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Insertion of carbon dioxide and isocyanide into tantalum–amide and tantalum–methyl bonds

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Dedicated to Professor H. Brunner on the occasion of his 65th birthday.

Abstract

The methyl–amide complex [TaCp*(N^{t}Bu)Me(NMe$_2$)] (**1a**) was isolated by reaction of the chloro–methyl [TaCp*(N^{t}Bu)MeCl] complex with LiNMe$_2$. Reaction of the mono-amide compounds [TaCp*(N^{t}Bu)XY] (X = NMe$_2$, Y = Me (**1a**); X = NH^{t}Bu, Y = Me (**1b**), Cl (**1c**)) with CO_2 gives the η^2-carbamate derivatives [TaCp*(N^{t}Bu)(η^2-O$_2$CX)Y] (X = NMe$_2$, Y = Me (**2a**); X = NH^{t}Bu, Y = Me (**2b**), Cl (**2c**)). A similar reaction with the di-amide complex [TaCp*(N^{t}Bu)(NH^{t}Bu)$_2$] (**1d**) gives the di-carbamate derivative [TaCp*(N^{t}Bu){η^2-O$_2$C(NH^{t}Bu)}{η^1-O$_2$C(NH^{t}Bu)] (**2d**). Reaction of the methyl–carbamate (**2a**) with isocyanide CNAr (Ar = 2,6-Me$_2$C$_6$H$_3$) gives the η^2-iminoacyl–η^1-carbamate complex [TaCp*(N^{t}Bu){η^2-C(Me)=NAr}{η^1-O$_2$C(NMe$_2$)] (**3a**). Formation of the related compound [TaCp*(N^{t}Bu){η^2-C(Me)=NAr}{η^1-O$_2$C(NH^{t}Bu)}] (**3b**) was only detected by NMR spectroscopy in C$_6$D$_6$ or CDCl$_3$ whereas the reaction of **2b** in hexane gives the η^1-iminoacyl–η^2-carbamate complex [TaCp*(N^{t}Bu){η^1-C(Me)=NAr}{η^2-O$_2$C(NH^{t}Bu)}] (**3b′**). All of the new compounds were characterized by elemental analysis and ^{1}H- and ^{13}C-NMR spectroscopy.

Keywords: Carbon dioxide; Insertion reactions; Carbamate compounds

1. Introduction

Many studies of competitive insertion of carbon monoxide and isocyanides into different M–C [1–3], M–Si [4,5] and M–N [1c,6–8] bonds have been reported. However there are many fewer reports of the competitive reactivity of M–C, M–O, M–N and M–Si bonds in insertion reactions of N≡CR, O=CO, O=CR$_2$, S=CS, O=C=NR and other related unsaturated substrates [2,3]. Studies of CO_2 insertion reactions established that the M–amide bonds were more reactive than M–alkyl and M–alkoxo bonds, and that regioselective insertion into the M–amide bonds always takes place [3,9] except for the η^5-cyclopentadienyl silyl-η–amide zirconium dimethyl complex [Zr{η^5-C$_5$H$_4$SiMe$_2$–η-N^{t}Bu}Me$_2$] for which previous regioselective insertion into the Zr–Me bonds was reported [10]. Mechanistic studies revealed [2] that direct nucleophilic attack on CO_2 by the amido ligand followed by *O*-coordination to the metal is more plausible than the initial coordination of CO_2 to the metal.

We have reported recently [11] that single and double insertion of CN(2,6-Me$_2$C$_6$H$_3$) into the Ta–Me bond of [TaCp*(N^{t}Bu)MeX] (X = Me, Cl, OMe, O^{t}Bu, NH^{t}Bu) is controlled by the π-donor capacity and the steric demands of the X substituent. As an extension of our previous studies we decided to investigate the competitive insertion of CO_2 into Ta–amide bonds (amide = NMe$_2$, NH^{t}Bu) and of CN(2,6-Me$_2$C$_6$H$_3$) into the Ta–Me bond still present in the resulting carbamate compounds. The results of these studies are reported in this paper.

2. Results and discussion

The new methyl–amide complex [TaCp*(N^{t}Bu)-Me(NMe$_2$)] (**1a**), shown in Eq. (1), was isolated in high

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yield (84%) as a dark yellow oil from the reaction of $LiNMe_2$ with an Et_2O solution of the methyl–chloro derivative [TaCp*(N^{t}Bu)MeCl].

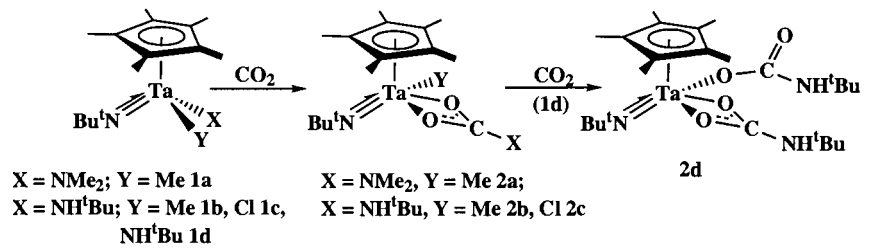
$$\text{TaCp*(N}^t\text{Bu)MeCl} + \text{LiNMe}_2 \xrightarrow{\text{Et}_2\text{O, 7 h}} \underset{\textbf{1a}}{\text{TaCp*(N}^t\text{Bu)Me(NMe}_2\text{)}} \quad (1)$$

The complex is air sensitive but can be stored for long periods under an inert atmosphere. Dynamic behaviour, not investigated in detail, was observed for **1a**, indicating that the amido ligand was rotating freely, making the two methyl groups equivalent to give a unique signal in both ^{1}H- (broad) and ^{13}C-NMR spectra at room temperature (see Section 4).

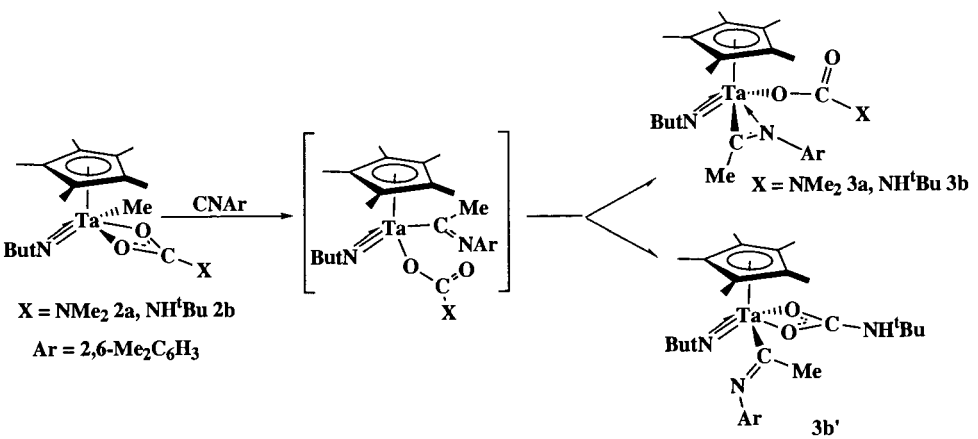
2.1. Reactions with CO_2

Reactions of CO_2 with the methyl–amide [TaCp*(N^{t}Bu)MeX] (X = NMe_2 (**1a**), NH^{t}Bu (**1b**) [11]), chloro–amide [TaCp*(N^{t}Bu)Cl(NH^{t}Bu)] (**1c**) [12] and diamide [TaCp*(N^{t}Bu)(NH^{t}Bu)$_2$] (**1d**) [12] complexes in hexane were studied. As shown in Scheme 1, the products isolated were the mono–carbamate [TaCp*(N^{t}Bu)-(η^2-O_2CX)Y] (X = NMe_2, Y = Me (**2a**); X = NH^{t}Bu, Y = Me (**2b**), Cl (**2c**)) and the di-carbamate complex [TaCp*(N^{t}Bu)(O_2CNH^{t}Bu)$_2$] (**2d**). Insertion of CO_2 into each Ta–amide bond was complete after 16 h at room temperature. No intermediates were detected when these reactions were monitored by NMR spectroscopy in C_6D_6 or $CDCl_3$ at room temperature. The carbamate species were the unique reaction products, formed in quantitative yield and more rapidly (6 h at room temperature) when $CDCl_3$ was used. The presence of free amine, which could favour the insertion [13], was not detected. The mono-insertion product expected in the reaction of **1d** with CO_2 could not be detected when this reaction was monitored by NMR spectroscopy, and the di-carbamate complex was the unique reaction product formed in quantitative yield. Transformation of methyl–carbamate into the corresponding amide–acetate complexes was not observed when their $CDCl_3$ solutions were heated for long periods, indicating that the carbamate complexes were the thermodynamic products of all these reactions. Insertion into the Ta–amide bond occurred by the direct attack of CO_2 at the nitrogen atom [2].

The ^{13}C-NMR and IR spectra of complexes **2a**–**c** were consistent with the η^2-coordination of the carbamate ligand [13], which shows one C(sp^2) resonance at $\delta \approx 165$–167 and one ν(COO) stretching vibration at $\approx 1586\ cm^{-1}$. The di-carbamate complex **2d** shows two ν(COO) and two ν(NH) absorptions in the solid (see Section 4), indicating that only one of the carbamate ligands is η^2-coordinated. However, the ^{1}H- and ^{13}C-NMR spectra in $CDCl_3$ show the presence of a unique type of carbamate ligand with two singlets due to both equivalent N–H and CMe_3 protons (^{1}H) and three



Scheme 1.



Scheme 2.

singlets due to the two equivalent *C*OO C(sp^2), *C*Me_3 and C*Me*$_3$ carbons (^{13}C) respectively, indicating that a rapid exchange between both η^2- and η^1-coordinate carbamate ligands takes place at room temperature (Scheme 2).

2.2. Reactions with isocyanide

The carbamate complexes [TaCp*(N^{t}Bu)(O_2CX)Me] (X = NMe_2 **2a**, NH^{t}Bu **2b**) still contain one Ta–Me bond susceptible to reaction with an isocyanide. Addition of one equivalent of CNAr (Ar = 2,6-$Me_2C_6H_3$) to a hexane solution of the dimethylamide compound **2a** resulted in the immediate formation of the η^2-iminoacyl–η^1-carbamate complex [TaCp*(N^{t}Bu){η^2-C(Me) = NAr}]{η^1-O_2C(NMe_2)}] (**3a**), isolated in high yield as a colorless solid soluble in aromatic and chlorinated solvents but only partially soluble in hexane. It was an air sensitive compound, decomposing slowly in the solid state under inert atmosphere without evolving CNAr. Accepting the metal coordination pathway, this insertion would require the transformation of the η^2- into η^1-coordinated carbamate ligand before insertion. After insertion two alternative processes, namely η^2-*O*,*O*-coordination of the carbamate ligand to give a four membered chelate ring or η^2-*C*, *N*-coordination of the iminoacyl ligand to give a three membered ring, are in competition. The η^2-*C*,*N*-coordination route was preferred to give complex **3a**. Its formulation is consistent with the low field resonance observed at δ 248.5 for the η^2-C=N carbon, similar to that found for alkoxo η^2-iminoacyl species [TaCp*(N^{t}Bu){η^2-C(R′)=NR}OR″] (R = 2,6-$Me_2C_6H_3$. R′ = Me, C(Me)=NR; R″ = Me, ^{t}Bu) [11] and the η^1-O_2C carbon resonance observed at δ 161.2 in the ^{13}C-NMR spectrum. Its IR spectrum showed two absorption bands at 1600 and 1639 cm^{-1}, corresponding to the ν(η^2-C=N) and ν(η^1-OOC) vibrations, respectively.

When a similar reaction with the ^{t}butylamide compound **2b** was monitored by ^{1}H-NMR in $CDCl_3$, formation of the corresponding compound **3b** was observed. However the same reaction carried out on a preparative scale in hexane gave the iminoacyl–carbamate derivative **3b′**, which was isolated as a colourless air sensitive solid. The ^{13}C-NMR spectrum of compound **3b** suggests the η^2-iminoacyl–η^1-carbamate relative of **3a** (see Section 4). However the NMR behaviour of compound **3b′** is slightly different, the most remarkable features being the higher field resonance observed at δ = 232.4 for the sp^2 C=N carbon [1c] and the resonance slightly displaced to lower field (δ = 167.7) corresponding to the sp^2 OOC carbon. Its IR spectrum showed two absorption bands at 1670 and 1656 cm^{-1} due to two different ν(C=N) moieties and one absorption at 1572 cm^{-1} due to the ν(η^2-OOC) vibration [14]. This behaviour is more consistent with its formulation as a η^1-iminoacyl–η^2-carbamate compound. Exchange between both coordination modes could not be detected as heating their solutions resulted in their decomposition.

The IR spectrum of complex **3b′** indicates the presence of two ν(C=N), two broad ν(N–H) and one ν(CO_2) absorption indicating that in the solid hydrogen bridges between the iminoacyl nitrogen and the ^{t}butylamido hydrogen are present. The same behaviour was observed in C_6D_6 but not in $CDCl_3$. Studies made in solution demonstrate that heating or dilution make the ν(N–H) band narrower and displaced to higher wave numbers, as expected for intermolecular hydrogen bridges [14].

3. Conclusions

Reaction of the methyl–amide [TaCp*(N^{t}Bu)MeX] (X = NMe_2 (**1a**), NH^{t}Bu (**1b**)), chloro–amide [TaCp*(N^{t}Bu)Cl(NMe_2)] (**1c**) and diamide [TaCp*(N^{t}Bu)(NH^{t}Bu)$_2$] (**1d**) complexes with CO_2 resulted in insertions into the Ta–amide bonds to give the mono-carbamate complexes [TaCp*(N^{t}Bu)(η^2-O_2CX)Y] (X = NMe_2, Y = Me (**2a**); X = NH^{t}Bu, Y = Me (**2b**), Cl (**2c**)) and the di-carbamate complex [TaCp*(N^{t}Bu)(O_2CNH^{t}Bu)$_2$] (**2d**). The carbamate ligand is always η^2-coordinate in the mono-carbamate derivatives whereas rapid exchange between η^2-and η^1-coordination was observed in solution at room temperature for the di-carbamate derivative **2d**. Insertion of CNAr (Ar = 2,6-$Me_2C_6H_3$) into the Ta–Me bond of the methyl–carbamate complexes **2a** and **2b** results in formation of the iminoacyl–carbamate complexes [TaCp*(N^{t}Bu)(O_2CY){C(Me) = NR}] (Y = NMe_2 (**3a**); NH^{t}Bu (**3b**)), which show varying η^2-η^1-coordination of the iminoacyl and carbamate substituents, depending on the amide group and the solvent. Formation of intermolecular hydrogen bridges was observed by IR and NMR spectrometry in the solid and in C_6D_6 solutions of the ^{t}butyl-carbamate derivative.

4. Experimental

All operations were carried out under a dry argon atmosphere either in a Vacuum Atmosphere Dri-lab or by standard Schlenk techniques. Hydrocarbon solvents were dried and freshly distilled: *n*-hexane from sodium potassium alloy and toluene and ether from sodium. Reagent grade CN(2,6-$Me_2C_6H_3$) (Fluka), $LiNMe_2$ (Aldrich) were purchased from commercial sources and were used without further purification. The starting complexes [TaCp*(N^{t}Bu)XY] (Y = Cl; X = Me [12]. Y = NH^{t}Bu; X = Me [11], Cl [12], NH^{t}Bu [12]) were synthesized by reported methods. Infrared spectra were

recorded on a Perkin–Elmer 583 spectrophotometer (4000–200 cm^{-1}). ^1H- and ^{13}C-NMR spectra were recorded on a Varian Unity VXR 300 MHz instrument, and chemical shifts were measured relative to residual ^1H and ^{13}C resonances of the deuterated solvents C_6D_6 (δ 7.15), $CDCl_3$ (δ 7.24) and C_6D_6 (δ 128), $CDCl_3$ (δ 77), respectively. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer.

4.1. [TaCp*(N^{t}Bu)Me(NMe$_2$)] (1a)

A mixture of [TaCp*(N^{t}Bu)ClMe] (2.00 g, 4.57 mmol) and $LiNMe_2$ (0.23 g, 4.57 mmol) was stirred in Et_2O (40 ml) for 7 h at room temperature (r.t.). The solvent was removed in vacuo and the residue was extracted into *n*-hexane (2 × 20 ml) to give **1a** as a brown oil after removal of the solvent in vacuo (Yield: 1.71 g, 84%).

Data for **1a**: IR (CsI, δ, cm^{-1}): 1280 (s). ^1H-NMR ($CDCl_3$, δ, ppm): 3.17 (s, 6H, NMe_2), 2.03 (s, 15H, C_5Me_5), 1.15 (s, 9H, CMe_3), −0.16 (s, 3H, Ta–Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 114.5 (C_5Me_5), 64.2 ($NCMe_3$), 50.8 (NMe_2), 33.4 (CMe_3), 20.5 (Ta–Me), 11.2 (C_5Me_5). Anal. Calc. for $C_{17}H_{33}N_2Ta$: C, 45.74; H, 7.45; N, 6.28. Found: C, 45.29; H, 7.36; N, 6.04.

4.2. [TaCp*(N^{t}Bu)(O$_2$CX)Y] X = NMe$_2$, Y = Me (2a); X = NH^{t}Bu, Y = Me (2b), Cl (2c)

Hexane (60 ml) solutions of compounds **1a** (1.50 g, 3.36 mmol), **1b** (1.50 g, 3.16 mmol) and **1c** (1.50 g, 3.03 mmol) were stirred for 16 h at r.t. under a CO_2 atmosphere. Then the solutions were filtered, the solvent evaporated under vacuum until 10 ml remained and the resulting solution was cooled at −30°C to yield, respectively, **2a** (1.20 g, 73%), **2b** (1.20 g, 73%) and **2c** (1.27 g, 78%) as colourless solids.

Data for **2a**: IR (KBr pellets, δ, cm^{-1}): 1586 (s), 1273 (s). ^1H-NMR ($CDCl_3$, δ, ppm): 2.85 (s, 6H, NMe_2), 1.95 (s, 15H, C_5Me_5), 1.10 (s, 9H, CMe_3), 0.12 (s, 3H, Ta–Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 166.2 (O_2C), 115.3 (C_5Me_5), 64.2 (CMe_3), 34.5 and 33.1 (NMe_2 and Ta–Me), 32.8 (CMe_3), 10.9 (C_5Me_5). Anal. Calc. for $C_{18}H_{33}N_2O_2Ta$: C, 44.07; H, 6.78; N, 5.71. Found: C, 43.91; H, 6.65; N, 5.83.

Data for **2b**: IR (KBr pellets, δ, cm^{-1}): 3143 (w), 1587 (s), 1274 (s). ^1H-NMR ($CDCl_3$, δ, ppm): 4.59 (s, 1H, NH), 1.97 (s, 15H, C_5Me_5), 1.31 (s, 9H, CMe_3), 1.09 (s, 9H, CMe_3), 0.08 (s, 3H, Ta–Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 166.5 (O_2C), 115.6 (C_5Me_5), 64.2 (CMe_3), 50.4 (CMe_3), 32.9 (CMe_3), 32.8 (Ta–Me), 29.1 (CMe_3), 11.0 (C_5Me_5). Anal. Calc. for $C_{20}H_{37}N_2O_2Ta$: C, 46.32; H, 7.21; N, 5.40. Found: C, 46.20; H, 7.26; N, 5.30.

Data for **2c**: IR (KBr pellets, δ, cm^{-1}): 3312 (w), 1586 (s), 1274 (s). ^1H-NMR ($CDCl_3$, δ, ppm): 4.88 (s, 1H, NH), 2.10 (s, 15H, C_5Me_5), 1.36 (s, 9H, CMe_3), 1.10 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 165.6 (O_2C), 119.2 (C_5Me_5), 65.7 (CMe_3), 50.9 (CMe_3), 32.7 (CMe_3), 29.2 (CMe_3), 11.4 (C_5Me_5). Anal. Calc. for $C_{19}H_{34}ClN_2O_2Ta$: C, 42.35; H, 6.36; N, 5.20. Found: C, 42.30; H, 6.41; N, 4.98.

4.3. [TaCp*(N^{t}Bu)(O$_2$CNH^{t}Bu)$_2$] (2d)

A hexane solution (60 ml) of **1d** (1.50 g, 2.82 mmol) was stirred for 16 h at r.t. under CO_2 atmosphere. Then the solution was filtered, the solvent evaporated under vacuum until 10 ml remained and the resulting solution was cooled at −30°C to yield **2d** as a white solid (1.31 g, 75%).

Data for **2d**: IR (KBr pellets, δ, cm^{-1}): 3399 (w), 3230 (w), 1630 (s), 1597 (s), 1285 (s). ^1H-NMR ($CDCl_3$, δ, ppm): 4.94 (s, 2H, NH), 2.10 (s, 15H, C_5Me_5), 1.24 (s, 18H, CMe_3), 1.11 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 162.4 (2 O_2C), 118.9 (C_5Me_5), 64.9 (CMe_3), 50.1 (2 CMe_3), 33.2 (CMe_3), 29.1 (2 CMe_3), 11.1 (C_5Me_5). Anal. Calc. for $C_{24}H_{44}N_3O_4Ta$: C, 46.53; H, 7.16; N, 6.78. Found: C, 46.65; H, 7.10; N, 6.55.

4.4. [TaCp*(N^{t}Bu)(η^1-O$_2$CNMe$_2$){η^2-C(Me)=NAr}] (Ar = 2,6-Me$_2$C$_6$H$_3$) (3a)

A hexane (30 ml) solution of [TaCp*(N^{t}Bu)-Me(O_2CNMe_2)] (**2a**) (1.00 g, 2.04 mmol) and CNAr (Ar = 2,6-$Me_2C_6H_3$) (0.27 g, 2.04 mmol) was stirred for 1 h at r.t. The solution was filtered, the solvent removed under vacuum until 5 ml remained and the resulting solution cooled at −20°C to yield **3a** as a white solid (0.97 g, 76%).

Data for **3a**: IR (KBr pellets, δ, cm^{-1}): 1639 (s), 1600 (s), 1269 (s). ^1H-NMR ($CDCl_3$, δ, ppm): 6.94 (m, 3H, $Me_2C_6H_3$), 2.58 (s, 6H, NMe_2), 2.48 (s, 3H, MeCN), 2.14 (s, 15H, C_5Me_5), 2.04 and 1.98 (s, 3H, $Me_2C_6H_3$), 1.08 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 248.5 (MeCN), 161.2 (O_2C), 142.2, 130.2, 129.1, 127.8, 127.6 and 125.2 ($Me_2C_6H_3$), 115.7 (C_5Me_5), 65.0 (CMe_3), 36.5 (NMe_2), 33.6 (CMe_3), 22.5, 18.9 and 18.8 (MeCN and $Me_2C_6H_3$), 11.6 (C_5Me_5). Anal. Calc. for $C_{27}H_{42}N_3O_2Ta$: C, 51.84; H, 7.41; N, 6.72. Found: C, 51.66; H, 7.27; N, 6.59.

4.5. [TaCp*(N^{t}Bu){η^1-O$_2$C(NH^{t}Bu)}{η^2-C(Me)=NAr}] (Ar = 2,6-Me$_2$C$_6$H$_3$) (3b)

A $CDCl_3$ solution of **2b** (0.020 g, 0.041 mmol) and CNAr (Ar = 2,6-$Me_2C_6H_3$) (0.005 g, 0.042 mmol) was charged into a teflon-valved NMR tube and the reaction, which was complete after 15 min, was monitored by ^1H-NMR spectroscopy to give **3b** as the unique product.

Data for **3b**: ^1H-NMR ($CDCl_3$, δ, ppm): 6.98 (m, 3H, $Me_2C_6H_3$), 4.43 (s, 1H, NH), 2.51 (s, 3H, MeCN), 2.13 (s, 15H, C_5Me_5), 2.05 and 1.97 (s, 3H, $Me_2C_6H_3$), 1.09 and 0.95 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ,

ppm): 247.9 (MeCN), 159.7 (O_2C), 142.5, 130.1, 129.4, 128.2, 127.7 and 125.8 ($Me_2C_6H_3$), 115.9 (C_5Me_5), 65.0 (Ta=$NCMe_3$), 49.1 ($NHCMe_3$), 34.1 and 28.7 (CMe_3), 22.7, 18.8 and 18.7 (MeCN and $Me_2C_6H_3$), 11.6 (C_5Me_5).

4.6. [TaCp*(N^tBu)(η^2-O_2CNH^tBu){η^1-C(Me)=NAr}] (Ar = 2,6-$Me_2C_6H_3$) (**3b′**)

A hexane (30 ml) solution of **2b** (0.60 g, 1.16 mmol) and CN(2,6-$Me_2C_6H_3$) (0.15 g, 1.16 mmol) was treated using the procedure described above for **3a** to give **3b′** as a white solid (0.63 g, 84%).

Data for **3b′**: IR (KBr pellets, δ, cm^{-1}): 3442 (w), 3232 (w, broad), 1670 (s), 1656 (s), 1572 (s), 1522 (s), 1284 (s). ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.84 (m, 3H, $Me_2C_6H_3$), 4.72 (s, 1H, NH), 2.44 (s, 3H, MeCN), 2.24 and 1.90 (s, 3H, $Me_2C_6H_3$), 1.99 (s, 15H, C_5Me_5), 1.44 and 1.33 (s, 9H, CMe_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 232.4 (MeCN), 167.7 (O_2C), 144.5, 136.9, 128.2, 128.1 and 124.2 ($Me_2C_6H_3$), 118.6 (C_5Me_5), 62.8 (Ta=$NCMe_3$), 50.8 ($NHCMe_3$), 30.0 and 29.7 (CMe_3), 22.6, 19.2 and 14.1 (MeCN and $Me_2C_6H_3$), 11.2 (C_5Me_5). Anal. Calc. for $C_{29}H_{46}N_3O_2Ta$: C, 53.62; H, 7.14; N, 6.47. Found: C, 54.42; H, 7.06; N, 6.20.

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References

[1] (a) J.J. Alexander, in: F.R. Hartley (Ed.), The Chemistry of the Metal–Carbon Bond, Ch. 5, vol. 2, Wiley, New York, 1985. (b) M.F. Lappert, N.T. Luong-Thi, C.J. Milne, Organomet. Chem. 174 (1979) C35. (c) L.D Durfee, I.P. Rothwell, Chem. Rev. 88 (1988) 1059. (d) J.D. Debad, P. Legzdins, F.W.B. Einstein, R.J. Batchelor, Organometallics 12 (1993) 2094. (e) J.L. Petersen, L. Kloppenburg, Organometallics 16 (1997) 3548.
[2] J.F. Hartwig, R.G. Bergman, R.A. Andersen, J. Am. Chem. Soc. 113 (1991) 6499.
[3] P. Legzdins, S.J. Rettig, K.J. Ross, Organometallics 13 (1994) 569.
[4] (a) F.H. Elsner, T.D. Tilley, A.L. Rheingold, S.J. Geib, J. Organomet. Chem. 358 (1988) 169. (b) C.M. Roddick, R.H. Heyn, T.D. Tilley, Organometallics 8 (1989) 324.
[5] (a) Z. Wu, L.H. McAlexander, J.B. Diminnie, Z. Xue, Organometallics 17 (1998) 4853. (b) Z. Wu, J.B. Diminnie, Z. Xue, Organometallics 18 (1999) 1002.
[6] M.H. Chisholm, C.E. Hammond, D. Ho, J.C. Huffman, J. Am. Chem. Soc. 108 (1986) 7860.
[7] A. Dormond, A. Aaliti, C. Moise, J. Chem Soc. Chem. Commun. 1231 (1985).
[8] A. Castro, M. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, F. Sánchez, J. Organomet. Chem. 595 (2000) 36.
[9] X. Yin, J.R. Moss, Coord. Chem. Rev. 181 (1999) 27.
[10] L. Kloppenburg, J.L. Petersen, Organometallics 15 (1996) 7.
[11] J. Sánchez-Nieves, P. Royo, M.A. Pellinghelli, A. Tiripicchio, Organometallics 19 (2000) 3161.
[12] P. Royo, J. Sánchez-Nieves, J. Organomet. Chem. 597 (2000) 61.
[13] (a) M.H. Chisholm, M.W. Extine, J. Am. Chem. Soc. 99 (1977) 782. (b) M.H. Chisholm, M.W. Extine, J. Am. Chem. Soc. 99 (1977) 792. (c) M.H. Chisholm, L.-S. Tan, J.C. Huffman, J. Am. Chem. Soc. 104 (1982) 4879.
[14] (a) T. Okamura, K. Sakauye, N. Ueyama, A. Nakamura, Inorg. Chem. 37 (1998) 6731. (b) J.D. Carr, S.J. Coles, W.W. Hassan, M.B. Hurthouse, K.M.A. Malik, J.H.R. Tucker, J. Chem. Soc. Dalton Trans. 57 (1999).