SYNTHESES OF NEW TITANIUM(IV) AND RHODIUM(I) GUANIDINIDO COMPLEXES

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contribution to the area of organometallic chemistry and catalysis.

The new titanium guanidinido complexes [TiCp*Me$_2${(PhN)$_2$CNH$_2$}] (**1**), and [TiCp*Cl$_2$-{(PhN)$_2$CNH$_2$}] (**2**) (Cp* = η^5-C$_5$Me$_5$) have been synthesized. The reaction of complex **1** with [Rh(μ-OH)(cod)]$_2$ affords the rhodium guanidinido complex [Rh{(PhNH)(PhN)CNH}(cod)]$_2$ (**3**). The molecular structures of complexes **1** and **3** were studied by X-ray diffraction methods. Complex **3** can also be prepared by reaction of [Rh(μ-OH)(cod)]$_2$ with *N*,*N′*-diphenyl-guanidine.

Keywords: N ligands; Titanium; Rhodium; Guanidines; Half-sandwich complexes; X-ray diffraction.

The development of new ancillary ligands for modulating electronic and steric properties of the metal center has been vital to the discovery of new metal-mediated organic transformations, which is one of the main issues in organometallic chemistry. In the search for new ligands to tune the reactivity of the metal center, a variety of new multidentate anionic ligands bearing nitrogen donor atoms, including diamide[1–3], amidinide[4–8], and guanidinide[9] ligands, have been studied.

Guanidinide anions are closely related to amidinides but the presence of the NR_2 group in these ligands results in the possibility of a zwitterionic resonance structure II (Scheme 1) generated by delocalization of the lone pair at the non-coordinated nitrogen in the π-system. This could contribute to the stabilization of electron-deficient metal centers through enhanced electron donation[10].

Guanidinide anions have received limited attention in coordination and organometallic chemistry. Majority of the studies of guanidinido complexes of early transition metals have focused on the tetrasubstituted guanidinide ligands[11]. We are interested in disubstituted guanidinide ligands because of their potential in molecular architecture constructions.
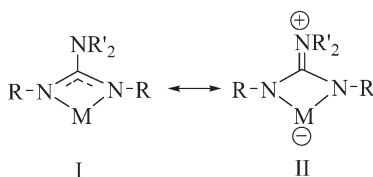
SCHEME 1

We report here the preparation of disubstituted guanidinido titanium and rhodium complexes as well as their structural characterization.

EXPERIMENTAL

General Procedures

The preparation and handling of the studied compounds was performed on rigorous exclusion of air and moisture under nitrogen atmosphere, using a standard vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen atmosphere.

The following reagents were prepared by literature procedures: [TiCp*Me$_3$] (ref.[12]), [TiCp*Cl$_3$] (ref.[13]). Commercially available N,N'-diphenylguanidine (Aldrich) was used as received.

^{1}H and ^{13}C NMR spectra were recorded on a 200 Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as references. Chemical shifts (δ, ppm) are reported relative to SiMe$_4$, coupling constants, J, are given in Hz.

[TiCp*Me$_2${(PhN)$_2$CNH$_2$}] (1)

To a solution of [TiCp*Me$_3$] (0.482 g, 2.11 mmol) in toluene at –40 °C, N,N'-diphenylguanidine (0.446 g, 2.11 mmol) was added. The solution was allowed to warm up to room temperature and then stirred for 2 h. The solvent was removed under vacuum and the residue extracted with pentane. Cooling down the solution to –25 °C yielded red crystals of **1** (0.637 g, 71%). ^{1}H NMR (C$_6$D$_6$, 293 K, 200 MHz): 0.91 (s, 6 H, Me); 1.76 (s, 15 H, Cp*); 3.66 (br, 2 H, NH$_2$); 6.83 (m, 2 H, Ar); 7.07 (m, 8 H, Ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 12.3 (s, Cp*), 68.3 (s, Me), 123.7 (s, Cp*), 126.2 (s, Ar), 127.5 (s, Ar), 129.2 (s, Ar), 147.7 (s, Ar$_{ipso}$), 156.1 (s,

N_3C). For $C_{25}H_{33}N_3Ti$ (420.4) calculated: 70.91% C, 7.85% H, 9.92% N; found: 70.53% C, 7.85% H, 9.65% N.

[TiCp*Cl₂{(PhN)₂CNH₂}] (2)

To a mixture of [TiCp*Cl₃] (0.212 g, 0.73 mmol) and *N,N'*-diphenylguanidine (0.155 g, 0.73 mmol) in toluene, NEt₃ (0.102 ml, 0.73 mmol) was added. The solution was stirred at room temperature for 2 h and then filtered. Slow diffusion of pentane into the toluene solution yielded dark red crystals of **2** (0.234 g, 69%). ¹H NMR (CDCl₃, 293 K, 200 MHz): 2.14 (s, 15 H, Cp*); 4.30 (s, 2 H, NH₂); 7.12 (m, 2 H, Ar); 7.38 (m, 8 H, Ar). ¹³C{¹H} NMR (CDCl₃): 14.6 (s, Cp*), 125.4 (s, Ar), 127.2 (s, Ar), 129.6 (s, Ar), 134.9 (s, Cp*), 146.8 (s, Ar$_{ipso}$), 158.1 (s, N₃C). For $C_{23}H_{27}Cl_2N_3Ti$ (464.3) calculated: 59.50% C, 5.86% H, 9.05% N; found: 58.90% C, 5.90% H, 8.88% N.

[Rh{(PhNH)(PhN)CNH}(cod)]₂ (3)

To a solution of [Rh(μ-OH)(cod)]₂ (0.125 g, 0.27 mmol) in toluene at room temperature, *N,N'*-diphenylguanidine (0.124 g, 0.55 mmol) was added. The solution was stirred at room temperature for 2 h. The solvent was then removed under vacuum and the residue extracted with diethyl ether (Et₂O) overnight. Cooling the solution down to –23 °C yielded red crystals of complex **3**·2Et₂O (0.175 g, 64%). ¹H NMR (CDCl₃, 293 K, 200 MHz): 1.70 (m, 4 H, cod); 2.40 (m, 4 H, cod); 4.03 (m, 4 H, cod); 4.54 (br, 2 H, NH₂); 6.88 (m, 6 H, Ar); 7.20 (m, 4 H, Ar). ¹³C{¹H} NMR (C₆D₆): 31.4 (s, cod), 77.8 (d, $^1J_{Rh-C}$ = 12.95, cod), 122.8 (s, Ar), 123.9 (s, Ar), 129.9 (s, Ar), 146.7 (s, Ar$_{ipso}$), 165.7 (s, N₃C). For $C_{42}H_{48}N_6Rh_2$·2Et₂O (990.9) calculated: 60.60% C, 6.91% H, 8.48% N; found: 60.26% C, 6.55% H, 8.41% N.

X-ray Crystallography

A summary of crystal data and refinement parameters for compounds **1** and **3** are given in Table I. The single crystals for **1** and **3**·2Et₂O were mounted on a glass fiber and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromatized MoKα radiation source (λ = 0.71073 Å). Data were integrated using the SAINT program[14], and absorption correction was performed with the SADABS program[15]. The SHELXTL-NT software package[16] was used for space group determination, structure solution and refinement by full-matrix least-square methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a riding model and included in the refinement at calculated positions. For **1**, the asymmetric unit consists of one half molecule of the complex. CCDC 634534 (for **1**) and 634535 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The titanium derivative [TiCp*Me₃] reacts with 1 equivalent of *N,N'*-diphenylguanidine to yield the titanium complex [TiCp*Me₂{(PhN)₂CNH₂}] (**1**)

TABLE I
Crystal data and structure refinement for complexes **1** and **3**

Complex	1	3
Empirical formula	$C_{25}H_{30}N_3Ti$	$C_{42}H_{48}N_6Rh_2 \cdot 2C_4H_{10}O$
M, g mol^{-1}	420.42	990.92
T, K	180(2)	180(2)
Wavelength, Å	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	P_{nma}	$P\text{-}\bar{1}$
a, Å	13.902(2)	13.637(4)
b, Å	19.145(3)	16.153(5)
c, Å	8.679(1)	20.955(7)
α, °		83.429(6)
β, °		88.695(6)
γ, °		89.432(6)
V, Å^3	2309.9(6)	4584(3)
Z	4	4
D_c, g cm^{-3}	1.209	1.436
μ(MoKα), mm^{-1}	0.385	0.766
$F(000)$	892	2064
Crystal size, mm	$0.45 \times 0.45 \times 0.36$	$0.41 \times 0.23 \times 0.11$
θ range, °	2.13 to 26.37	1.80 to 26.37
Index ranges	$-17 \le h \le 14$	$-17 \le h \le 15$
	$-23 \le k \le 23$	$-20 \le k \le 19$
	$-10 \le l \le 10$	$-25 \le l \le 26$
Reflections collected	13723	23543
Independent reflections	2436 [$R_{int} = 0.0551$]	18420 [$R_{int} = 0.0967$]
Max. and min. transmission	0.8731 and 0.8451	0.9205 and 0.7441
Data/restraints/parameters	2436/0/147	18710/0/1064
GOF on F^2	1.041	0.941
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0472$, $wR_2 = 0.1213$	$R_1 = 0.0868$, $wR_2 = 0.1909$
Largest diff. peak and hole, e Å^{-3}	0.296 and −0.495	3.022 and −1.497

(Scheme 2). Complex **1** was isolated as an air-sensitive red compound. It is soluble in most common organic solvents. It has been characterized by usual spectroscopic techniques as well as by X-ray diffraction methods.
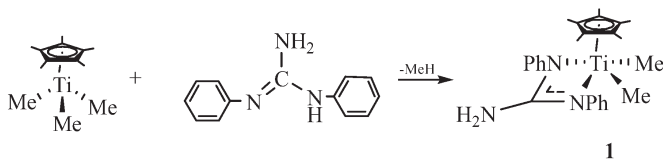
SCHEME 2

The NMR spectra show that the coordination environment around the titanium atom is quite symmetric. The ^{1}H NMR spectrum indicates that the methyl groups bound to the titanium center are equivalent and give rise to a singlet signal at 0.91 ppm. The broad absorption at 3.66 ppm with a relative integral corresponding to two protons is assigned to the NH_2 moiety. The ^{13}C NMR shows that both phenyl groups of the guanidinide ligand are equivalent (see Experimental). All those data, point to the coordination of the guanidinide groups through the two nitrogen atoms bonded to the phenyl groups, as shown in Scheme 2.

The proposed coordination mode has been confirmed by X-ray diffraction. An ORTEP drawing of **1** is shown in Fig. 1, and some selected bond distances and angles are summarized in Table II. The structure consists of
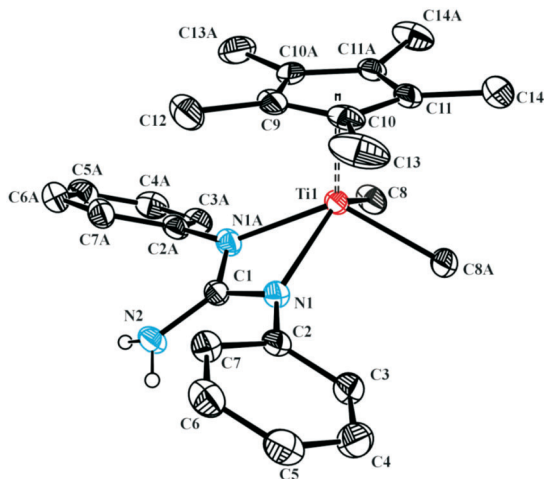

FIG. 1
Perspective ORTEP drawing (30% probability level) of the molecular structure of complex **1**

discrete molecules separated by van der Waals distances. The coordination around the metal is best described in terms of pseudo-square planar pyramid geometry. The titanium atom is η^5-bonded to the cyclopentadienyl ring. The guanidinide ligand is bound to the metal in a bidentate fashion. Both methyl groups are in cis position to each other. The Ti(1)–N(1) bond distance (2.165(2) Å) compares well with that found in other titanium benzamidinido[17] or guanidinido complexes[11]. The Ti–C bond length (Ti(1)–C(8) 2.138(2) Å) is comparable to that found in methyl titanium complexes[18]. The angles around the central atom of the guanidinide ligand total 359.94, indicating the planarity of the CN_3 unit[19]. The question should be addressed whether the lone pair of the uncoordinated nitrogen is located on this

TABLE II
Selected bond distances (in Å) and angles (in °) for complexes **1** and **3**

Complex **1**		Complex **3**	
Bond distances			
Ti(1)–N(1)	2.165(2)	Rh(1)–N(4)	2.085(10)
N(1)–C(1)	1.334(2)	Rh(1)–N(1)	2.121(9)
N(2)–C(1)	1.366(4)	Rh(2)–N(3)	2.130(10)
N(1)–C(2)	1.411(3)	Rh(2)–N(2)	2.076(8)
Ti(1)–C(8)	2.138(2)	N(1)–C(8)	1.331(13)
		C(8)–N(2)	1.349(13)
		C(8)–N(10)	1.394(14)
		N(3)–C(24)	1.304(13)
		C(24)–N(4)	1.329(13)
		C(24)–N(11)	1.404(15)
Bond angles			
C(8)–Ti(1)–C(8)#1	85.28(15)	N(1)–C(8)–N(2)	123.5(10)
N(1)#1–C(1)–N(1)	111.9(2)	N(1)–C(8)–N(10)	121.5(10)
N(1)–C(1)–N(2)	124.02(12)	N(2)–C(8)–N(10)	114.1(10)
N(1)–Ti(1)–N(1)#1	61.41(10)	N(3)–C(24)–N(4)	123.9(12)
C(1)–N(1)–Ti(1)	93.29(14)	N(3)–C(24)–N(11)	118.1(10)
C(1)–N(1)–C(2)	122.95(18)	N(4)–C(24)–N(11)	117.2(10)

atom or delocalized into the ligand. The bond between the central carbon of the ligand and the coordinated nitrogen atoms (1.334(2) Å) is somewhat shorter than the N(2)–C(1) bond (1.366(4) Å) but the small difference suggests an important contribution of form II to the ligand bonding (Scheme 1).

[TiCp*Cl$_3$] reacts with 1 equivalent of *N,N*-diphenylguanidine to yield the titanium derivative [TiCp*Cl$_2${(PhN)$_2$CNH$_2$}] (**2**) (Scheme 3). Complex **2** was isolated as a highly air-sensitive dark red compound. It is soluble in toluene or THF and less soluble in pentane. It has been characterized by usual spectroscopic techniques. According to the NMR data, the coordination mode of the guanidinide ligand to the titanium center in **2** is analogous to that in complex **1** (see data in Experimental) and, in accordance, a structure arrangement similar to that depicted in Scheme 3 is proposed for this complex.
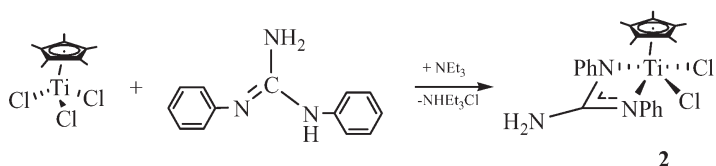
In order to test the potential of complex **1** to serve as appropriate building block for construction of heterometallic complexes of early and late transition metals, we have carried out the reaction of the titanium complex **1** with [Rh(μ-OH)(cod)]$_2$ on an NMR-tube scale. Complex **1** reacts with the rhodium complex [Rh(μ-OH)(cod)]$_2$ in C$_6$D$_6$ at room temperature to yield, according to the ^{1}H NMR spectrum, a new rhodium complex [Rh{(PhN)$_2$CNH$_2$}(cod)]$_2$ (**3**), as a result of the guanidinide ligand transfer from the titanium to the rhodium center.

Complex **3** can be synthesized in a more straightforward reaction from the hydroxido complex [Rh(μ-OH)(cod)]$_2$ with *N,N*-diphenylguanidine in 1:2 molar ratio (Scheme 4). It was isolated as an air-stable red crystalline
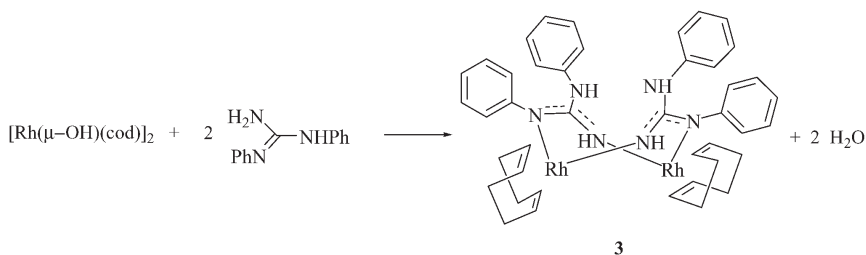
solid, soluble in most common organic solvents, and characterized by usual spectroscopic techniques as well as X-ray diffraction. Figure 2 shows an ORTEP diagram of **3**. Selected bond distances and angles are summarized in Table II. The geometry around each metal centre is distorted square planar. Each rhodium center is η^4-bound to a chelating cod ligand and to two nitrogen atoms of the bridging guanidinide ligands. The Rh–N distance average 2.101 Å. The cod ligand is coordinated to the rhodium center in the usual η^4-bonding mode and the C–C distances are within the expected range for Rh(I) complexes.

The analysis of the carbon–nitrogen bond distances within the guanidinide ligands can be tentatively used as a diagnostic tool regarding the extent of delocalization of the lone pair of the uncoordinated nitrogen. The bonds between the central carbon of the ligand and the coordinated nitrogen atoms average 1.328 Å while the bonds between the uncoordinated nitrogen atoms and the central carbon of the guanidinide ligands are on average considerably longer (1.399 Å). Therefore, we can propose that in complex **3** the contribution of form I to the ligand bonding is higher than that in complex **1** (Scheme 1).

The ^{1}H and ^{13}C NMR spectra indicate that in CDCl$_3$ or toluene-d_8 solution the coordination of the guanidinide ligand to the rhodium center is different from that observed in the solid state. Both the ^{1}H and ^{13}C NMR
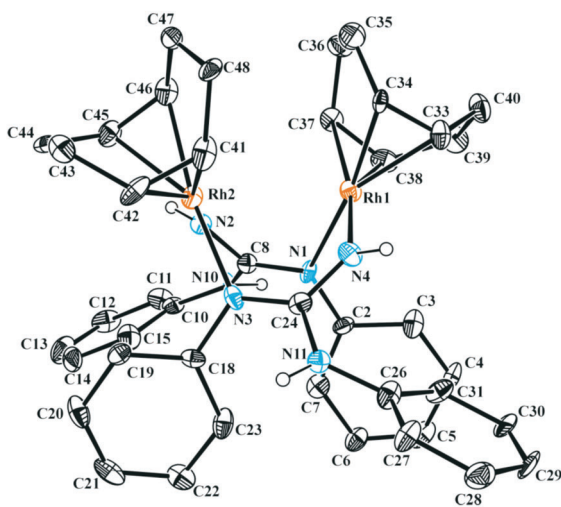

Fig. 2
Perspective ORTEP drawing (30% probability level) of the molecular structure of complex **3**

spectra indicate quite a symmetric coordination environment and would be in agreement with the coordination of the guanidinide ligand in a chelating fashion through the PhN moieties (Fig. 3). This coordination mode is analogous to that found for the benzamidinido complex [Rh{CPh(PhN)$_2$}-(cod)] (ref.[20]).
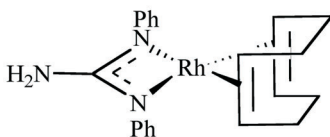

<small>Fig. 3</small>
Proposed coordination mode of complex **3** in solution

A ^{1}H VTNMR experiment carried out in toluene-d_8 indicates that no significant changes in the spectra pattern are observed from –80 to +80 °C.

In summary, we report here the synthesis of a titanium guanidinido complex and its reaction with [Rh(μ-OH)(cod)]$_2$, which results in transfer of the guanidinide ligand from the titanium to the rhodium center. These are the first complexes of rhodium and titanium with this ligand. They can be interesting starting materials for syntheses of new organometallic derivatives.

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