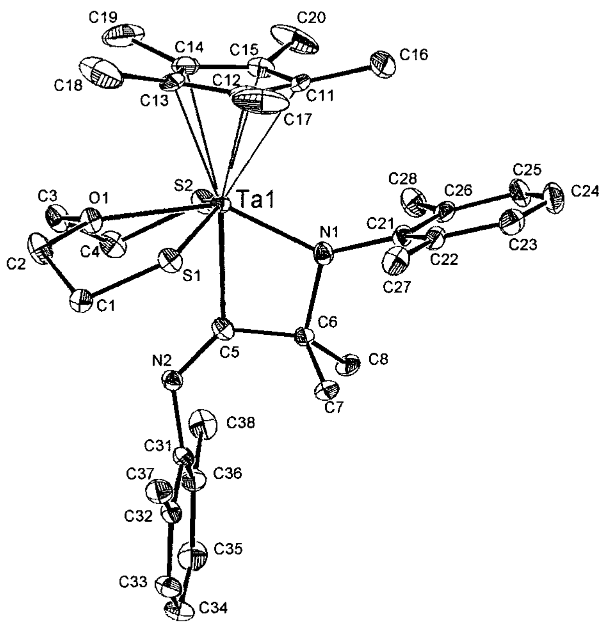


Figure 4. Perspective ORTEP drawing of the molecular structure of complex **5**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5

Ta(1)−S(1)	2.488(3)	S(1)−Ta(1)−O(1)	74.7(2)
Ta(1)−S(2)	2.468(3)	S(1)−Ta(1)−S(2)	143.6(1)
Ta(1)−O(1)	2.324(7)	O(1)−Ta(1)−S(2)	74.3(2)
Ta(1)−N(1)	2.010(9)	S(1)−Ta(1)−N(1)	98.6(3)
Ta(1)−C(5)	2.24(1)	S(2)−Ta(1)−N(1)	96.5(3)
N(1)−C(6)	1.53(1)	N(1)−Ta(1)−C(5)	63.6(4)
N(2)−C(5)	1.31(1)	Ta(1)−N(1)−(C21)	141.5(7)
C(5)−C(6)	1.44(1)	Ta(1)−C(5)−N(2)	135.4(8)
N(2)−C(31)	1.40(1)	N(2)−C(5)−C(6)	129.3(10)
C(5)−C(6)	1.44(1)	C(1)−S(1)−Ta(1)	102.5(4)
S(1)−C(1)	1.80(1)	C(4)−S(2)−Ta(1)	102.9(4)
S(2)−C(4)	1.78(1)	S(2)−Ta(1)−S(1)	143.61(10)
		N(1)−Ta(1)−O(1)	145.9(3)
		C(5)−N(2)−C(31)	128.7(9)
		C(6)−N(1)−Ta(1)	102.6(6)

represents an ORTEP diagram of the molecular structure, while selected bond distances and angles are listed in Table 4.

The molecular structure of **5** is best described as pseudo-octahedral, with the Cp* ligand and the carbon atom of the iminoacyl moiety placed in the apical positions. The iminoacyl group is adopting an η^1-bonding mode, an uncommon motif in early transition metals.[15] The dithiolate ligand is trihapto, with the sulfur atoms trans to each other while the oxygen atom is in trans position to the nitrogen atom. The tantalum atom is 0.599(3) Å out of the plane defined by the S(1), S(2), O(1), and N(1) atoms.

The distances from the tantalum atom to the cyclopentadienyl ring carbon atoms are in the normal range,[16] while the Ta−S bond distances are somewhat longer than that found in complexes **2**, **3**, and **4**. The Ta−N bond distance, 2.010(9) Å, is comparable to that found in other nitrogen ligand tantalum complexes.[17] The distance from the tantalum to the iminoacyl carbon atom is 2.24(1) Å.

To confirm the proposed mechanism through which formation of **5** occurs, the reaction of complex **3** with xylylisocyanide was monitored in an ^{1}H NMR experiment. Reaction takes place in C_6D_6 at room temperature to yield complex **6** as the first detectable product, indicating that the second methyl migration on the proposed initially formed iminoacyl complex would be very fast (See Scheme 1). The ^{1}H NMR spectrum exhibits two singlet signals at 2.28 and 2.36 ppm which are assigned to the methyl groups of the xylyl moiety and the two methyl groups which have undergone the insertion reaction. Equivalence of those methyls suggests formation of an imine ligand in accord with the above commented mechanism in the formation of complex **5**. On the other hand, there are four multiplet signals at 2.04, 2.57, 2.87, and 3.20 ppm corresponding to the methylene protons of the thiolate ligand. The aromatic protons give rise to a multiplet signal at 6.96 ppm. The spectrum shows that the ligands have a symmetric distribution around the metallic center. Afterward, an evolution of the signals was observed in the spectrum, and finally the resonances that correspond to complex **5** appear, indicating that the formation of this complex as the final product takes place.

In addition, the reaction of complex **3** with 1 equiv of xylylisocyanide was carried out in toluene over a period of 3 h. In these experimental conditions, complex **6** was isolated, after appropriate workup, as an air-sensitive yellow solid (see Experimental Section). Their ^{1}H NMR spectrum agrees with that previous described in the ^{1}H NMR experiment, and in addition, the ^{13}C NMR spectrum is also in agreement with the proposal and shows as outstanding feature: the singlet placed at 82.5 ppm, which is tentatively assigned to the quaternary carbon atom of the imine ligand. The high field of this resonance point to an η^2-coordination mode of the imine group.[18]

In contrast with the reactivity observed for complex **3**, the analogous compound **4** does not react with 2,6-$Me_2C_6H_3$−NC under the same reaction conditions. This lack of reactivity may be due to the stronger coordination of the central sulfur atom than the central oxygen atom in **3** to the tantalum center that inhibits the initial coordination of the isocyanide, preventing its further reactivity.

In conclusion new families of monocyclopentadienyl tantalum complexes with assisted dithiolate ligands from both metathetical and protonolysis processes have been described. In addition, the reaction of a dimethyl-containing species with xylylisocyanide proceeds via successive insertions to give rise to both η^2-imine and azatantalacyclobutane species. Further studies are in progress aimed at establishing the reactivity of these complexes as well as the synthesis of new complexes of early transition elements with these ligands.

Experimental Details

General Procedures. The preparation and handling of described compounds was performed with rigorous exclusion

---

[15] Jubb, J.; Song, J.; Richeson, D.; Gambarotta, S. In *Comprehensive Organometallic Chemistry*; Lappert, M. F., Ed.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, pp 582−585.

[16] Castro, A.; Galakov, M. V.; Gómez, M.; Gómez-Sal, P.; Martín, A.; Sánchez, F. *J. Organomet. Chem.* **2000**, *595*, 36.

[17] Jiménez Pindado, G.; Thornton-Pett, M.; Bochman, M. *J. Chem. Soc., Dalton Trans.* **1998**, 393.

[18] Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rotwell, I. P. *Organometallics* **1990**, *9*, 75.

Table 5. Crystal Data and Structure Refinement for 2, 3, 4, and 5

	2	**3**	**4**	**5**
empirical formula	$C_{14}H_{23}Cl_2S_3Ta$	$C_{16}H_{29}OS_2Ta$	$C_{32}H_{58}S_6Ta_2$	$C_{34}H_{47}N_2OS_2Ta$
fw	539.35	482.46	997.04	744.81
temp, K	293(2)	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	orthorhombic	monoclinic	triclinic
space group	*Pbca*	*Pbca*	$P2_1/n$	$P\bar{1}$
a, Å	8.7870(10)	8.6809(10)	14.1220(10)	8.723(2)
b, Å	14.3020(10)	14.970(3)	8.9040(10)	13.193(3)
c, Å	28.5760(10	27.043(2)	30.4000(10)	14.402(3)
α, deg				81.63(3)
β, deg			102.45(1)	83.40(3)
γ, deg				80.56(3)
V, Å^3	3591.2(5)	3514.3(9)	3732.7(5)	1610.5(6)
Z	8	8	4	2
ρ_{calcd}, g cm^{-3}	1.995	1.824	1.774	1.536
μ, cm^{-1}	67.56	64.87	62.15	35.71
transmn coeff	0.530−1.000	0.690−1.000	0.091−1.000	0.531−1.000
F(000)	2096	1904	1968	756
cryst size, mm	0.2 × 0.2 × 0.1	0.4 × 0.3 × 0.1	0.2 × 0.2 × 0.1	0.3 × 0.3 × 0.2
index ranges	$0 \le h \le 11$ $0 \le k \le 18$ $0 \le l \le 37$	$0 \le h \le 11$ $0 \le k \le 19$ $0 \le l \le 35$	$-18 \le h \le 18$ $0 \le k \le 11$ $0 \le l \le 40$	$-11 \le h \le 11$ $-17 \le k \le 17$ $0 \le l \le 19$
no. of rflns measd	4324	4244	8984	7800
no. of rflns obsd [$I > 2\sigma(I)$]	2148	2272	6128	5491
no. of params refined	116	181	361	372
no. of restraints	0	0	0	0
S (goodness-of-fit) on F^2	1.043	1.021	1.060	1.460
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0759 wR2 = 0.2010	R1 = 0.0512 wR2 = 0.0972	R1 = 0.0681 wR2 = 0.1996	R1 = 0.0678 wR2 = 0.1418
largest diff peak and hole, e Å^{-3}	3.716 and −3.442	1.076 and −1.050	6.057 and −5.544	3.945 and −2.633

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

of air and moisture under nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere.

The following reagents were prepared by literature procedures: Cp*$TaCl_4$,[19] Cp*$TaMe_4$.[20] The commercially available compounds Cp*H, LiMe in diethyl ether, 2-mercaptoethyl sulfide, and 2-mercaptoethyl ether were used as received from Aldrich.

^1H and ^{13}C NMR spectra were recorded on a 200 Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$.

IR spectra were recorded in the region 4000−400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer as Nujol mulls using PET cells.

Cp*TaCl$_2$(SCH$_2$CH$_2$)$_2$O (1). To a solution of Cp*$TaCl_4$ (0.443 g, 0.97 mmol) and 2-mercaptoethyl ether (0.120 mL, 0.97 mmol) was added 0.269 mL (1.93 mmol) of NEt_3, and the mixture was stirred at 80 °C for 3 h. After filtration, the solvent was removed under vacuum and the solid washed with pentane, yielding complex **1** (0.265 g, 53%) as a yellow crystalline solid. IR (cm^{-1}): 1194 (m), 1021 (s), 971 (m), 951 (s), 779(s), 638 (w), 432 (w). ^1H NMR (C_6D_6, 18 °C): δ 2.27 (s, 15 H, Cp*), 3.50 (t, $^3J_{CH}$ = 5.62 Hz, 4 H, CH_2S), 4.08 (t, $^3J_{CH}$ = 5.62 Hz, 4 H, CH_2O). $^{13}C\{^1H\}$ NMR: 13.4 (s, Cp*), 35.5 (s, CH_2S), 81.3 (s, CH_2O), 125.3 (s, Cp*). Anal. Calcd for $C_{14}H_{23}Cl_2OS_2Ta$: C, 32.13; H, 4.39. Found: C, 32.29; H, 4.64.

Cp*TaCl$_2$(SCH$_2$CH$_2$)$_2$S (2). To a solution of Cp*$TaCl_4$ (0.640 g, 1.40 mmol) in 10 mL of toluene were added 0.18 mL (1.40 mmol) of 2-mercaptoethyl sulfide and 0.390 mL (2.80 mmol) of NEt_3. The mixture was stirred at 80 °C for 2 h, and then the solvent was removed under vacuum. The solid was washed with pentane, yielding an orange product that was characterized as **2** (0.457 g, 60%). IR (cm^{-1}): 1170 (m), 1022 (s), 962 (m), 911 (m), 834 (s), 647 (s), 476 (w). ^1H NMR (C_6D_6, 18 °C): δ 2.20 (s, 15 H, Cp*), 3.16 (m, 2H, CH_2), 3.37 (m, 2 H, CH_2), 3.73 (m, 4 H, CH_2). $^{13}C\{^1H\}$ NMR: 12.9 (s, Cp*), 40.3 (s, CH_2), 41.9 (s, CH_2), 125.5 (s, Cp*). Anal. Calcd for $C_{14}H_{23}Cl_2S_3Ta$: C, 31.19; H, 4.30. Found: C, 31.31; H, 4.13.

Cp*TaMe$_2$(SCH$_2$CH$_2$)$_2$O (3). A solution of Cp*$TaMe_4$ (0.535 g, 1.42 mmol) in 10 mL of toluene was stirred, at 80 °C, for 2 h with 0.176 mL (1.42 mmol) of 2-mercatoethyl ether. Then the solvent was removed and the oily residue washed with 6 mL of pentane, yielding an orange complex, which was characterized as **3** (0.428 g, 64%) IR (cm^{-1}): 1170 (m), 1023 (s), 921 (m), 858 (m), 614 w), 464 (m). ^1H NMR (C_6D_6, 18 °C): δ 0.15 (s, 6 H, Ta-Me), 1.97 (s, 15 H, Cp*), 2.81 (m, 2 H, CH_2S), 2.88 (m, 2 H, CH_2S), 3.31 (m, 2 H, CH_2O), 4.07 (m, 2 H, CH_2O). $^{13}C\{^1H\}$ NMR: 12.2 (s, Cp*), 30.6 (s, CH_2S), 42.1 (s, Ta-Me), 79.3 (s, CH_2O), 117.6 (s, Cp*). Anal. Calcd for $C_{16}H_{29}OS_2Ta$: C, 39.83; H, 6.01. Found: C, 39.62; H, 5.69.

Cp*TaMe$_2$(SCH$_2$CH$_2$)$_2$S (4). A solution of Cp*$TaMe_4$ (0.385 g, 1.02 mmol) and 2-mercaptoethyl sulfide (0.133 mL, 1.02 mmol) was heated to 80 °C for 2 h. The solvent was evaporated to dryness and the solid washed with pentane, rendering a yellow solid, which was characterized as **4** (0.338 g, 65%). IR (cm^{-1}): 1185 (s), 1023 (s), 919 (m), 859 (m), 674 (w), 460 (s). ^1H NMR (C_6D_6, 18 °C): δ −0.18 (s, 6H, Ta-Me), 1.95 (s, 15 H, Cp*), 2.35 (m, 2H, CH_2), 2.85 (m, 2 H, CH_2), 3.00 (m, 4 H, CH_2).$^{13}C\{^1H\}$ NMR: 11.9 (s, Cp*), 30.3 (s, Ta-Me), 33.9 (s, CH_2), 42.7 (s, CH_2), 118.3 (s, Cp*). Anal. Calcd for $C_{16}H_{29}S_3Ta$: C, 38.55; H, 5.86. Found: C, 38.50; H, 5.84.

Cp*Ta(xylylNC(Me)$_2$C=Nxylyl)(SCH$_2$CH$_2$)$_2$O (5). A solution of Cp*$TaMe_2(SCH_2CH_2OCH_2CH_2S)$, 0.212 g (0.44 mmol), and 0.177 g (1.32 mmol) of xylylisocyanide in 3 mL of toluene was left at room temperature for 15 h. The solvent was then removed under vacuum and the residue washed with pentane, yielding 0.103 g (32%) of an orange solid, which was characterized as **5**. IR (cm^{-1}): 1619 (m), 1585 (m), 1421 (s), 1411 (s), 1346 (s), 1228 (s), 1202 (s), 1171 (m), 1052 (m), 864 (m), 771 (vs), 762 (vs). ^1H NMR (C_6D_6, 18 °C): δ 1.28 s, (6 H, Me−C), 1.64 (s, 15 H, Cp*), 2.18 (s, 6 H, Me−C), 2.52 (s, 6 H, Me−C), 2.61 (m, 2 H, CH_2S), 3.31 (m, 2 H, CH_2S), 3.84 (m, 2 H, CH_2O),

---

[19] Burt, R. J.; Chatt, J.; Leigh, G. J.; Teuben, J. H.; Whesterhof *J. Organomet. Chem.* **1977**, *129*, C33.

[20] Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, 240.

4.23 (m, 2 H, CH_2O), 6.75 (m, 4 H, Ar), 6.95 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR: 11.7 (s, Cp*), 19.8 (Me−C), 21.2 (s, Me−C), 22.2 (s, (Me−C), 31.8 (s, CH_2S), 81.3 (s, C−N), 82.6 (s, CH_2O), 121.0 (s, Cp*), 121.0 (s, C−H), 125.1 (s, C−H), 126.7 (s, C−H), 128.4 (s, C−H), 139.9 (s, C_{ipso}), 146.12 (s, C_{ipso}), 240.1 (s, C═N). Anal. Calcd for $C_{34}H_{47}N_2OS_2Ta$: C, 54.84; H, 6.31; N, 3.76. Found: C, 54.36; H, 6.21; N, 3.28.

Cp*Ta(η^2-xylylNCMe$_2$)(SCH$_2$CH$_2$)$_2$O (6). To a solution of complex **3** (0.310 g, 0.643 mmol) in 5 mL of toluene was added 0.126 g (0.964 mmol) of xylylisocyanide. After 3 h at room temperature the solvent was removed under vacuum and the residue washed with pentane (10 mL) to yield a yellow solid, which was characterized as complex **6**. Yield: 0.205 g, 52%. IR (cm^{-1}): 1586 (w), 1295 (s), 1261 (vs), 1228 (vs), 1182 (m), 1102 (m), 1056 (s), 956 (m), 923 (w), 579 (w), 492 (w). ^1H NMR (C_6D_6, 18 °C): δ 1.81 (s, 15 H, Cp*), 2.28 (s, 6 H, Me−C), 2.36 (s, 6 H, Me−C), 2.04 (m, 2 H, CH_2S), 2.57 (m, 2 H, CH_2S), 2.87 (m, 2 H, CH_2O), 3.20 (m, 2 H, CH_2O), 6.96 (m, 3 H, Ar). $^{13}C\{^1H\}$ NMR: 11.5 (s, Cp*), 20.1 (Me−C), 26.7 (s, Me−C), 31.8 (s, CH_2S), 81.2 (s, CH_2O), 82.5 (s, C−N), 117.3 (s, Cp*), 124.3 (s, C−H), 136.4 (s, C−H), 137.6 (s, C_{ipso}), 149.4 (s, C_{ipso}). Anal. Calcd for $C_{25}H_{38}NOS_2Ta$: C, 48.93; H, 6.24; N, 2.28. Found: C, 48,38; H, 6,55; N, 2,24.

Crystal Structure Determination and Refinement of Complexes 2, 3, 4, and 5. Recrystallization by slow diffusion of pentane into a toluene solution of the complexes produced some poor-quality crystals. The crystals were mounted in a sealed 0.3-mm Lindeman glass capillary tube. Intensity data were collected on a NONIUS-MACH3 four-circle diffractometer, equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), using the $\omega/2\theta$ scan technique at 298 K. Unit-cell parameters were determined from automatic centering of 25 reflections and refined by the least-squares method. Data were corrected in the usual fashion for Lorentz and polarization effects, and an empirical absorption correction was made. The crystal data and details of the data collection and structure analyses are summarized in Table 5.

The structures of **2** and **5** were solved by Patterson synthesis, whereas structures of **3** and **4** by direct methods, using the SHELXS computer program,[21] and refined on F^2 by full-matrix least-squares techniques with the SHELXL-97 computer program.[22] All non-hydrogen atoms were refined with anisotropic thermal parameters for all compound except compound **2**, where carbon atoms were refined with isotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model.

Acknowledgment. We thank the Dirección General de Enseñanza Superior e Investigación Científica (Grant No. PB98-0159-C02-01-02) for financial support and also the Junta de Comunidades de Castilla-La Mancha for a fellowship (C.H.).

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles for complexes **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000626Y

---

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(22) Sheldrick, G. M. *SHELX93*: *Program for Determination of Crystal Structure*; University of Göttingen: Germany, 1994.