(THFMgNPh)$_6$ as an imide transfer agent: synthesis of titanium and zirconium imido complexes

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Abstract

Reaction of the magnesium imide (THFMgNPh)$_6$ (1) with either $(\eta^5\text{-}C_5H_5)_2TiCl_2$ or $(\eta^5\text{-}C_5H_5)TiCl_3$ affords the μ-imido complexes $(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-NPh})_2Ti(\eta^5\text{-}C_5H_5)_2$ (2) or $[(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-NPh})]_2$ (3) in good yield. In contrast, the reaction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with 1 exclusively leads to $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-NPh})]_2$ (4). The amido complex $(\eta^5\text{-}C_5H_5)_2Zr(Cl)NHPh \cdot 0.5$ toluene (5) was also isolated from this latter reaction in low yield. The crystal structures of 2, 3 and 5 were determined. These results demonstrate that 1 is an effective and useful transfer agent for the [NPh]$^{2-}$ moiety. Crystallographic data with Cu Kα radiation ($\lambda = 1.54178$ Å) for 2, and Mo Kα radiation ($\lambda = 0.71073$ Å) for 3 and 5, at 130 K: 2, $a = 7.986(6)$ Å, $b = 16.576(2)$ Å, $c = 17.184(2)$ Å, $Z = 4$, orthorhombic, space group $P2_12_12_1$; 3, $a = 8.677(4)$ Å, $b = 14.527(8)$ Å, $c = 17.032(10)$ Å, $Z = 4$, orthorhombic, space group $Pbca$; 5, $a = 6.564(3)$ Å, $b = 19.869(9)$ Å, $c = 13.440(4)$ Å, $\beta = 101.12(3)°$, $Z = 4$, monoclinic, space group $P2_1/n$.

Keywords: Titanium; Zirconium; Magnesium; Imido complexes; Crystal structure; Cyclopentadienyl

1. Introduction

Organomagnesium compounds in the form of Grignard reagents RMgX (R = alkyl or aryl group; X = halide) or diorganomagnesium species MgR$_2$ are widely used in organic and organometallic chemistry [1]. In their reactions they bear a resemblance to organolithium reagents, which perform a similar function in many instances. In sharp contrast the synthetic application of corresponding derivatives of related nitrogen based ligands such as amides or imides has been confined almost exclusively to lithium compounds [2]. Magnesium based compounds have rarely been used as transfer agents for −NR$_2$ or −NR groups. It has, however, been demonstrated in many cases that organomagnesium reagents are less prone to effect reduction of a substrate than their lithium analogues or to form 'ate' complexes, particularly in the case of transition metal compounds [3]. It may therefore be useful to investigate the use of magnesium amides or imides as possible transfer agents for these ligands. Of particular interest is the possible use of the recently reported [4] magnesium imide (THFMgNPh)$_6$ (1) as a transfer agent for the imido

group NPh to, for example, a transition metal center to give the corresponding metal imido complex. Complexes of this type have attracted considerable interest, particularly those of the electrophilic early transition metals of Groups 4 and 5. Such complexes have shown potential in both alkane and arene C−H bond activation [5] as well as 2 + 2 cycloadditions [5c,5f,6], catalytic amination of alkynes [7], and adduct chemistry [5c,5d,6a,8]. (THFMgNPh)$_6$ (1) can easily be prepared [4] in good yield from the straightforward reaction of aniline with commercially available 'dibutylmagnesium'. The use of 1 as an imide transfer agent provides an alternative synthetic route to transition metal imido complexes. Usually the syntheses of such complexes involve formation of an amido precursor followed by an amide abstraction step, for example, either via deprotonation or methylation to give the imido species [5b,7a,9].

2. Experimental details

2.1. General procedures

All reactions were performed using modified Schlenk techniques under an inert atmosphere of N$_2$ or in a Vacuum Atmospheres HE43-2 drybox. Solvents were

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freshly distilled under N_2 from Na/K or sodium/potassium benzophenone ketyl and degassed twice before use. NMR spectra were obtained on a General Electric QE-300 NMR spectrometer and referenced to an internal standard. IR spectra were obtained on a Perkin-Elmer 1430 spectrometer. $(\eta^5\text{-}C_5H_5)TiCl_3$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$, $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and the solution of Bu_2Mg (1:1 mixture of n-and sec-Bu) 1.0 M in heptane were purchased commercially and used as received. Aniline, methylene chloride and $(Me_2N)_3PO$ were distilled off calcium hydride before use.

2.2. $(THFMgNPh)_6$ (1)

$MgBu_2$ (40.3 mmol in heptane solution, 40 ml) was added dropwise to aniline (3.75 g, 40.3 mmol) dissolved in THF (50 ml) and the solution was stirred for 12 h. The resulting white solid was filtered and washed with hexane (3 × 25 ml) to yield $(THFMgNPh)_6$ (6.17 g, 5.64 mmol, 84%). ^1H NMR (300 MHz, C_6D_6) δ 7.17 (t, $J = 7.2$ Hz, 2H, m-H), 6.97 (dd, $J = 1.2$, 8.1 Hz, 2H, o-H), 6.35 (t, $J = 7.2$ Hz, 1H, p-H), 3.58 (s, br, 4H, OCH_2), 1.15 (s, br, 4H, CH_2). ^{13}C NMR (300 MHz, C_6D_6) δ 168.5 (s, ipso-C), 129.5 (d, m-C), 125.0 (d, o-C), 110.4 (d, p-C), 70.0 (t, OCH_2) 25.3 (t, CH_2).

2.3. $\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)_2Ti(\eta^5\text{-}C_5H_5)_2$ (2)

$(\eta^5\text{-}C_5H_5)_2TiCl_2$ (0.68 g, 2.73 mmol) was dissolved in toluene (80 ml). $(THFMgNPh)_6$ (0.51 g, 0.46 mmol) was added via solid addition funnel and the solution was refluxed for 16 h. The solution was then filtered through Celite and the filtrate was concentrated under reduced pressure to ca. 50 ml. Suitable crystals for

X-ray diffraction were obtained upon slow cooling to $-20°C$. (0.57 g, 1.12 mmol, 82% based on Ti). M.p. 160°C (decomp.). ^1H NMR (300 MHz, C_6D_6) δ 7.09 (t, $J = 7.5$ Hz, 4H, m-H), 6.80 (t, $J = 7.2$ Hz, 2H, p-H), 6.44 (d, $J = 7.8$ Hz, 4H, o-H), 6.21 (s, 5H, $(\eta^5\text{-}C_5H_5)$), 6.06 (s, 5H, $(\eta^5\text{-}C_5H_5)$), 6.04 (s, 5H, $(\eta^5\text{-}C_5H_5)$). ^{13}C NMR (300 MHz, C_6D_6) δ 128.9 (d, m-C), 122.6 (d, p-C), 120.4 (d, o-C), 119.8 (d, $(\eta^5\text{-}C_5H_5)$), 118.2 (d, $(\eta^5\text{-}C_5H_5)$), 113.9 (d, $(\eta^5\text{-}C_5H_5)$). IR (Nujol) ν 1575(w), 1230(m), 1010(ms), 800(vs), 750(m), 700(m) cm^{-1}.

2.4. $[(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)]_2$ (3)

$(\eta^5\text{-}C_5H_5)TiCl_3$ (0.88 g, 4.0 mmol) was dissolved in toluene (50 ml). $(THFMgNPh)_6$ (0.75 g, 0.67 mmol) was added via solid addition funnel and the solution was refluxed for 4.5 h. The solution was then filtered through Celite and the filtrate was concentrated under reduced pressure to ca. 25 ml. Dark orange crystals (0.73 g, 1.52 mmol, 76% based on Ti) were obtained upon slow cooling to $-20°C$. M.p. 257°C. ^1H NMR (300 MHz, C_6D_6) δ 7.00 (dt, $J = 1.2$, 7.8 Hz, 2H, m-H), 6.79 (dd, $J = 1.2$, 7.2 Hz, 2H, o-H), 6.75 (dt, $J = 1.2$, 8.2 Hz, 1H, p-H), 6.08 (s, 5H, $(\eta^5\text{-}C_5H_5)$). ^{13}C NMR (300 MHz, C_6D_6) δ 129.3 (d, m-C), 125.4 (d, p-C), 121.2 (d, o-C), 118.5 (d, $(\eta^5\text{-}C_5H_5)$). IR (Nujol) ν 1580(m), 1240(s), 1065(m), 1015(m), 890(w), 815(s), 755(s), 685(s), 625(m), 580(m) cm^{-1}.

2.5. $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}NPh)]_2$ (4)

$(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (1.17 g, 4 mmol) was dissolved in toluene (50 ml). $(THFMgNPh)_6$ (0.75 g, 0.67 mmol)

Table 1
Crystallographic data for compounds 2, 3 and 5

	2	3	5
Formula	$C_{27}H_{25}ClN_2Ti_2$	$C_{22}H_{20}Cl_2N_2Ti_2$	$C_{19.5}H_{20}ClNZr$
M_r	508.7	479.2	395.0
a (Å)	7.986(1)	8.677(4)	6.564(3)
b (Å)	16.576(2)	14.527(8)	19.869(9)
c (Å)	17.184(2)	17.032(10)	13.440(4)
β (°)			101.12(3)
V (Å³)	2274.8(5)	2147(2)	1720.0(12)
Z	4	4	4
Space group	$P2_12_12_1$	$Pbca$	$P2_1/n$
λ (Å)	Cu K α (1.54178)	Mo K α (0.71073)	Mo K α (0.71073)
d(calc) (g cm^{-3})	1.485	1.482	1.525
μ (mm^{-1})	7.180	1.003	0.792
Range of transmission factors	0.58–0.79	0.98–0.99	0.89–0.92
2θ range (°)	0 to 112	0 to 50	0 to 50
No. of reflections measured with $F > 4\sigma(F)$	1510	1271	1981
Parameters refined	289	105	177
$R(F)$ (%)	3.75	4.36	5.92
$Rw(F)$ (%)	3.64	4.59	6.20
GoF	1.25	1.24	1.28

was added via solid addition funnel and the solution was refluxed for 2 h. At reflux temperature the solution quickly darkens and very fine green crystals are precipitated. The solution was filtered and the green solid washed with THF (3 × 20 ml) and dried to give **4** (0.73 g, 1.16 mmol, 58% based on Zr). Cooling of the toluene filtrate to 4°C yielded additional **4** as a very fine crystalline powder (0.10 g). ^{1}H NMR (300 MHz, C_6D_6) δ 7.06 (t, $J = 7.8$ Hz, 2H, m-H), 6.71 (t, $J = 7.8$ Hz, 1H, p-H), 6.34 (d, $J = 8.4$ Hz, 2H, o-H), 6.00 (s, 10H, (η^5-C_5H_5)). IR (Nujol) ν 1580(m), 1245(s), 1010(m),

865(w), 805(s), 750(sh, s), 690(mw), 630(mw), 565(br, m) cm^{-1}. Owing to the insolubility of **4** in common organic solvents, recrystallization and satisfactory elemental analysis could not be performed. Further concentration of the toluene solution to ca. 15 ml and slow cooling to -20°C yielded fine yellow crystals of (η^5-C_5H_5)$_2$Zr(Cl)NHPh $\cdot$ 0.5 toluene (**5**). M.p. 168°C. ^{1}H NMR (300 MHz, C_6D_6) δ 7.20 (t, $J = 7.5$ Hz, 2H, m-H), 6.97 (d, $J = 7.5$ Hz, 2H, o-H), 6.86 (t, $J = 7.5$ Hz, 1H, p-H), 5.76 (s, 10H, (η^5-C_5H_5)). ^{13}C NMR (300 MHz, C_6D_6) δ 156.3 (s, $ipso$-C), 129.1 (d, m-C),

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for **2**, **3** and **5**

	x	y	z	U_{eq}
Compound 2				
Ti(1)	9965(2)	5242(1)	2173(1)	19(1)
Ti(2)	9628(2)	4230(1)	796(1)	19(1)
N(1)	10662(7)	5203(3)	1010(3)	19(2)
N(2)	8914(7)	4180(3)	1850(3)	21(2)
Cl	7181(2)	4587(1)	112(1)	34(1)
C(1)	11689(9)	5728(4)	572(3)	19(2)
C(2)	13426(9)	5723(4)	600(4)	24(2)
C(3)	14373(10)	6244(4)	162(4)	29(2)
C(4)	13623(9)	6794(4)	−331(4)	25(2)
C(5)	11901(10)	6782(5)	−396(4)	31(3)
C(6)	10941(10)	6264(4)	52(4)	27(2)
C(7)	7839(9)	3637(4)	2222(4)	22(2)
C(8)	7891(10)	3515(4)	3038(4)	27(2)
C(9)	6868(10)	2956(4)	3387(4)	34(3)
C(10)	5719(10)	2517(4)	2960(4)	31(3)
C(11)	5619(10)	2638(4)	2161(4)	28(2)
C(12)	6663(10)	3189(4)	1800(4)	28(2)
C(13)	7146(10)	5665(5)	1922(4)	35(3)
C(14)	8180(11)	6277(5)	1704(4)	34(3)
C(15)	9009(10)	6587(4)	2370(4)	35(3)
C(16)	8396(10)	6149(4)	3012(4)	29(3)
C(17)	7262(9)	5568(4)	2735(4)	29(2)
C(18)	11221(10)	4988(5)	3399(4)	33(3)
C(19)	11808(10)	4374(5)	2917(4)	32(3)
C(20)	12794(9)	4704(4)	2338(4)	26(2)
C(21)	12842(9)	5557(5)	2467(4)	28(2)
C(22)	11895(9)	5713(5)	3131(4)	31(3)
C(23)	9693(11)	3105(4)	−78(4)	39(3)
C(24)	10939(12)	3653(5)	−301(5)	47(3)
C(25)	12118(11)	3698(4)	286(6)	49(3)
C(26)	11606(10)	3192(5)	884(5)	37(3)
C(27)	10163(12)	2820(4)	646(4)	44(3)
Compound 3				
Ti(1)	13458(8)	156(5)	4634(4)	249(2)
Cl(1)	29921(13)	11705(8)	963(7)	429(4)
N(1)	−6745(39)	5540(21)	4847(19)	270(11)
C(1)	33430(54)	−5297(59)	13186(51)	410(24)
C(2)	21315	−1722	17888	386(22)
C(3)	7987	−7176	16561	288(20)
C(4)	11865	−14122	11038	305(20)
C(5)	27589	−12961	8952	326(21)
C(6)	−5598(49)	19170(27)	13131(25)	325(14)
C(7)	−12561(50)	25320(31)	18196(25)	380(15)
C(8)	−27755(48)	24191(31)	20330(25)	355(15)
C(9)	−35981(55)	17082(33)	17189(29)	482(18)
C(10)	−29186(52)	10865(32)	12089(27)	417(16)
C(11)	−13656(45)	11853(27)	10044(22)	251(12)

Table 2 (continued)

	x	y	z	U_{eq}
Compound 5				
Zr	1436(1)	7537(1)	8263(1)	19(1)
Cl	3614(3)	7613(1)	6937(1)	30(1)
N	−1051(11)	7020(3)	7374(5)	23(2)
C(1)	1614(18)	6494(6)	9298(8)	47(4)
C(2)	1973(17)	7031(6)	9960(7)	49(4)
C(3)	3884(18)	7306(5)	9917(7)	46(4)
C(4)	4670(15)	6948(5)	9190(7)	41(4)
C(5)	3259(17)	6444(5)	8825(7)	41(4)
C(6)	1619(16)	8669(5)	9105(8)	39(4)
C(7)	1589(17)	8793(4)	8101(8)	42(4)
C(8)	−359(18)	8595(4)	7547(8)	45(4)
C(9)	−1483(16)	8354(5)	8241(10)	51(4)
C(10)	−269(17)	8394(5)	9214(8)	45(4)
C(11)	−1295(13)	6371(4)	6971(6)	23(3)
C(12)	−3185(15)	6021(5)	6861(7)	34(3)
C(13)	−3380(16)	5374(5)	6478(7)	36(3)
C(14)	−1760(16)	5049(4)	6170(7)	37(4)
C(15)	95(14)	5387(4)	6260(7)	30(3)
C(16)	357(13)	6042(4)	6632(6)	25(3)
C(17)	3847	74	4109	60(3)
C(18)	5326	407	3831	48(6)
C(19)	7270	495	4453	84(4)
C(20)	7632	259	5450	55(6)
C(21)	4106	−152	5202	37(5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

121.5 (d, *o*-C). 120.9 (d, *p*-C), 112.7 (d, $(\eta^5\text{-}C_5H_5)$). IR (Nujol) ν 1590(w), 1250(m), 1150(br, mw), 1010(m), 840(w), 800(m), 720(s), 685(m) cm^{-1}.

$(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (0.64 g, 2.2 mmol) was dissolved in THF (40 ml). (THFMgNPh)$_6$ (0.41 g, 0.36 mmol) was added via solid addition funnel and the solution was refluxed for 16 h. The solution was filtered and the green solid washed with THF (3 × 20 ml) and dried to give 4 (0.48 g, 0.77 mmol, 70% based on Zr).

Further attempts at the preparation of $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}NPh)]_2$ (6) involved the reaction between 2 (0.76 g, 1.49 mmol) in THF (40 ml) and Na(C$_5$H$_5$) (0.38 g, 4.32 mmol) under reflux for 48 h. After filtering through Celite, the solution was pumped to dryness under reduced pressure. The resulting dark orange oil was extracted with methylene chloride (50 ml). Addition of hexane (10 ml) and then concentration of the solution to ca. 25 ml yielded 2 upon cooling in a −20°C freezer.

2.6. X-ray crystallography

A dark orange needle of 2 (0.04 × 0.08 × 0.20 mm) suitable for data collection was mounted in the cold stream (130 K) of a Siemens P4RA diffractometer equipped with an LT-2 low temperature device. All unique diffraction maxima $(+h, +k, +l)$ with $2\theta <$ 112° were measured by fixed speed, 2θ–θ scans (10° min^{-1}) with nickel foil monochromated Cu K α radiation ($\lambda = 1.54178$ Å) from a Siemens rotating anode

operating at 15 kW. A 6% linear decay in the intensities of the two check reflections occurred during data collection, and the data were scaled accordingly. 1511 of the unique data (1727) were judged observed ($F > 4\sigma(F)$). The structure was solved in space group $P2_12_12_1$ using direct and difference Fourier methods (SHELXTL PLUS) [10]. The hydrogen atoms were added in calculated positions and refined by use of a riding model and fixed isotropic thermal parameters equal to 0.04 Å^2. The absolute structure was determined. An absorption correction (XABS) [11] was applied. Refinement [12] was by full-matrix least-squares methods based on F, with anisotropic thermal parameters for all non-hydrogen atoms. The final difference map showed no peaks or holes greater than 0.36 eÅ^{-3}.

A dark brown prism of 3 (0.45 × 0.15 × 0.04 mm) selected for data collection was mounted in the cold stream (130 K) of a Siemens R3m/v diffractometer fitted with an Enraf-Nonius low temperature apparatus. The radiation employed was graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) operating at 2 kW. The structure was solved in space group *Pbca* using Patterson and difference Fourier methods, developed and refined routinely. The $(\eta^5\text{-}C_5H_5)$ ring was disordered into two orientations related by rotation around the ring axis. During refinement the two sets of $(\eta^5\text{-}C_5H_5)$ rings were constrained as rigid pentagons. Hydrogen atoms were added in calculated positions, assuming C–H of 0.96 Å, and refined by use of a riding model and fixed isotropic thermal parameters equal to

0.05 $\mathring{A}^2$ except for those atoms affected by disorder. An absorption correction (XABS) was made. Refinement was by full-matrix least-squares methods based on F, with anisotropic thermal parameters for all non-hydrogen atoms except those of the $(\eta^5\text{-}C_5H_5)$ ring. The final difference map showed no peaks or holes greater than 0.41 e$\mathring{A}^{-3}$.

A yellow needle of **5** ($0.30 \times 0.12 \times 0.12$ mm) suitable for data collection was similarly mounted on the Siemens R3m/v diffractometer. The structure was solved in space group $P2_1/n$ (No. 14) using direct and difference Fourier methods. A half molecule of toluene resides on a center of symmetry and was included with its positional parameters fixed, thermal parameters free. Hydrogen atoms were added geometrically, assuming C–H and N–H of 0.96 $\mathring{A}$, and refined by use of a riding model and fixed isotropic thermal parameters equal to 0.05 $\mathring{A}^2$ except for those atoms affected by disorder. An absorption correction (XABS) was made. Refinement was by full-matrix least-squares methods based on F, with anisotropic thermal parameters for all non-hydrogen atoms except those of the toluene. The final difference map contains three unassigned features ranging from 1.7 to 1.1 e$\mathring{A}^{-3}$ in the vicinity of the disordered toluene. No other significant features were present.

Selected crystallographic data, atom coordinates and selected structural parameters for **2**, **3** and **5** are provided in Tables 1–3 respectively.

3. Results and discussion

The main objective of the work described here was to demonstrate that $(THFMgNPh)_6(\mathbf{1})$ is a useful imido transfer agent toward transition metal complexes. A summary of this work is illustrated in Scheme 1. The reaction of the magnesium imide $(THFMgNPh)_6(\mathbf{1})$ with $(\eta^5\text{-}C_5H_5)_2TiCl_2$ in a 1:6 ratio in refluxing toluene proceeded cleanly, but did not give the symmetric dimer $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}NPh)]_2(\mathbf{6})$ but rather dark orange crystals of the asymmetric μ-phenylimido complex $(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)_2Ti(\eta^5\text{-}C_5H_5)_2$ (**2**) in excellent yield. X-ray diffraction studies of **2** were undertaken to confirm its structure. When $(\eta^5\text{-}C_5H_5)TiCl_3$ was similarly reacted with **1**, the expected symmetric imido dimer $[(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)]_2(\mathbf{3})$ was obtained in good yield. The structure of **3** has previously been determined [9a], although no details were given. In addition the direct preparation of **3** by using **1** is simpler than the previously reported route, which requires two steps and necessitates the isolation of an intermediate amido complex [9a]. These results involving the reactions of **1** provide the first example of the practical synthetic utility of magnesium imides. It is apparent that this magnesium imide is both a capable and effective imide transfer agent. The phenylimido group can be

Table 3
Selected bond lengths ($\mathring{A}$) and angles (°) for compounds **2**, **3** and **5**

Compound 2			
Ti(1)···Ti(2)	2.911(2)	Ti(1)–N(1)–Ti(2)	95.6(2)
Ti(1)–N(1)	2.075(5)	Ti(1)–N(2)–Ti(2)	95.6(2)
Ti(1)–N(2)	2.028(5)	Ti(1)–N(1)–C(1)	130.5(4)
Ti(2)–N(1)	1.849(5)	Ti(1)–N(2)–C(7)	133.4(4)
Ti(2)–N(2)	1.900(5)	Ti(2)–N(1)–C(1)	133.7(4)
Ti(2)–Cl	2.357(2)	N(1)–Ti(1)–N(2)	79.7(2)
N(1)–C(1)	1.413(8)	N(1)–Ti(2)–N(2)	89.0(2)
N(2)–C(7)	1.398(9)	N(1)–Ti(2)–Cl	104.5(2)
Ti(1)–C	2.405(5)	N(2)–Ti(2)–Cl	103.7(2)
Ti(2)–C	2.366(5)	Ti(2)–N(2)–C(7)	130.5(4)
Compound 3			
Ti(1)···T(2)	2.819(4)	Ti(1)–N(1)–Ti(1A)	94.9(1)
Ti(1)–N(1)	1.920(4)	Ti(1)–N(1)–C(11)	131.7(3)
Ti(1)–N(1A)	1.906(3)	Ti(1A)–N(1)–C(11)	133.2(3)
Ti(1A)–N(1A)	1.906(3)	N(1)–Ti(1)–N(1A)	85.1(1)
Ti(1)–Cl(1)	2.290(2)	Cl(1)–Ti(1)–N(1)	106.0(1)
N(1)–C(11)	1.409(5)	Cl(1)–Ti(1)–N(1A)	106.1(1)
Ti(1)–C	2.369(av.)		
Compound 5			
Zr–Cl	2.494(3)	Zr–N–C(11)	133.8(5)
Zr–N	2.096(6)	Cl–Zr–N	96.5(2)
N–C(11)	1.397(10)		

transferred to titanium cleanly, and in a straightforward reaction, to give the complexes **2** and **3** in good isolated yields.

The structure of the titanium complex **2** is shown in Fig. 1, selected bond lengths and angles are given in Table 3. It is a bimetallic species with the titanium centers linked by bridging phenylimido groups giving a central Ti_2N_2 heterocyclic ring. The Ti(1) atom is bound to two $(\eta^5\text{-}C_5H_5)$ rings, whereas Ti(2) is bound to an $(\eta^5\text{-}C_5H_5)$ ring and a Cl atom. The Ti····Ti distance (2.911(2) $\mathring{A}$) is not unusually short for a binuclear titanium(IV) complex, and similar distances have been observed in related species [13]. Although the four-membered Ti_2N_2 ring is planar (maximum deviation from the averaged plane 0.001 $\mathring{A}$) the lengths of the Ti–N bonds differ significantly owing to the different substitution of the metal atoms. This is also reflected in different N–Ti–N angles of 79.7(2)° at Ti(1) and 89.0(2)° at Ti(2). For symmetrical μ-imido complexes, the Ti–N bond lengths are invariably equivalent (ca. 1.90 $\mathring{A}$) [13b]. However, for **2** both Ti(1)–N bonds exhibit considerable lengthening (Ti(1)–N(1) = 2.075(5) $\mathring{A}$ and Ti(1)–N(2) = 2.028(5) $\mathring{A}$) in comparison with those of Ti(2), where Ti(2)–N(1) = 1.849(5) $\mathring{A}$ and Ti(2)–N(2) = 1.900(5) $\mathring{A}$). The latter distances are closest to those normally observed in titanium imido complexes, which are usually in the range 1.86–1.94 $\mathring{A}$ [13,14]. The distortion of the Ti–N bond lengths in **2** is not unique; a similar variation in bond lengths has been observed in a related mixed amido/imido Ti_2N_2 heterocycle, although in this complex the titaniums have

different oxidation states [14]. For the $(\eta^5\text{-}C_5H_5)$ rings attached to Ti(1), the average Ti–C bond distances are comparatively longer than those of the $(\eta^5\text{-}C_5H_5)$ ring attached to Ti(2). Although there are no close contacts in the structure of **2** it is likely that the steric requirements of the $(\eta^5\text{-}C_5H_5)$ rings attached to Ti(1) do contribute to the lengthening of these bonds. Also, the respective Ti–C and Ti–N bond distances may reflect the relative electronegativity of each titanium. Both the Ti–N and Ti–C bond lengths indicate that Ti(2) has more electropositive character than Ti(1). In support of this the ^{1}H NMR spectrum of **2** displays resonances in which the $(\eta^5\text{-}C_5H_5)$ rings attached to Ti(1) are observed upfield of the unique $(\eta^5\text{-}C_5H_5)$ ring on Ti(2). This difference is primarily due to the Cl substituent at Ti(2).

Although the structure of **3** has been previously determined [9a], virtually no details were provided. Selected bond distances and angles for **3** are given in Table 3 and the structure is depicted in Fig. 2. The dimer is located on a crystallographic center of inversion. The geometry at the titanium atom is somewhat distorted from tetrahedral. The Ti $\cdots$ Ti distance is 2.819(4) Å. Though this distance is shorter than that determined for **2**, it is in the normal range expected for such a titanium(IV) complex [13b]. Unlike the asymmetric Ti$_2$N$_2$ heterocycle **2**, both Ti–N bond lengths for **3** are almost equal and in the range reported for other titanium μ-imido compounds [13,14], as are the Ti–N–Ti and N–Ti–N angles. However, these bond distances differ slightly from each other, indicating the bridging μ-imido ligands may be bonding asymmetrically [13b].

Having prepared the titanium μ-imido compounds **2** and **3** it was decided to extend this synthetic route to analogous zirconocene imido complexes. When **1** was reacted with $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in refluxing tol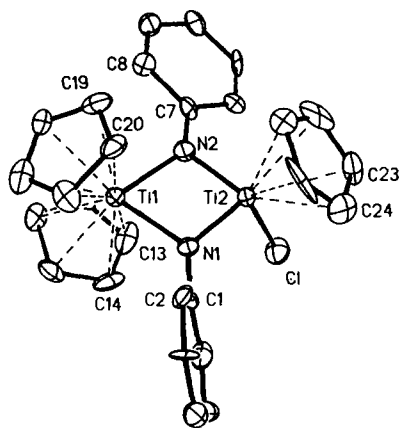uene a pale green precipitate formed. This compound was identified spectroscopically as the dimeric μ-imido product $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}NPh)]_2$(**4**). Attempts to characterize **4** more fully were unsuccessful, owing to the relative insolubility of this compound. Formulation of **4** as an imido-bridged dimer is based on other structurally characterized Group 4 species such as $[(\eta^5\text{-}C_5H_5)_2ZrN(4\text{-}{}^tBuC_6H_4)]_2$ [5c,5f]. A second product, obtained in low yield, was the amido complex $(\eta^5\text{-}C_5H_5)_2(Cl)ZrNHPh$ (**5**).

The structure of the zirconocene amido complex **5** is shown in Fig. 3. Not unexpectedly, the Zr atom exhibits pseudotetrahedral geometry. There is nothing unusual in the Zr–N (2.096(6) Å) and Zr–Cl bond lengths. A similar Zr–N bond length has been observed in the related [15] amido complex $(\eta^5\text{-}C_5H_5)_2Zr(NHPh)OSO_2CF_3$ and the Zr–Cl distance (2.494(3) Å) is not unusually long, these bond distances range from 2.41 to 2.51 Å [16]. There is only one other feature of note; a weak hydrogen bonding interaction (H $\cdots$ Cl = 2.72 Å) exists between the amido hydrogen and the chlorine of an adjacent molecule.

Although **4** is dimeric, it is the related monomeric imido complexes of Group 4 which have attracted more interest, owing to the fact that the imido moiety in transient $(\eta^5\text{-}C_5H_5)_2ZrNR$ constitutes a reactive site for C–H bond activation [5] and 2 + 2 cycloaddition [5c,5f,6] chemistry. In an attempt to obtain a base-stabilized monomeric imide, $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ was treated with **1** in THF solution. This reaction does not proceed at ambient temperature, and the starting material was recovered in quantitative yield. Repetition of the reaction in refluxing THF led only to the isolation of **4** as product. Formation of a μ-phenylimido dimer $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}NPh)]_2$ instead of a monomeric THF adduct is not surprising. Similar results have been obtained with other substituents and they were explained
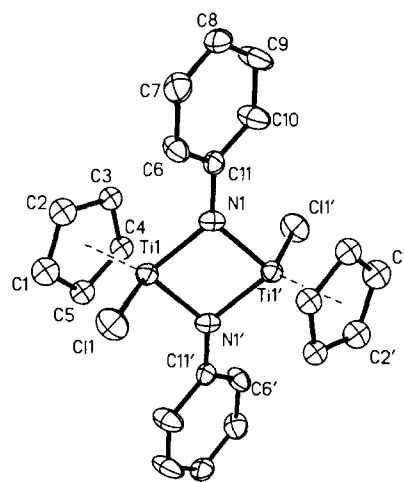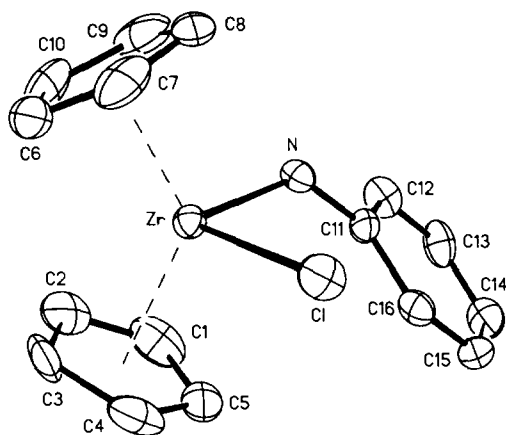

Fig. 2. Molecular structure of $[(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)]_2$ (**3**) with atoms shown as 50% probability ellipsoids. Hydrogen atoms are not shown for clarity.

Fig. 1. Molecular structure of $(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)_2Ti(\eta^5\text{-}C_5H_5)_2$ (**2**) with atoms shown as 50% probability ellipsoids. Hydrogen atoms are not shown for clarity.

Fig. 3. Molecular structure of $(\eta^5\text{-}C_5H_5)_2(Cl)ZrNHPh$ (5) with atoms shown as 50% probability ellipsoids. Hydrogen atoms are not shown for clarity.

on steric grounds [5c,5f,6d,16]. Sterically encumbering imido substituents lead to the formation of monomeric adducts, whereas less bulky substituents give dimeric species [5f,5c]. Compound **4** does not react with $(Me_2N)_3PO$ in refluxing THF.

Reaction of the magnesium imide **1** with $(\eta^5\text{-}C_5H_5)_2MCl_2$(M=Ti or Zr) metals demonstrates that the NPh group is readily transferred in both cases. However, the formation of **2** from the reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ implies that the $(\eta^5\text{-}C_5H_5)^-$ ligand can be displaced in addition to, or instead of, chloride. This reaction is not observed in the case of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. This may be due in part to titanium(IV) complexes having more labile ligands than those of the corresponding zirconium species [17]. It is unclear why formation of **2** is favored over the imido dimer $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}NPh)]_2$ (**6**). Possible steric congestion in the dimer **6**,

due to close contacts between phenyl and cyclopentadienyl rings, may be a contributing factor. In an attempt to obtain the imido dimer **6**, $Na(C_5H_5)$ was reacted with **2** in both refluxing THF and toluene solutions, but the formation of **6** could not be detected in either case. This result perhaps suggests that the dimeric titanocene imide **6** may be too sterically crowded to be readily formed.

The formation of **2** from the 6:1 reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with **1** indicates that this reaction is not a straightforward coupling of L_2MCl_2 (L=Cl, $(\eta^5\text{-}C_5H_5)$; M=Ti, Zr) with an MgNPh entity to form $MgCl_2$ and a transient L_2MNPh intermediate which then dimerizes to give a M_2N_2 heterocyclic product. Transient $L_2M=NR$ moieties have been reported to be intermediates in the synthesis of metal imido compounds [5,6]. If such an intermediate were present, then either **3** or **6** might have been expected as possible products from the coupling of **1** with $(\eta^5\text{-}C_5H_5)_2TiCl_2$, as formation of **2** requires both $(\eta^5\text{-}C_5H_5)_2TiNPh$ and $(\eta^5\text{-}C_5H_5)(Cl)TiNPh$. However, neither **3** nor **6** is an observed product in the reaction of **1** and $(\eta^5\text{-}C_5H_5)_2TiCl_2$, indicating that a transient $L_2Ti=NPh$ intermediate may not be formed during this reaction. If this is the case, then the M_2N_2 species **2** must form via an alternative route. For the coupling reaction of **1** with $(\eta^5\text{-}C_5H_5)_2TiCl_2$ a reasonable sequence for the initial part of this coupling may be envisaged. Though speculative, it probably involves initial coordination of the nucleophilic imido nitrogen to the metal center then formation of an M–N bond. This would then lead to the sequential loss of a halide to magnesium. Either dimerization of the resulting intermediate or reaction with a second equivalent of either $(\eta^5\text{-}C_5H_5)_2TiCl_2$ or MgNPh then leads to the observed products. The latter part of this reaction, which gives the Ti_2N_2 heterocycle, is less well understood.
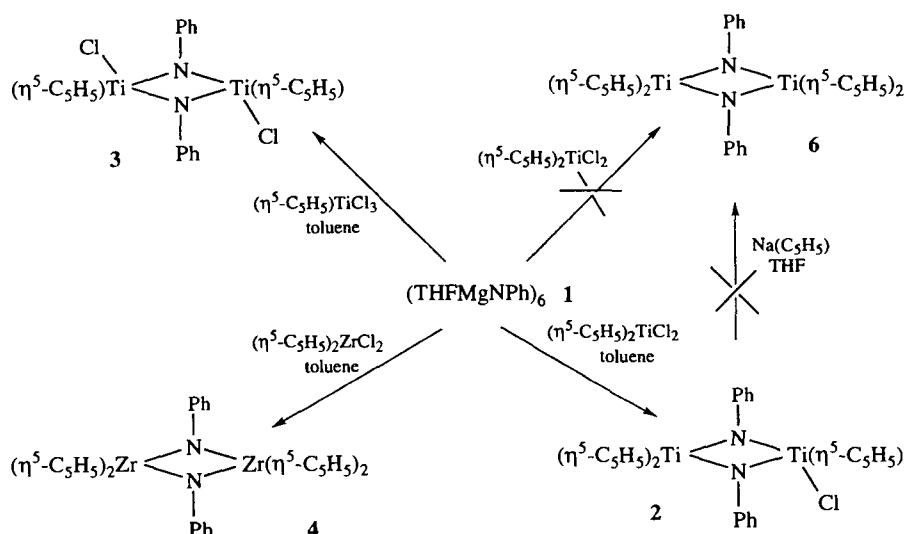
Scheme 1.

4. Conclusion

Coupling the magnesium imide $(THFMgNPh)_6(1)$ with either $(\eta^5\text{-}C_5H_5)_2TiCl_2$ or $(\eta^5\text{-}C_5H_5)TiCl_3$ gives a clean reaction yielding the respective μ-imido complexes 2 and 3 in good to excellent isolated yield. This reactivity can also be extended to give an analogous zirconium complex 4 from the coupling $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. These results demonstrate that the magnesium imide $(THFMgNPh)_6$ (1) can successfully be utilized as an imido transfer agent in synthesis. The NPh group is able to be transferred from magnesium to a transition metal center in a straightforward coupling reaction. Further investigations of the potential synthetic applications of magnesium imides are in hand.

5. Supplementary material available

Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles and hydrogen atom coordinates for 2, 3 and 5 (28 pages) are available. Ordering information is given on any current masthead page.

Acknowledgments

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