Synthesis of Novel Mono(pentamethylcyclopentadienyl)tantalacycloalkyl and -tantalacycloalkylidene Complexes. Crystal Structure of [TaCp*Cl_2\{η^3-C_6H_4(2-CH_2NMeCH_2)\}]

Irene de Castro, Mikhail V. Galakhov, Manuel Gómez, Pilar Gómez-Sal, and Pascual Royo*

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

Received July 10, 1995[⊗]

TaCp*Cl_4 reacts with 1 equiv of Li[2-(CH_2NMe_2)C_6H_4] to give the trichloroaryltantalum(V) complex [TaCp*Cl_3\{η^2-C_6H_4(2-CH_2NMe_2)\}] (**1**), containing the chelated arylamine ligand. Reaction of complex **1** with an additional 1 equiv of the lithium reagent causes C−H bond activation at one of the methylamino groups with β-H elimination, leading to the formation of the cyclometalated species [TaCp*Cl_2\{η^3-C_6H_4(2-CH_2NMeCH_2)\}] (**2**). Complex **2** reacts with a further 2 equiv of the lithium reagent giving the cyclometalated alkylidene complex [TaCp*\{η^2-C_6H_4(2-CH_2NMe_2)\}\{η^2-C_6H_4(2-CH_2NMeCH)\}] (**3**), via α-H elimination. Thermally stable complex **2** reacts with 1 equiv of $LiNMe_2$ and LiNH^{t}Bu to give the new chloroamidotantalacycloalkyl complexes [TaCp*Cl\{η^2-C_6H_4(2-CH_2NMeCH_2)\}(NMe_2)] (**4**) and [TaCp*Cl\{η^2-C_6H_4(2-CH_2NMeCH_2)\}(NH^{t}Bu)] (**5**). The imido complex [TaCp*\{η^2-C_6H_4(2-CH_2NMeCH_2)\}(N^t-Bu)] (**6**) is obtained by reacting the monoamido derivative **5** with an additional 1 equiv of LiNH^{t}Bu, whereas the related reaction of complex **4** with $LiNMe_2$ leads, via α-H elimination, to the tantalacycloalkylidene complex [TaCp*\{η^2-C_6H_4(2-CH_2NMeCH)\}(NMe_2)] (**7**). A similar reaction is also observed when complex **2** is treated with 1 equiv of $LiN(SiMe_3)_2$, giving the chlorotantalacycloalkylidene complex [TaCp*Cl\{η^2-C_6H_4(2-CH_2NMeCH)\}] (**8**); no amido complex was isolated in this case. All compounds were characterized by IR and NMR spectroscopy. The structure of **2** was solved from diffractometer data by a combination of direct and Fourier methods and refined by full-matrix least squares.

Introduction

Increased attention is being focused on group 5 metal alkylidene complexes, stimulated by their use in understanding the chemistry of important catalytic processes, particularly those related to olefin metathesis.[1] More recently, tantalum alkylidenes have been used in ring-opening metathesis polymerization.[2] The pronounced effect of some ancillary ligands on alkylidene reactivity, supported by theoretical studies with related oxo[3] ligands encouraged the development of synthetic studies related to group 5 metal imido complexes.[4] Ligands such as *o*-(methylamino)aryl are able to form cyclometalated complexes[5] containing a five-membered chelate ring that stabilizes electron-deficient metal centers, being convenient substrates to study interesting intramolecular C−H bond activation reactions. Many different metal complexes with this type of ligand have been reported,[6a] and more recently new alkylidene- and alkylidynetantalum derivatives have been isolated.[6b,c]

In this paper, we describe the results obtained by using the 2-[(dimethylamino)methyl]phenyl ligand in the synthesis of new tantalum(V) complexes and their transformation into new cyclometalated tantalum alkylidene derivatives by activation of C−H bonds in one of the methylamino groups of the ligand, promoted by different reagents. We also report the structural characterization of the new complexes and the X-ray molecular structure of [TaCp*Cl_2\{η^3-C_6H_4(2-CH_2NMeCH_2)\}].

Results and Discussion

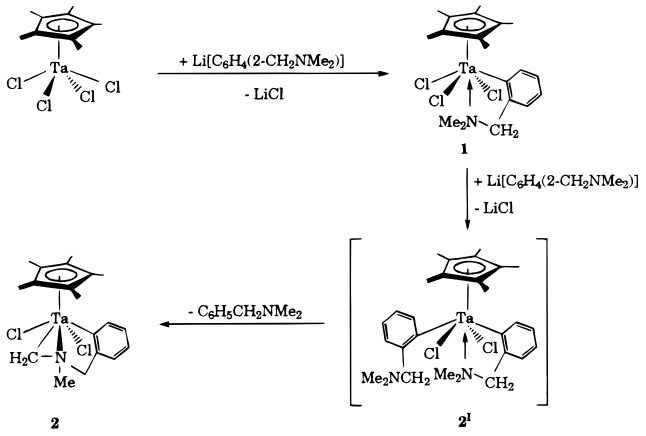
Upon reaction of TaCp*Cl_4 (Cp* = C_5Me_5) with 1 equiv of Li[2-(CH_2NMe_2)C_6H_4] in toluene at room temperature, orange crystals of compound **1** are obtained in high yield following filtration of the solution to remove LiCl (Scheme 1). Spectroscopic data and elemental analyses for **1** are consistent with its formulation as the alkylated compound [TaCp*Cl_3\{C_6H_4(2-CH_2NMe_2)\}]. Coordination of the nitrogen electron pair to the electron-deficient metal center in complex **1** seems to be reasonable because coordination of the donor solvent is not observed when the NMR spectrum is registered in THF-d_8. The NMR data (see Experimental Section) show that the protons within both Me_2N and NCH_2Ta are equivalent, consistent with the presence

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) Schrock, R. R. *Science* **1983**, *219*, 13.
(2) (a) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (b) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.
(3) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448.
(4) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
(5) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451 and references therein.
(6) (a) Abbenhuis, H. C. L.; van Belzen, R.; Grove, D. M.; Klomp, A. J. A.; van Mier, G. M. P.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 210 and references therein. (b) Abbenhuis, H. C. L.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 446. (c) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Kooijman, H.; Spek, A. L.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 996.

0276-7333/96/2315-1362$12.00/0

Scheme 1



of a plane of symmetry defined by the tantalacycle. If the arylamine ligand is coordinated in a bidentate fashion, giving a stabilized cyclometalated complex, which contains a five-membered chelate ring, it has to occupy one equatorial and one axial position, in a plane perpendicular to the cyclopentadienyl ring. Complex **1** is a thermally stable, air-sensitive compound soluble in aromatic hydrocarbons.

When the same reaction is carried out by using 2 equiv of the alkylating agent, a dark red-garnet crystalline solid is obtained, characterized as [TaCp*Cl_2\{η^3-C_6H_4(2-CH_2NMeCH_2)\}] (**2**). As illustrated in Scheme 1, the formation of compound **2** takes place by elimination of *N*,*N*-dimethylbenzylamine through C−H bond activation of one of the methyl groups of the coordinated amine, a spontaneous transformation at room temperature which prevents isolation of the diarylated intermediate. The alleviation of the steric hindrance in the crowded diarylated complex is probably the determining step which causes spontaneous β-H elimination to occur. A related transformation has been reported[6a] for [$TaCl_2(\eta^3$-arylNMe_2)$(CH_2Ph)_2$] (arylNMe_2 = C_6H_4CH(Me)NMe_2-2 and 1-$C_{10}H_6$NMe_2-8), which led to the same $MeNCH_2$ unit by thermal C−H activation with concomitant formation of toluene. Compound **2** can also be formed by treating **1** with 1 equiv of the lithium reagent. The ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature shows an AB spin system for the tantalum-bonded methylene group Ta*C*H_2NMe (δ_{av} = 3.26 ppm, $\Delta\delta$ = 0.14 ppm, $^2J_{H-H}$ = 4.7 Hz) and one singlet for the N*C*H_2Ar protons, whereas at −60 °C in $CDCl_3$ (500 MHz) this singlet is resolved in another AB spin system (δ_{av} = 4.44 ppm, $\Delta\delta$ = 0.05 ppm, $^2J_{H-H}$ = 14.5 Hz) without any change of line width. The ^{13}C NMR spectrum of **2** shows one signal due to the phenyl C_{ipso} atom bonded to the metal at δ 205.6 ppm and two signals at δ 84.2 ppm ($^1J_{C-H}$ = 155.2 Hz) and at δ 70.7 ppm ($^1J_{C-H}$ = 136.5 Hz) which were assigned to the Ta*C*H_2NMe and NMe_2*C*H_2Ar resonances, respectively.

The molecular structure of complex **2** was studied by X-ray diffraction methods on a crystal obtained by cooling a saturated toluene solution to −20 °C. A problem of disorder involving probably two kinds of molecules was observed in the structural resolution of the methylene carbon. Figure 1 shows the approximately pseudo-octahedral structure of **2**, and Table 1 summarizes the selected bond distances and angles for both molecules. As Figure 1 shows, the four positions of the equatorial plane, which is almost parallel to the cyclopentadienyl ring (dihedral angle 3°), are occupied by two chlorines, the aryl-bonded carbon, and the amine nitrogen atom. The Ta(1)−N(1) and Ta(1)−C(21) bond distances are 2.240(4) and 2.218(6) Å, respectively, consistent with single bonds. The Ta(1)−Cl(1) distance trans to nitrogen (2.364(1) Å) is shorter than the Ta(1)−Cl(2) distance trans to the aryl carbon (2.453(2) Å). The structural resolution locates the methylene carbon of the NCH_2 unit in two different positions. One of the molecules shows the carbon atom C(2) (60% population) of the activated methylamino group located in the axial position trans to the cyclopentadienyl ring. The intramolecular coordination of the NCH_2 group generates a triangular Ta−C−N unit with a very narrow N(1)−Ta(1)−C(2) angle of 40.2(3)° and Ta(1)−C(2) (2.26(1) Å) and Ta(1)−N(1) (2.240(4) Å) single bond distances, whereas a long C(2)−N(1) (1.55(1) Å) distance is observed. This unit is therefore best described as a Ta−CH_2 σ-bond combined with a σ-donor N−Ta interaction. The second molecule shows the carbon atom C(2b) (40% population) with a Ta−C(2b) distance (3.01 Å) too long for a bonding interaction and a shorter N(1)−C(2b) distance (1.45 Å), which could be better considered as a Ta(III) complex with a coordinated iminium ion[6a] N^+=CH_2. The two types of C(2)H_2 groups were however not observed in the ^{1}H NMR spectrum recorded in solution at low temperature (500 MHz) nor in the ^{13}C CP MAS spectrum (75.3 MHz).

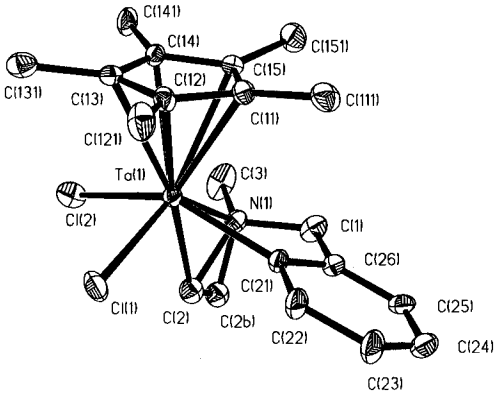


Figure 1. ORTEP view of the molecular structure of TaCp*Cl_2\{η^3-C_6H_4(2-CH_2NMeCH_2)\} (**2**) with the atom-numbering scheme. Atoms labeled C(2) (60%) and C(2b) (40%) correspond to a disorder position.

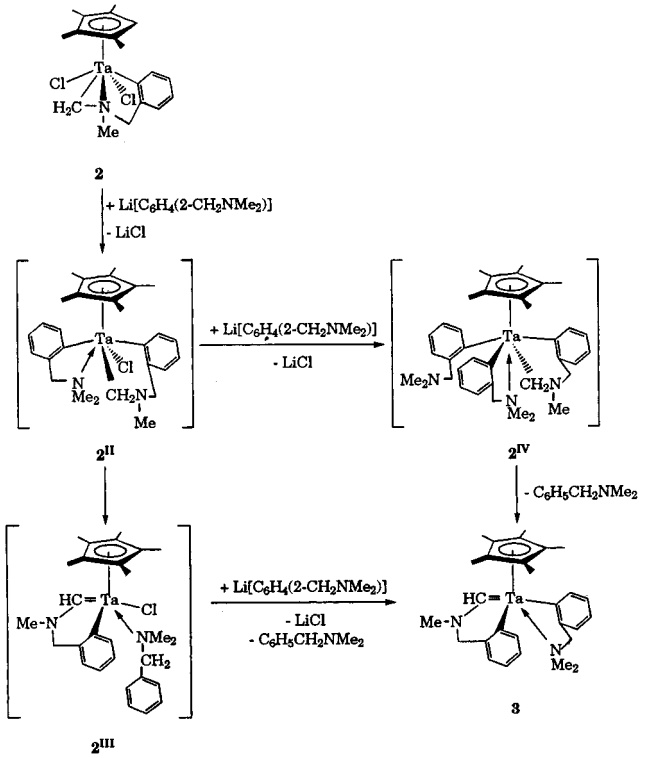
Table 1. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for 2[a]

Bond Distances			
Ta(1)−Cl(1)	2.364(1)	Ta(1)−CE	2.139
Ta(1)−Cl(2)	2.453(2)	N(1)−C(1)	1.486(9)
Ta(1)−N(1)	2.240(4)	N(1)−C(2)	1.55(1)
Ta(1)−C(21)	2.218(6)	N(1)−C(3)	1.486(9)
Ta(1)−C(2)	2.26(1)	C(26)−C(1)	1.495(9)
Ta(1)−C(2b)	3.01(1)	N(1)−C(2b)	1.45(1)

Bond Angles			
Cl(1)−Ta(1)−Cl(2)	87.7(6)	C(21)−Ta(1)−CE	104.7
Cl(1)−Ta(1)−C(21)	88.8(2)	C(2)−Ta(1)−N(1)	40.2(3)
Cl(1)−Ta(1)−C(2)	91.2(2)	C(2)−Ta(1)−CE	158.8
Cl(1)−Ta(1)−CE	109.9	N(1)−Ta(1)−CE	118.6
Cl(2)−Ta(1)−N(1)	84.9(1)	Ta(1)−C(2)−N(1)	69.3(4)
Cl(2)−Ta(1)−C(2)	74.0(3)	Ta(1)−C(21)−C(26)	117.8(4)
Cl(2)−Ta(1)−CE	107.3	C(1)−N(1)−C(3)	109.6(5)
C(21)−Ta(1)−N(1)	73.0(2)	C(2)−N(1)−C(1)	116.0(6)
C(21)−Ta(1)−C(2)	73.4(3)	C(2b)−N(1)−C(1)	101.4(8)
C(3)−N(1)−C(2b)	100.3(8)		

[a] CE is the centroid of the C_5Me_5 ring.

Scheme 2



Compound **2** reacts further with an additional 2 equiv of the lithium reagent to give purple crystals of compound **3**, characterized as [TaCp*{η^2-C_6H_4(2-CH_2-NMe_2)}{η^2-C_6H_4(2-CH_2NMeCH)}]. Formation of **3** could be explained by a similar sequence of reactions involving in this case the α-H elimination process from a previously alkylarylated tantalacycle intermediate (Scheme 2). The same reaction also occurs when 4 equiv of the lithium reagent are added to the starting complex TaCp*Cl_4. None of the postulated intermediates shown in Schemes 1 and 2 could be isolated either from the reaction of TaCp*Cl_4 with only 3 equiv of the lithium reagent or by the reaction of **2** with 1 equiv of aryllithium; the latter reaction gives a mixture of compound **3** together with unreacted **2**. Compound **3** contains a cyclometalated bidentate arylamine ligand, similar to that found in complex **1**, and a cyclometalated bidentate arylalkylidene ligand.

The alkylidene character of the activated methylamine group is confirmed by its ^{1}H and ^{13}C NMR spectra, which show the *H*C═Ta resonance at δ 7.83 ppm and H*C*═Ta doublet at δ 227.8 ppm ($^1J_{C-H}$ = 170.3 Hz), respectively. This J_{C-H} and those described below, which are the highest coupling constants reported for alkylidenetantalum compounds, are in the range known for olefins substituted by electronegative groups. So a high value of J_{C-H} could be due to the presence of the amino substituent and the more electronegative phenyl groups bonded to the metal, although the available data do not allow a definitive answer to this behavior. The ^{13}C NMR spectrum shows the presence of two phenyl C_{ipso} carbons (δ 195.2 and 190.1 ppm) bonded to tantalum, two types of $^{13}CH_2$ carbons at δ 74.0 ppm (t q, $^1J_{C-H}$ = 134 Hz) and at δ 77.0 ppm (t sept, $^1J_{C-H}$ = 132 Hz) assigned to the resonances of Me*N*CH_2Ar and Me_2*N*CH_2-Ar, respectively, in accord with the multiplicity of these signals. The ^{1}H NMR spectrum of **3** at room temperature shows two inequivalent *Me*$_2$N groups and two AB systems: δ_{av} = 4.13 ($\Delta\delta$ = 0.23 ppm, $^2J_{H-H}$ = 16 Hz) and δ_{av} = 3.31 ($\Delta\delta$ = 0.8 ppm, $^2J_{H-H}$ = 13.5 Hz) assigned to the methylene protons of Me_2N*C*H_2Ar and MeN*C*H_2-Ar, respectively. The ^{1}H chemical shifts of the CH_2 group in the arylamine ligand are very similar for complexes **1** (δ = 4.19 ppm) and **3** (δ_{av} = 4.13 ppm), whereas that of the (arylamino)alkylidene ligand is clearly different (δ_{av} = 3.31 ppm) and also a great inequivalency ($\Delta\delta$ = 0.8 ppm) is observed for its two MeN*C*H_2Ar protons. We were not able to isolate crystals of complex **3** adequate for X-ray diffraction studies, to confirm its assumed pseudo-square pyramidal structure.

Complexes **2** and **3** can be regarded as the products arising by β- and α-hydrogen abstraction, respectively, from one of the methyl groups of the NMe_2 unit by a strong Lewis base such as the lithium derivative of the anionic arylamine ligand. In order to obtain additional data on this type of C−H activation process in compounds containing the bidentate arylamine ligand, we studied the reactions of **2** with different lithium amides.

As shown in Scheme 3, the reaction of **2** with 1 equiv of LiNMe_2 in toluene gives a brown-orange crystalline solid identified by its elemental analysis and spectroscopic data as the amido derivative [TaCp*Cl{η^2-C_6H_4(2-CH_2N*Me*CH_2)}(NMe_2)] (**4**). Compound **4** is thermally stable, very air and moisture sensitive, and very soluble in aliphatic and aromatic hydrocarbons. When complex **2** is reacted with 2 equiv of LiNMe_2, the expected diamido complex is spontaneously converted, via α-hydrogen elimination from one of the methylamine groups of the cyclometalated arylalkyl ligand, into the related cycloalkylidene derivative. The resulting compound was characterized from its elemental analysis and spectroscopic data as [TaCp*{η^2-C_6H_4(2-CH_2NMeCH)}(NMe_2)] (**7**), an air- and moisture-sensitive brown-red crystalline solid very soluble in aliphatic and aromatic hydrocarbons. The ^{1}H and ^{13}C NMR data for the new amido compounds **4** and **7** are very similar to those of the related complexes **2** and **3**, respectively (see Experimental Section). The variable-temperature NMR spectra of **4** and **7** show different dynamic behavior for the methyl amido groups. At room temperature the ^{1}H NMR spectrum of **4** shows the presence of two inequivalent interchanging methyl groups. The kinetic parameters obtained by ^{1}H DNMR[7] (log A = 12.3 ± 0.6, E_a = 17.5 ± 0.9 kcal/mol, $\Delta H^{\ddagger}$ = 17.6 ± 0.9 kcal/mol, $\Delta S^{\ddagger}$ = −0.3 ± 2.8 eu, $\Delta G^{\ddagger 298K}$ = 17.7 kcal/mol)[8] are consistent with the rotation of the amido group about the Ta−N bond, whereas the ^{1}H and ^{13}C{^{1}H} NMR spectra of **7** show only one signal for both methylamido groups at 183 K.[9] This behavior suggests that in compound **4** there is a significant π-donation from the nitrogen lone pair to the electron-deficient tantalum center, increasing the multiplicity of the Ta−N bond whereas in compound **7** the higher electron density of the metal prevents similar π-donation.

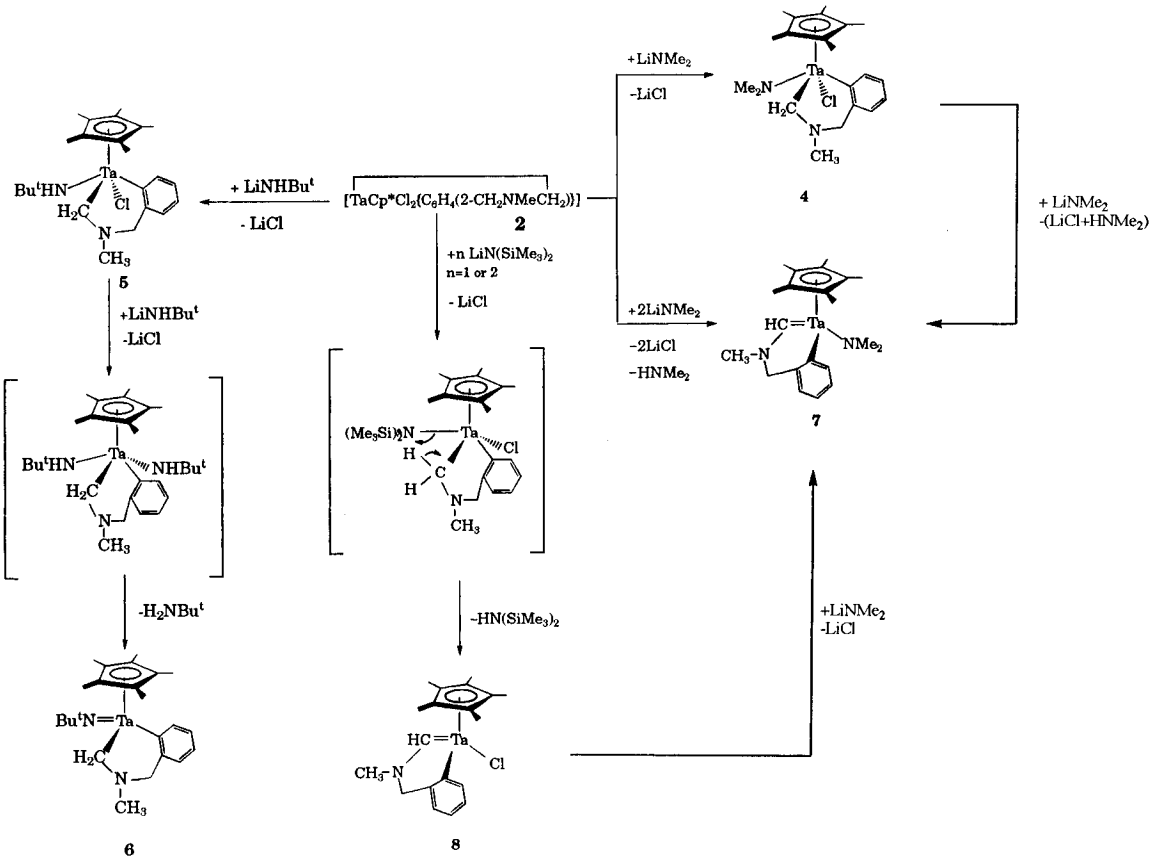
The same spontaneous α-hydrogen elimination takes place when a bulkier amide is used. Reactions of

(7) (a) Abragam, S. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, U.K., 1961. (b) Jackman, K. M.; Cotton, F. A. *DNMR Spectroscopy*; Academic Press: New York, 1975.

(8) The kinetic parameters were obtained between 298 and 340 K from Arrhenius and Eyring equations by using the approximation of slow interchange of two positions.

(9) Using a Varian-Unity 500 Plus NMR spectrometer.

Scheme 3



compound **2** with either 1 or 2 equiv of $LiN(SiMe_3)_2$ lead to a single chloro arylalkylidene complex [TaCp*Cl{η^2-C_6H_4(2-CH_2NMeCH)}] (**8**), isolated as a brown-orange air-sensitive solid, soluble in THF, OEt_2, and aliphatic and aromatic hydrocarbons. Complex **8** is converted to **7** by reaction with $LiNMe_2$. Spectroscopic data for **8** (see Experimental Section) confirm that its molecular structure is similar to that described for the related amido complex **7**.

When primary amides are used, the preferential α-hydrogen elimination of the amido proton takes place. Reaction of compound **2** with 1 equiv of $LiNH^tBu$ enables the isolation of the amido derivative [TaCp*Cl{η^2-C_6H_4(2-CH_2NMeCH$_2$)}(NH^tBu)] (**5**) as a very air sensitive red-violet microcrystalline solid. However, when the reaction time is extended for more than 4 h, compound **5** is slowly transformed into the imido complex [TaCp*{η^2-C_6H_4(2-CH_2NMeCH$_2$)}(N^tBu)] (**6**). Compound **6** is rapidly and quantitatively formed when 2 equiv of $LiNH^tBu$ are used, with simultaneous elimination of *tert*-butylamine (Scheme 3). Compounds **5** and **6** were characterized by their elemental analyses and spectroscopic data (see Experimental Section), and all the byproducts were qualitatively identified by GCMS of samples of the final solutions.

Conclusions

The behavior observed shows that tantalum cyclometalated complexes with a coordinated NMe_2 chelating unit undergo spontaneous β-C−H activation of one of the methylamine groups by reaction with the lithium derivative of the anionic ligand, leading to (alkylamino)-aryl cyclometalated compounds. A further α-C−H activation takes place in the same alkyl carbon atom when the (alkylamino)aryl complex is treated with strong Lewis bases, such as the lithium derivative of the anionic ligand. Different products are obtained when lithium amides are used. Preferential metathesis with elimination of lithium chloride results from the reaction with 1 equivalent of primary ($LiNH^tBu$) or secondary ($LiNMe_2$) amides leading to the chloro amido compounds [TaCp*Cl{η^2-C_6H_4(2-CH_2NMeCH$_2$)}(amide)] (amide = NMe_2, NH^tBu), whereas α-C−H activation takes place with the bulkier amide $LiN(SiMe_3)_2$, resulting in the formation of the chloro (arylamino)alkylidene complex [TaCp*Cl{η^2-C_6H_4(2-CH_2NMeCH)}]. Addition of a second 1 equiv of a secondary amide produces the α-C−H activation of the ligand, leading to the (arylamino)alkylidene complex [TaCp*{η^2-C_6H_4(2-CH_2-NMeCH)}(NMe_2)], whereas preferential deprotonation of the amide is observed in the case of primary amides, leading to the imido complex [TaCp*{η^2-C_6H_4(2-CH_2-NMeCH$_2$)}(N^tBu)].

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk techniques and solids handled in a Vacuum Atmosphere glovebox equipped with an HE-63-P Dri-Train. Solvents were dried over appropriate reagents and distilled under argon before use by employing the drying agents in parentheses: toluene (sodium) and *n*-hexane (sodium−potassium alloy). $TaCp^*Cl_4$,[10] Li[C_6H_4(2-CH_2NMe_2)],[11] and LiN-

(10) Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157.
(11) Jastrzebski, J. T. B. H.; van Koten, G. *Inorg. Synth.* **1989**, *26*, 152.

$(SiMe_3)_2$[12] were prepared according to literature procedures. LiNH^{t}Bu was prepared by treatment of $NH_2{}^t$Bu with Li^{n}Bu. $LiNMe_2$ was purchased from commercial sources (Aldrich) and used as received.

Infrared spectra were reocrded on a Perkin-Elmer 583 spectrophotometer (4000−200 cm^{-1}) as Nujol mulls between CsI pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity-300 instrument, and chemical shifts are reported in δ units (positive chemical shifts to a higher frequency) relative to a TMS standard. The ^1H DNMR spectra were recorded on a Varian Unity-500 Plus instrument. C, H, and N analyses were performed with a Perkin-Elmer 240C microanalyzer.

Preparation of TaCp*Cl$_3$[C$_6$H$_4$(2-CH$_2$NMe$_2$)] (1). A suspension of Li[C_6H_4(2-CH_2NMe_2)] (0.15 g, 1.09 mmol) in toluene (30 mL) was added to a stirred suspension of TaCp*Cl_4 (0.50 g, 1.09 mmol) in toluene (50 mL). After being stirred for 1.5 h at room temperature, the mixture was filtered and the resulting orange solution was concentrated and cooled at −20 °C overnight to give crystals of the monoaryl derivative. The data for **1** are as follows. Yield: 0.54 g (90%). IR (Nujol mull; ν, cm^{-1}): 1580 (w), 1176 (m), 1048 (m), 1018 (s), 977 (s), 845 (s), 750 (s), 610 (m), 519 (s), 456 (m), 417 (m), 290 (s), 253 (s). ^1H NMR (δ ppm, in C_6D_6): 7.94 (d, 1H, *o*-H, H_4C_6), 7.13 (m, 2H, H_4C_6), 7.03 (d, 1H, H_4C_6), 4.19 (s, 2H, C$H_2C_6H_4$), 2.89 (s, 6H, Me_2N), 2.29 (s, 15H, C_5Me_5). ^{13}C NMR (δ ppm, in C_6D_6): 203.4 (m, C_i, C_6H_4), 144.8 (m, C_6H_4), 141.0 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 130.8 (s, C_5Me_5), 129.3 (m, C_6H_4), 126.7 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 125.6 (dm, $^1J_{C-H}$ = 156 Hz, C_6H_4), 73.5 (t, $^1J_{C-H}$ = 136 Hz, C$H_2C_6H_4$), 52.8 (q, $^1J_{C-H}$ = 140 Hz, *Me*$_2$N), 14.0 (q, $^1J_{C-H}$ = 129 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{19}H_{27}Cl_3NTa$: C, 40.98; H, 4.89; N, 2.51. Found: C, 40.95; H, 4.89; N, 2.48.

Preparation of [TaCp*Cl$_2${η^3-C$_6$H$_4$(2-CH$_2$NMeCH$_2$)}] (2). Method 1. A suspension of Li[C_6H_4(2-CH_2NMe_2)] (0.31 g, 2.18 mmol) in toluene (30 mL) was added to a stirring suspension of TaCp*Cl_4 (0.50 g, 1.09 mmol) in toluene (50 mL). After 2 h at room temperature, a dark red-garnet solution was obtained. This solution was filtered off, concentrated, and cooled at −20 °C to give the *ortho*-phenyleneazacycloalkyl **2** as red-garnet crystals.

Method 2. Li[C_6H_4(2-CH_2NMe_2)] (0.12 g, 0.87 mmol) in toluene (30 mL) was added to a stirring solution of **1** (0.48 g, 0.87 mmol) in toluene (40 mL); the initially orange solution became dark red, and stirring was continued for 2 h. The isolated product characterized as metallacycle **2** with *N*,*N*-dimethylbenzylamine, $C_6H_5CH_2NMe_2$, as byproduct.

The data for **2** are as follows. Yield: 0.47 g (82%). IR (Nujol mull; ν, cm^{-1}): 1574 (w), 1250 (m), 1163 (m), 1050 (s), 1024 (s), 979 (s), 830 (m), 750 (s), 518 (w), 456 (m), 322 (s), 258 (m). ^1H NMR (δ ppm, in C_6D_6): 7.36 (d, 1H, *o*-H, H_4C_6), 7.00 (m, 2H, H_4C_6), 6.74 (d, 1H, H_4C_6), 3.62 (s, 2H, C$H_2C_6H_4$), 3.33 (d, 1H, $^2J_{H-H}$ = 4.7 Hz, CH_2Ta), 3.19 (d, 1H, $^2J_{H-H}$ = 4.7 Hz, CH_2-Ta), 2.45 (s, 3H, NMe), 1.79 (s, 15H, C_5Me_5). ^{13}C NMR (δ ppm, in C_6D_6): 205.6 (m, C_i, C_6H_4), 139.9 (dm, $^1J_{C-H}$ = 156 Hz, C_6H_4), 137.9 (m, C_6H_4), 126.8 (m, C_6H_4), 126.0 (s, C_5Me_5), 124.6 (m, C_6H_4), 124.5 (m, C_6H_4), 84.2 (t, $^1J_{C-H}$ = 155.2 Hz, CH_2Ta), 70.7 (t, $^1J_{C-H}$ = 136.5 Hz, C$H_2C_6H_4$), 51.4 (q, $^1J_{C-H}$ = 139 Hz, N*Me*), 11.6 (q, $^1J_{C-H}$ = 127 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{19}H_{26}Cl_2NTa$: C, 43.87; H, 5.01; N, 2.69. Found: C, 43.95; H, 5.01; N, 2.73.

Preparation of [TaCp*(η^2-C$_6$H$_4$(2-CH$_2$NMe$_2$)}{η^2-C$_6$H$_4$(2-CH$_2$NMeCH)}] (3). Toluene (100 mL) was added to a mixture of TaCp*Cl_4 (1.00 g, 2.18 mmol) and Li[C_6H_4(2-CH_2NMe_2)] (1.23 g, 8.73 mmol) at room temperature, and the mixture was stirred for 12 h. The suspension was removed by filtration, and the resulting solution was concentrated to ca. 20 mL. On cooling, a crystalline product was isolated and characterized as **3**. The data for **3** are as follows. Yield: 1.09 g (86%). IR (Nujol mull; ν, cm^{-1}): 1574 (w), 1066 (s), 1024 (s), 848 (s), 644 (m), 608 (m), 484 (m), 446 (m), 351 (m). ^1H NMR (δ ppm, in C_6D_6): 7.83 (s, 1H, *H*C═Ta), 7.78 (d, 1H, *o*-H, H_4C_6), 7.65 (d, 1H, *o*-H, H_4C_6), 7.21 (m, 2H, H_4C_6), 7.12−7.05 (m, 4H, H_4C_6), 4.25 (d, 1H, $^2J_{H-H}$ = 16 Hz, C$H_2C_6H_4$), 4.02 (d, 1H, $^2J_{H-H}$ = 16 Hz, C$H_2C_6H_4$), 3.71 (d, 1H, $^2J_{H-H}$ = 13.5 Hz, C$H_2C_6H_4$), 2.91 (d, 1H, $^2J_{H-H}$ = 13.5 Hz, C$H_2C_6H_4$), 2.74 (s, 3H, NMe), 1.97 (s, br, 3H, Me_2N), 1.85 (s, br, 3H, Me_2N), 1.75 (s, 15H, C_5Me_5). ^{13}C NMR (δ ppm, in C_6D_6): 227.8 (d, $^1J_{C-H}$ = 170.3 Hz, H*C*═Ta), 195.2 (m, C_i, C_6H_4), 190.1 (m, C_i, C_6H_4), 149.7 (m, C_6H_4), 148.3 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 146.9 (m, C_6H_4), 142.1 (dd, $^1J_{C-H}$ = 51 Hz, C_6H_4), 124.7 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 124.2 (dd, $^1J_{C-H}$ = 157 Hz, C_6H_4), 123.4 (dd, $^1J_{C-H}$ = 151 Hz, C_6H_4), 122.9 (dd, $^1J_{C-H}$ = 151 Hz, C_6H_4), 110.6 (s, C_5Me_5), 77.0 (t, $^1J_{C-H}$ = 132 Hz, C$H_2C_6H_4$), 74.0 (t, $^1J_{C-H}$ = 133.6 Hz, C$H_2C_6H_4$), 50.4 (q, $^1J_{C-H}$ = 135 Hz, N*Me*$_2$), 49.1 (q, $^1J_{C-H}$ = 136 Hz, N*Me*), 12.2 (q, $^1J_{C-H}$ = 127 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{28}H_{37}N_2Ta$: C, 57.73; H, 6.40; N, 4.80. Found: C, 57.65; H, 6.50; N, 4.64.

Preparation of [TaCp*Cl{η^2-C$_6$H$_4$(2-CH$_2$NMeCH$_2$)}-(NMe$_2$)] (4). $LiNMe_2$ (0.04 g, 0.87 mmol) was added to a toluene (50 mL) solution of **2** (0.45 g, 0.87 mmol), and the mixture was stirred overnight at room temperature. The LiCl formed was removed by filtration and the resulting solution concentrated. Cool *n*-hexane (5 mL) was slowly added, and the product crystallized out as an orange crystalline solid after 12 h at −40 °C. The data for **4** are as follows. Yield: 0.36 g (78%). IR (Nujol mull; ν, cm^{-1}): 1577 (w), 1254 (m), 1129 (s), 1024 (s), 959 (s), 697 (m), 452 (m), 402 (m), 262 (s). ^1H NMR (δ ppm, in C_6D_6): 7.13−7.00 (m, 3H, H_4C_6), 6.86 (d, 1H, H_4C_6), 3.88 (d, 1H, $^2J_{H-H}$ = 14 Hz, C$H_2C_6H_4$), 3.64 (d, 1H, $^2J_{H-H}$ = 14 Hz, C$H_2C_6H_4$), 3.75 (s, 3H, TaNMe_2), 3.64 (s, 3H, TaNMe_2), 3.13 (d, 1H, $^2J_{H-H}$ = 5 Hz, CH_2Ta), 1.95 (d, 1H, $^2J_{H-H}$ = 5 Hz, CH_2Ta), 2.57 (s, 3H, NMe), 1.74 (s, 15H, C_5Me_5). ^{13}C NMR (δ ppm, in THF-d_8): 201.8 (m, C_i, C_6H_4), 141.2 (m, C_6H_4), 139.9 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 127.1 (dd, $^1J_{C-H}$ = 155 Hz, C_6H_4), 124.2 (dd, $^1J_{C-H}$ = 158 Hz, C_6H_4), 123.5 (dd, $^1J_{C-H}$ = 154 Hz, C_6H_4), 121.3 (s, C_5Me_5), 83.9 (t, $^1J_{C-H}$ = 150 Hz, CH_2Ta), 72.1 (t, $^1J_{C-H}$ = 137 Hz, C$H_2C_6H_4$), 55.5 (q, $^1J_{C-H}$ = 135 Hz, TaN*Me*$_2$), 51.2 (q, $^1J_{C-H}$ = 134 Hz, TaN*Me*$_2$), 49.3 (q, $^1J_{C-H}$ = 138 Hz, N*Me*), 11.9 (q, $^1J_{C-H}$ = 129 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{21}H_{32}ClN_2Ta$: C, 47.68; H, 6.09; N, 5.29. Found: C, 48.10; H, 5.97; N, 5.19.

Preparation of [TaCp*Cl{η^2-C$_6$H$_4$(2-CH$_2$NMeCH$_2$)}(NH^t-Bu)] (5). Toluene (50 mL) was added to a mixture of **2** (1.00 g, 1.92 mmol) and LiNH^{t}Bu (0.15 g, 1.92 mmol); the mixture was stirred at room temperature for 1 h followed by filtration to remove the suspended solid. Concentration of the filtrate to ca. 20 mL, followed by cooling to −20 °C for 18 h, gave a red-violet microcrystalline solid. The data for **5** are as follows. Yield: 0.90 g (84%). IR (Nujol mull; ν, cm^{-1}): 3337 (m), 1356 (m), 1204 (m), 1025 (s), 969 (s), 826 (s), 670 (m), 595 (m), 536 (m), 445 (m), 421 (m), 405 (w), 281 (s). ^1H NMR (δ ppm, in C_6D_6): 7.30 (d, 1H, *o*-H, H_4C_6), 7.04 (m, 2H, H_4C_6), 6.87 (d, 1H, H_4C_6), 6.51 (s, 1H, TaN*H*CMe$_3$), 3.85 (d, 1H, $^2J_{H-H}$ = 14.5 Hz, C$H_2C_6H_4$), 3.67 (d, 1H, $^2J_{H-H}$ = 14.5 Hz, C$H_2C_6H_4$), 3.09 (d, 1H, $^2J_{H-H}$ = 5.5 Hz, CH_2Ta), 2.39 (d, 1H, $^2J_{H-H}$ = 5.5 Hz, CH_2Ta), 2.69 (s, 3H, NMe), 1.71 (s, 15H, C_5Me_5), 1.34 (s, 9H, TaNHC*Me*$_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in C_6D_6): 197.7 (s, C_i, C_6H_4), 140.9 (s, C_6H_4), 139.1 (s, C_6H_4), 125.3 (s, C_6H_4), 123.7 (s, C_6H_4), 119.0 (s, C_5Me_5), 82.2 (s, CH_2Ta), 71.1 (s, C$H_2C_6H_4$), 61.4 (s, TaNHCMe_3), 47.7 (s, N*Me*), 32.6 (s, TaNHC*Me*$_3$), 11.4 (s, C_5*Me*$_5$). Anal. Calcd for $C_{23}H_{36}ClN_2Ta$: C, 49.60; H, 6.51; N, 5.03. Found: C, 49.05; H, 6.38; N, 4.91.

Preparation of [TaCp*{η^2-C$_6$H$_4$(2-CH$_2$NMeCH$_2$)}(N^t-Bu)] (6). Toluene (50 mL) was added to a mixture of **2** (1.33 g, 2.55 mmol) and LiNH^{t}Bu (0.41 g, 5.11 mmol) at room temperature. After being stirred for 12 h, the resulting suspension was filtered off and a violet solution was obtained. Partial evaporation of solvent and subsequent cooling at −20 °C gave a pale violet microcrystalline solid. The data for **6** are as follows. Yield: 1.20 g (90%). IR (Nujol mull; ν, cm^{-1}):

(12) Amonoo-Neizer, E. H.; Shaw, R. A.; Skovlin, D. O.; Smith, B. C. *Inorg. Synth.* **1966**, *8*, 19.

1350 (m), 1270 (s), 1210 (m), 1058 (m), 1026 (m), 966 (m), 826 (m), 610 (m), 534 (m), 484 (w), 458 (w), 340 (s). ^{1}H NMR (δ ppm, in C_6D_6): 8.15 (d, 1H, *o*-H, H_4C_6), 7.30 (t, 1H, H_4C_6), 7.08 (m, 2H, H_4C_6), 3.66 (d, 1H, $^2J_{H-H}$ = 14.5 Hz, $CH_2C_6H_4$), 2.85 (d, 1H, $^2J_{H-H}$ = 8.8 Hz, CH_2Ta), 2.68 (s, 3H, NMe), 2.51 (d, 1H, $^2J_{H-H}$ = 14.5 Hz, $CH_2C_6H_4$), 1.83 (s, 15H, C_5Me_5), 1.20 (s, 9H, $TaNCMe_3$). ^{13}C{^{1}H} NMR (δ ppm, in C_6D_6): 184.5 (s, C_i, C_6H_4), 150.4 (s, C_6H_4), 141.2 (s, C_6H_4), 125.7 (s, C_6H_4), 124.5 (s, C_6H_4), 123.1 (s, C_6H_4), 112.4 (s, C_5Me_5), 67.8 (s, CH_2Ta), 67.0 (s, $CH_2C_6H_4$), 64.6 (s, $TaNCMe_3$), 52.2 (s, N*Me*), 34.0 (s, $TaNCMe_3$), 11.8 (s, C_5Me_5). Anal. Calcd for $C_{23}H_{35}N_2Ta$: C, 53.07; H, 6.78; N, 5.30. Found: C, 53.16; H, 6.63; N, 5.28.

Preparation of [TaCp*{η^2-C_6H_4(2-CH_2NMeCH)}(NMe_2)] (7). To a toluene (10 mL) solution of $LiNMe_2$ (0.18 g, 3.50 mmol) was added a toluene (50 mL) solution of **2** (0.91 g, 1.75 mmol), and the mixture was stirred for 12 h at room temperature. The suspension was filtered, and the solution was evaporated to dryness. The resulting brown oil was extracted with *n*-hexane (2 × 5 mL). After cooling, a brown-red crystalline solid was recovered and identified as complex **7**. The data for **7** are as follows. Yield: 0.69 g (80%). IR (Nujol mull; ν, cm^{-1}): 1548 (w), 1244 (m), 1147 (m), 1026 (m), 950 (s), 586 (m), 436 (m), 405 (w). ^{1}H NMR (δ ppm, in C_6D_6): 8.31 (s, 1H, *H*C═Ta), 7.83 (d, 1H, *o*-H, H_4C_6), 7.26 (m, 2H, H_4C_6), 7.21 (d, 1H, H_4C_6), 4.64 (d, 1H, $^2J_{H-H}$ = 15 Hz, $CH_2C_6H_4$), 3.66 (d, 1H, $^2J_{H-H}$ = 15 Hz, $CH_2C_6H_4$), 3.10 (s, 3H, NMe), 2.92 (s, 6H, $TaNMe_2$), 1.93 (s, 15H, C_5Me_5). ^{13}C NMR (δ ppm, in C_6D_6): 222.1 (d, $^1J_{C-H}$ = 169 Hz, H*C*═Ta), 188.4 (m, C_i, C_6H_4), 152.9 (m, C_6H_4), 137.8 (dd, $^1J_{C-H}$ = 153 Hz, C_6H_4), 126.7 (dd, $^1J_{C-H}$ = 158 Hz, C_6H_4), 124.4 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 122.2 (dd, $^1J_{C-H}$ = 153 Hz, C_6H_4), 112.2 (s, C_5Me_5), 81.4 (t, $^1J_{CH}$ = 133 Hz, $CH_2C_6H_4$), 54.6 (q, $^1J_{C-H}$ = 135 Hz, N*Me*), 47.2 (q, $^1J_{C-H}$ = 134 Hz, $TaNMe_2$), 11.5 (q, $^1J_{C-H}$ = 126 Hz, C_5Me_5). Anal. Calcd for $C_{21}H_{31}N_2Ta$: C, 51.22; H, 6.36; N, 5.69. Found: C, 51.43; H, 6.44; N, 5.37.

Preparation of [TaCp*Cl{η^2-C_6H_4(2-CH_2NMeCH)}] (8). A solution of $LiN(SiMe_3)_2$ (0.14 g, 0.82 mmol) in toluene (15 mL) was added dropwise to a solution of **2** (0.43 g, 0.82 mmol) in toluene (50 mL), and the mixture was stirred at room temperature for 12 h. After filtration to remove the resulting LiCl, the brown solution was concentrated to ca. 25 mL and cooled at −20 °C to give a brown-orange solid characterized as **8**. The data for **8** are as follows. Yield: 0.32 g (81%). IR (Nujol mull; ν, cm^{-1}): 1577 (w), 1251 (m), 1025 (s), 1004 (s), 962 (m), 832 (m), 621 (m), 598 (s), 431 (m), 379 (m), 329 (s). ^{1}H NMR (δ ppm, in C_6D_6): 8.16 (s, 1H, *H*C═Ta), 7.86 (d, 1H, *o*-H, H_4C_6), 7.24−7.18 (m, 3H, H_4C_6), 4.50 (d, 1H, $^2J_{H-H}$ = 16.5 Hz, $CH_2C_6H_4$), 4.13 (d, 1H, $^2J_{H-H}$ = 16.5 Hz, $CH_2C_6H_4$), 3.12 (s, 3H, NMe), 1.94 (s, 15H, C_5Me_5). ^{13}C NMR (δ ppm, in C_6D_6): 226.0 (d, $^1J_{C-H}$ = 178 Hz, H*C*═Ta), 188.1 (m, C_i, C_6H_4), 153.4 (m, C_6H_4), 138.0 (dd, $^1J_{C-H}$ = 156 Hz, C_6H_4), 129.2 (m, C_6H_4), 124.5 (dd, $^1J_{C-H}$ = 157 Hz, C_6H_4), 121.8 (dd, $^1J_{C-H}$ = 154 Hz, C_6H_4), 115.0 (s, C_5Me_5), 76.6 (t, $^1J_{C-H}$ = 134 Hz, $CH_2C_6H_4$), 52.6 (q, $^1J_{C-H}$ = 135 Hz, N*Me*), 11.8 (q, $^1J_{C-H}$ = 126 Hz, C_5Me_5). Anal. Calcd for $C_{19}H_{25}ClNTa$: C, 47.17; H, 5.21; N, 2.90. Found: C, 47.43; H, 5.18; N, 3.03.

Structure Determination of 2. Crystallographic and experimental details of the X-ray crystal structure determination for compound **2** are given in Table 2, and final atomic coordinates for the non-hydrogen atoms are given in Table 3 (22 °C). Crystals suitable for the X-ray analyses were obtained from a toluene-saturated solution of **2** at −20 °C. A single crystal of **2** was sealed in a Lindemann glass capillary under dry argon and mounted on an Enraf-Nonius CAD-4 automatic four-circle diffractometer with bisecting geometric and using a graphite-oriented monochromator, with Mo Kα radiation (λ(Mo Kα) = 0.710 73 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No extinction corrections was made. The structure was solved by a combination of direct methods and Fourier synthesis and refined (on *F*) by full-matrix least-squares calculations. Absorption correction was made using DIFABS methods.[13]

Table 2. Experimental Data for the X-ray Diffraction Study of 2

mol formula	$C_{19}H_{26}TaCl_2N$
mol wt	520.13
cryst system	monoclinic
space group	$P2_1/n$
cryst dimers, mm	0.36 × 0.25 × 0.20
unit cell dimens	
a, Å	8.819(4)
b, Å	12.197(5)
c, Å	18.170(6)
β, deg	102.63(2)
V, Å^3	1907(2)
V, Å^3	1907(2)
Z	4
D_{calcd}, g·cm^{-3}	1.812
F(000)	1016
μ(Mo Kα), cm^{-1}	59.78
scan mode	$\omega/2\theta$
2θ range	$4 \le 2\theta \le 50$
reflcns measd	3773
range of *hkl*	$0 < h < 10$
	$0 < k < 14$
	$-21 < l < 21$
indepdt reflcns obsd	3122 [$I \ge 3\sigma(I)$]
R	0.037
R_w	0.039
max peak in final diff map, e/Å^3	0.819
min peak in final diff map, e/Å^3	−1.08

Table 3. Final Atomic Coordinates for the Non-Hydrogen Atoms and Equivalent Isotropic Displacement Parameters with Esd's in Parentheses for 2

atom	*x*	*y*	*z*	*B* (Å^2)[a]
Ta(1)	0.51916(2)	0.29557(2)	0.83814(1)	2.354(4)
Cl(1)	0.5046(2)	0.4821(1)	0.8712(1)	4.22(3)
Cl(2)	0.5501(2)	0.3578(1)	0.71388(9)	4.43(4)
N(1)	0.3385(5)	0.1827(4)	0.7727(3)	3.2(1)
Cl(1)	0.6820(7)	0.1973(4)	0.9478(3)	3.0(1)
C(12)	0.7537(7)	0.3002(4)	0.9410(3)	2.9(1)
C(13)	0.8019(6)	0.3032(4)	0.8715(3)	2.9(1)
C(14)	0.7610(6)	0.2020(4)	0.8350(3)	2.7(1)
C(15)	0.6862(6)	0.1367(4)	0.8811(3)	2.9(1)
C(21)	0.3566(6)	0.2557(5)	0.9117(3)	2.8(1)
C(22)	0.3424(8)	0.3128(5)	0.9772(4)	4.1(1)
C(23)	0.2359(8)	0.2798(6)	1.0192(4)	4.9(2)
C(24)	0.1399(8)	0.1926(6)	0.9976(4)	5.0(2)
C(25)	0.1476(7)	0.1352(5)	0.9322(4)	4.2(1)
C(26)	0.2544(7)	0.1672(5)	0.8907(3)	3.3(1)
C(111)	0.6392(8)	0.1517(6)	1.0169(4)	4.6(2)
C(121)	0.7900(8)	0.3864(5)	1.0023(4)	4.5(1)
C(131)	0.8966(7)	0.3919(5)	0.8474(4)	3.9(1)
C(141)	0.8059(7)	0.1623(6)	0.7642(4)	4.1(1)
C(151)	0.6499(8)	0.0157(5)	0.8703(4)	4.9(2)
C(1)	0.2647(7)	0.1088(5)	0.8197(4)	4.3(1)
C(3)	0.3666(9)	0.1217(6)	0.7061(4)	5.9(2)
C(2)	0.277(1)	0.3019(8)	0.7645(6)	3.7(2)*
C(2b)	0.207(2)	0.251(1)	0.737(1)	4.4(3)*

[a] Starred *B* values are for atoms that were refined isotropically. *B* value for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3)[$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$].

A problem of disorder appeared in the resolution, the carbon atom labeled C(2) being located in two different positions C(2) and C(2b) with occupancies of 60% and 40%, respectively. Attempts to solve two different molecules in a less symmetric space group seemed first to be possible, but the refinement did not give good results.

All non-hydrogen atoms were refined anisotropically except carbon C(2) and C(2b). In the last cycle of refinement, the hydrogen atoms, except those corresponding to the disordered carbon atoms, were introduced from geometric calculations

(13) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1983**, *39*, 158.

with thermal parameters equivalent to the one of the carbon to which they are attached.

Final values of $R = 0.037$ and $R_w = 0.039$ were obtained with $R_w = [/\sum w//F_o/ - /2/w/F_o/^2]^{1/2}$ and $w = 4F_o^2[\sigma/F_o/]^2$. Anomalous dispersion corrections and atomic scattering factors were taken from ref 14. Calculations were performed with the SDP package[15] and the programs Multan[16] and Dirdif[17] on a Microvax II computer.

Acknowledgment. We are grateful to the DGICYT (Grant PB92-0178-C) for financial support.

Supporting Information Available: Tables of hydrogen atom coordinates and *B* values (Table S1), thermal parameters (Table S2), and complete bond distances and angles (Table S3) and variable-temperature ^{1}H NMR spectra of complexes **3** (Figure S1) and **4** (Figure S2) (7 pages). Ordering information is given on any current masthead page.

OM950524L

(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(15) B. A. Frenz, and Associates Inc. SPD; Texas A&M and Enraf Nonius, College Station, TX 77840, Delft, Holland, 1985.

(16) Main, P.; Fiske, S. E.; Hull, S. L.; Lessinger, L.; Germain, C.; Declerq, J. P.; Woolfsoon, M. M. MULTAN, Universities of York and Louvain, 1980.

(17) Beurskens, P. T.; Bossman, W. P.; Doesburg, H. M.; Gould, R. O.; van der Heurk, T. E. M.; Prick, P. A. S.; Noordik, J. H.; Beurskens, G.; Parthasarathu, V. DIRDIF Manual 81, Technical Report 1981/82, Crystallographic Laboratory, University of Nijmegen, Toernooiveld, The Netherlands, 1981.