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(Article begins on next page)

Heterometallic complexes with cube-type [MTi$_3$N$_4$] cores containing Group 10 metals in a variety of oxidation states

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Table of Contents Entry:

The metalloligand [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] is capable of stabilizing Group 10 metals in the oxidation states 0, II or IV.
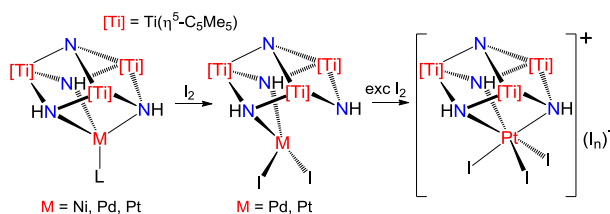
Abstract:

Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with one equivalent of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) in toluene at 60-80 °C and subsequent addition of diphenylacetylene, *trans*-stilbene or triphenylphosphane afforded the nickel(0) complexes $[LNi\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (L = PhC≡CPh (**2**), PhCH=CHPh (**3**), PPh₃ (**4**)). The nickel(II) complex $[I_2Ni\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**5**) was prepared by analogous addition of iodine to the solution obtained from the heating of **1** and $[Ni(cod)_2]$. Treatment of **1** with one equivalent of $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in toluene at room temperature led to the palladium(0) complex $[(dba)Pd\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**6**). Compound **6** reacted immediately with chloroform-d_1 to give the palladium dichloride derivative $[Cl_2Pd\{(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]$ (**7**), which was prepared by treatment of **1** with $[PdCl_2(cod)]$ at room temperature. Addition of iodine to a toluene solution of **6** afforded the analogue palladium(II) derivative $[I_2Pd\{(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]$ (**8**). Complex **6** reacted with two equivalents of dimethylacetylenedicarboxylate (dmad) to give the metallacyclopentadiene palladium(II) complex $[\{(MeOOC)_4C_4\}Pd\{(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]$ (**9**) via oxidative coupling. The treatment of **1** with $[Pt(nbe)_3]$ (nbe = norbornene) in toluene at room temperature gave the platinum(0) complex $[(nbe)Pt\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**10**). Compound **10** reacted with excess iodine to afford the platinum(IV) ionic derivative $[I_3Pt\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2(I_3)(I_5)$ (**11**) via an intermediate platinum(II) complex $[I_2Pt\{(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]$ (**12**). The X-ray crystal structures of **5**, **8**, **9** and **11** have been determined.

Introduction

Heterometallic sulfido complexes containing cube-type [M´M$_3$S$_4$] cores (M = Mo, W, Fe) constitute one of the most representative families within cluster chemistry.[1] A classical approach toward the rational synthesis of that type of complexes is based on the incorporation of a single metal into incomplete cube-type M$_3$S$_4$ aggregates.[2] These trinuclear complexes behave as metalloligands toward heterometals (M´) by using the lone pair electrons of the sulfur atoms. Thus, this synthetic route is especially appropriate for the incorporation of metal centers with a high affinity for soft ligands as late transition or post-transition metals in low or intermediate oxidation states. In particular, cube-type [M´Mo$_3$S$_4$] clusters containing Group 10 metals have been extensively investigated by Brorson and co-workers as molecular models in hydrodesulfurization catalysis,[3] and by the group of Hidai as efficient catalysts of organic transformations.[4,5]

In 1989, Roesky and co-workers reported the trinuclear titanium(IV) imido-nitrido complex [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**).[6] The structure of complex **1** shows an incomplete cube-type [Ti$_3$(μ-NH)$_3$(μ_3-N)] core, which strongly resembles those found in M$_3$S$_4$ clusters. On the basis of this similarity, we have intensively examined the incorporation of a variety of metal fragments into the preorganized structure of **1** to uncover a new family of heterometallic imido-nitrido compounds with cube-type [MTi$_3$N$_4$] cores. The trinuclear complex **1** is capable of acting as a neutral tridentate ligand through the NH imido groups toward many transition,[7] lanthanides,[8] and main-group[9] metals in a manner similar to other well-known facially coordinating trinitrogen six-electron donor ligands such as tris(pyrazolyl)methanes,[10] 1,4,7-triazacyclononanes,[11] and 1,3,5-triazacyclohexanes.[12] The great versatility of the metalloligand **1** is illustrated by the possibility of stabilizing complexes with metals in low (*e.g.*, Mo^0 and Ir^I) or high oxidation

3

states (*e.g.*, Ti^{IV} and Ta^{V}). Density functional theory (DFT) calculations performed on complexes of Group 6 and 9 metals in low oxidation states (0 and +1, respectively) showed that the presence of Ti^{IV} centers in the metalloligand **1** produces an additional stabilization through metal-metal couplings while maintaining the titanium and the incorporated heterometal in the initial oxidation states.[13] A similar electronic delocalization has been reported for a series of heterometallocubanes [MMo$_3$S$_4$] (M = Ni, Pd, Co),[14] although the assignment of formal oxidation states of the metal centers in those clusters remains inconclusive.[15] Therefore, **1** is capable of displaying π-acceptor properties in an analogous fashion to the cyclopentadienyl ligand and in contrast to the exclusive σ-donor interactions of trinitrogen organic systems.

Within this systematic study on the coordination chemistry of the metalloligand [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ$_3$-N)] (**1**), we were interested in assessing its ability to stabilize Group 10 metal centers in a variety of oxidation states. The potential π-acceptor character of **1** appears to be especially appropriate for the formation of complexes with those metals in the zero oxidation state. On the other hand, the use of polydentate nitrogen-based ligands is receiving considerable attention nowadays because of their ability to stabilize high-valent Group 10 species.[16] Herein, we report that the reactions of **1** with Group 10 metal(0) alkene complexes provide an access to aggregates with cube-type [MTi$_3$N$_4$] cores. The zerovalent heterometals in those adducts are readily oxidized to give nickel(II), palladium(II) or platinum(IV) complexes supported by the titanium metalloligand. The tendency of palladium(II) species to exhibit square-planar geometries afforded the first examples of bidentate coordination of **1** to a single metal center.

Results and discussion

Nickel complexes. The reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with one equivalent of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) in benzene-d_6 was monitored by ^1H NMR spectroscopy. No reaction was observed at room temperature and only after prolonged heating at 60 ºC, minor resonance signals assignable to free 1,5-cyclooctadiene (cod) were detected. Spectra taken after heating at 80 ºC for 3 days revealed complete consumption of the starting materials with concomitant formation of one compound that showed resonance signals for equivalent NH and $\eta^5\text{-}C_5Me_5$ ligands. However, the spectra revealed complicated multiplets for organic fragments instead of the expected resonances for free or coordinated 1,5-cyclooctadiene. Thus, while ^1H and $^{13}C\{^1H\}$ NMR data are consistent with a tridentate coordination of the titanium metalloligand to the nickel center (see below),[17] we were unable to provide more insight into the structure or composition of this complex with $[NiTi_3N_4]$ core. Noteworthy, in an independent NMR experiment, we found that $[Ni(cod)_2]$ in benzene-d_6 decomposed completely at 80 ºC to give free cod in solution and a mirror of nickel metal. Therefore, it appears that incorporation of Ni^0 into the incomplete cube-type structure of **1** requires thermal decomposition of the nickel precursor and is accompanied by chemical transformation of the 1,5-cyclooctadiene ligands.

In a preparative scale reaction, a 1:1 mixture of **1** and $[Ni(cod)_2]$ in toluene was initially heated at 60 ºC for 24 h and then at 80 ºC for 3 days to give a brown solution. Despite many attempts, a pure compound could not be isolated from this solution, but subsequent addition of donor molecules L to the *in situ* generated solution allowed the isolation of several nickel(0) derivatives. Thus, the treatment of this toluene solution with one equivalent of diphenylacetylene, *trans*-stilbene or triphenylphosphane at room temperature afforded complexes $[LNi\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (L = PhC≡CPh

(**2**), PhCH=CHPh (**3**), PPh$_3$ (**4**)) as air-sensitive red-brown solids in 43-80% yields (Scheme 1).
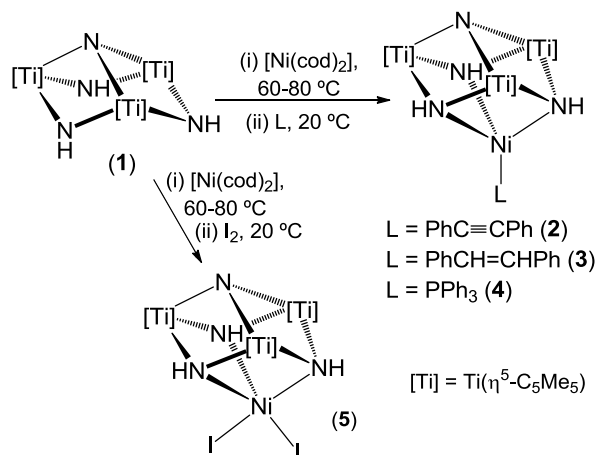
Scheme 1. Synthesis of nickel complexes.

Compounds **2-4** were characterized by spectroscopic and analytical methods. The IR spectra (KBr) reveal one ν_{NH} vibration in the range 3337-3327 cm^{-1}, which is similar to that determined for compound **1** (3352 cm^{-1}).[18] ^{1}H and ^{13}C{^{1}H} NMR spectra in benzene-d$_6$ at room temperature show resonance signals for equivalent NH and η^5-C$_5$Me$_5$ ligands. The NH resonance signals (δ = 10.38-9.17) in the ^{1}H NMR spectra are shifted to a higher field than that found for **1** (δ = 13.80).[18] We have noted an analogous shift in many adducts of **1** with a tridentate chelate coordination of the NH groups to the metal centers.[7-9] However, the resonances for the *ipso* carbon of the C$_5$Me$_5$ groups (δ = 116.9-115.3) in the ^{13}C{^{1}H} NMR spectrum are slightly shifted upfield with respect to that found for **1** (δ = 117.1).[18] This shift of the *ipso* carbon is unusual in complexes derived from **1** and indicates an increased electron density at the titanium centers upon coordination of the metalloligand. Indeed, this variation has been only found in the ^{13}C{^{1}H} NMR spectra of Group 9 derivatives, [(cod)M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (M = Rh, Ir) and [(C$_2$H$_4$)$_2$Rh{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (δ = 116.9-115.9), where DFT

calculations show the highest delocalization of the Group 9 metal d electrons with the Ti_3 core.[13b] Therefore, these chemical shifts suggest that the d^{10} nickel center in complexes **2-4** shares a considerable electron density with the metalloligand through the formation of metal-metal bonds with the Ti_3 triangle.

Further indication of the acceptor character of the metalloligand **1** in complexes **2** and **3** can be obtained from the spectroscopic data for the diphenylacetylene or *trans*-stilbene ligands coordinated to the nickel(0) centers. The $^{13}C\{^1H\}$ NMR spectrum of complex **2** displays one resonance at $\delta = 110.4$, which can be assigned to the acetylene carbons of the ligand. This resonance is shifted lower field compared to that of free diphenylacetylene ($\delta = 90.1$), but appears at higher field than those found in many nickel(0) complexes containing the diphenylacetylene ligand ($\delta = 141.3$-124.2).[19,20] Similarly, the $^{13}C\{^1H\}$ NMR spectrum of **3** shows one resonance for the olefinic carbons at $\delta = 63.3$, which is *ca.* 10 ppm at lower field than those reported for *trans*-stilbene ligands in several diphosphane nickel(0) complexes.[21] Those ^{13}C NMR chemical shifts are consistent with a lower degree of π back-donation to the alkyne or alkene ligands in complexes **2** and **3**. This is also corroborated by the IR spectrum (KBr) of **2**, which reveals a strong absorption at 1897 cm^{-1} for the ν_{CC} stretching vibration of the coordinated diphenylacetylene ligand. This band is shifted to lower energy relative to free diphenylacetylene ($\tilde{\nu}_{CC} = 2223$ cm^{-1}), but the reduction of the ν_{CC} stretching vibration ($\Delta\tilde{\nu} = 326$ cm^{-1}) in **2** is smaller than those observed in nickel(0) complexes with a high degree of π back-bonding into the alkyne ligand ($\Delta\tilde{\nu} = 482$-419 cm^{-1}).[19,22] The relatively high wavenumbers for the ν_{CO} stretching vibration observed in $[(CO)M'Mo_3S_4]$ ($M' = Ni$,[23] Pd[5b]) sulfido clusters have been explained by competition between the Mo_3 triangle and the CO ligands for M' electron density.[14]

The nickel(0) compounds **2**-**4** react immediately with chloroform-d_1 to give broad resonance signals in the ^{1}H NMR spectra probably due to paramagnetic nickel(II) derivatives. The oxidative reaction with iodine ($\geq$ 1 equivalent) of the toluene solution generated from heating **1** and [Ni(cod)$_2$] gave the nickel diiodide complex [I$_2$Ni{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**5**) (Scheme 1). Compound **5** was isolated as a brown solid in 63% yield if the reaction was performed under vigorous stirring for 30 min. Alternatively, slow diffusion of a toluene solution of I$_2$ into the solution obtained from heating a 1:1 mixture of **1** and [Ni(cod)$_2$] gave X-ray quality red-brown crystals of **5**·1/2C$_7$H$_8$ in 27% yield. The ^{1}H NMR spectrum of **5** in benzene-d_6 displays a broad resonance at 2.80 ppm ($\Delta\nu_{1/2}$ = 12 Hz) for the η^5-C$_5$Me$_5$ groups. While the presence of one resonance for the NH imido ligands was not detected in the ^{1}H NMR spectrum of **5**, the N-H stretch was identified in the IR spectrum (KBr) at 3328 cm^{-1}. The paramagnetic nature of **5** was confirmed by an Evans method determination of its effective magnetic moment (μ_{eff} = 2.47 μ_B, 293 K, C$_6$D$_6$ solution),[24] which indicated the presence of two unpaired electrons in the complex.

The solid-state structure of complex **5** is presented in Fig. 1, while selected distances and angles are given in Table 1. The molecular structure shows a [NiTi$_3$N$_4$] cube-type core with the nickel atom bonded to three NH imido groups of the {(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)} metalloligand and two iodine atoms. The coordination geometry about the nickel center may be described as intermediate between trigonal bipyramidal and square pyramidal (τ_5 = 0.57).[25] The Ni-I bond lengths (average 2.617(2) Å) in **5** compare well with those reported for the few crystallographically documented mononuclear nickel diiodide complexes [NiLI$_2$] containing tridentate nitrogen ligands.[26] Within the titanium

metalloligand, the distortions in bond distances and angles in **5** are small when compared to those of **1**.[6]
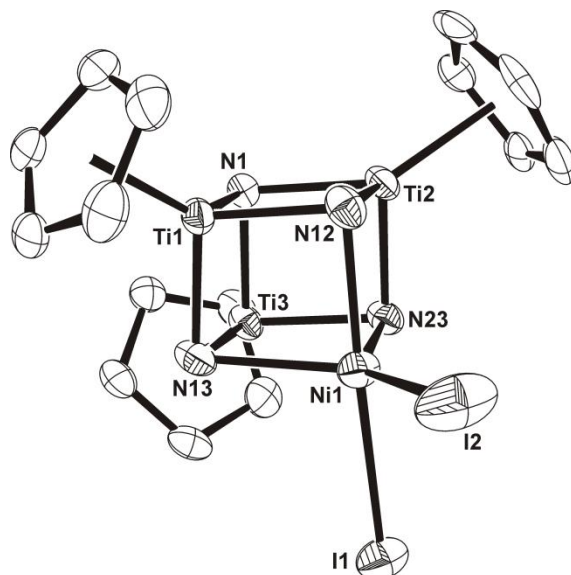
Fig. 1. Perspective view of **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity.

**Table 1** Selected lengths (Å) and angles (º) for complex **5**.

Ni(1)–N(12)	2.125(4)	Ni(1)–N(13)	2.197(4)
Ni(1)–N(23)	2.118(4)	Ni(1)–I(1)	2.618(1)
Ni(1)–I(2)	2.615(1)	Ti–N(1)[a]	1.914(13)
Ti–N[a]	1.945(14)	Ni(1)···Ti(1)	2.857(1)
Ni(1)···Ti(2)	2.841(1)	Ni(1)···Ti(3)	2.849(1)
N(12)–Ni(1)–N(13)	85.3(2)	N(12)–Ni(1)–N(23)	85.7(2)
N(13)–Ni(1)–N(23)	86.7(1)	I(1)–Ni(1)–I(2)	93.9(1)
N(12)–Ni(1)–I(1)	176.5(1)	N(12)–Ni(1)–I(2)	87.3(1)
N(13)–Ni(1)–I(1)	96.5(1)	N(13)–Ni(1)–I(2)	129.5(1)
N(23)–Ni(1)–I(1)	91.4(1)	N(23)–Ni(1)–I(2)	142.3(1)
N(1)–Ti–N[a]	85.8(4)	N–Ti–N[a]	97.6(8)
Ti–N(1)–Ti[a]	95.1(3)	Ti–N–Ti[a]	93.2(5)

[a] Averaged values.

Palladium complexes. Treatment of **1** with one equivalent of [Pd(dba)$_2$] or 0.5 equivalent of [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone or 1,5-diphenyl-1,4-pentadien-3-one) in toluene at room temperature led to the palladium(0) complex [(dba)Pd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**6**) and free dibenzylideneacetone (dba) (Scheme 2). The separation of compound **6** from the free organic diene dba was difficult because the similar solubility of both products in common solvents.[27] Only after being repeatedly washed with diethyl ether or acetonitrile, complex **6** could be obtained nearly free of dba ($\leq$ 5% by ^{1}H NMR spectroscopy) as a red solid in 55% yield.

The IR spectrum (KBr) of **6** reveals one ν_{NH} vibration at 3352 cm^{-1} and one strong absorption at 1640 cm^{-1} for the ν_{CO} stretching mode of the dba ligand.[28] ^{1}H and ^{13}C{^{1}H} NMR spectra in benzene-d$_6$ at room temperature show resonance signals for equivalent NH and η^5-C$_5$Me$_5$ ligands. The resonance for the *ipso* carbon of the C$_5$Me$_5$ groups (δ = 118.5) in the ^{13}C{^{1}H} NMR spectrum is shifted downfield with respect to that found for **1** (δ = 117.1).[18] This shift contrasts with those observed for the nickel compounds **2**-**4** and suggests a lower sharing of electron density of the palladium(0) center with the Ti$_3$ core.

The ^{1}H NMR spectrum of **6** shows two different sets of olefinic resonances, indicating that dba is coordinated to palladium through only one of its double bonds. Two well-resolved doublets at δ = 7.96 and 6.94 (^3J(H,H) = 15.9 Hz) correspond to the protons of the uncoordinated double bond of dba, whereas the protons of the olefin coordinated to palladium appear at δ = 5.28 and 5.16 (^3J(H,H) = 10.5 Hz). The ^{13}C{^{1}H} NMR spectrum shows two carbon resonances for the uncoordinated double bond (δ = 146.4 and 142.7) and two carbon resonances for the olefin coordinated to palladium (δ = 68.8 and 60.8).[29] The NMR data at room temperature rule out the exchange between coordinated and free olefins of the dba ligand observed in many palladium(0) complexes.[27b,30]
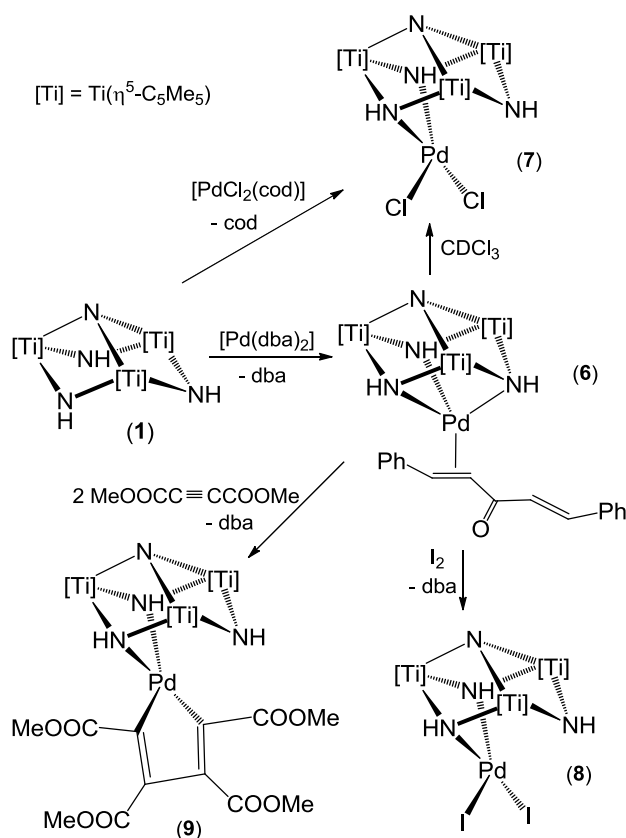
Scheme 2. Synthesis of palladium complexes.

Complex **6** readily reacts with chloroform-d_1 to give the palladium dichloride derivative $[Cl_2Pd\{(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]$ (**7**). Compound **7** was isolated as a brown solid in 84% yield by treatment of **1** with one equivalent of $[PdCl_2(cod)]$ in toluene at room temperature (Scheme 2). Addition of iodine ($\geq$ 1 equivalent) to a toluene solution of **6** afforded the analogue palladium(II) derivative $[I_2Pd\{(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]$ (**8**). Complex **8** was isolated as a brown solid in 44% yield if the reaction was carried out under vigorous stirring for 3 h or as X-ray quality red-brown crystals of $8\cdot I_2\cdot 0.75C_7H_8$ layering a toluene solution of **6** with a toluene solution of I_2. The solid-state structure is presented in Fig. 2 and selected distances and angles are given in Table 2. Two independent molecules of **8** are found in the asymmetric unit, which are associated by halogen bonds[31] between one iodide of each molecule and one diiodine

molecule. The remaining iodide in each molecule is further associated by halogen bonds to a neighboring I_2 molecule leading to right- and left-handed helical chains along the crystal (see Fig. S1 and Table S1 in the ESI).† The molecules of **8** show the palladium atoms bound to two NH imido and two iodide ligands, while the third NH group of the metalloligands are clearly not coordinated to the palladium centers (distances Pd(1)···N(13) 2.958(6) Å and Pd(2)··· N(56) 2.901(6) Å). The coordination geometry about the palladium atoms are slightly distorted square-planar (τ_4 = 0.08 and 0.09)[32] with N-Pd-N, I-Pd-I and N-Pd-I (*cis*) angles ranging from 88.0(2) to 92.5(3)°. The Pd-N and Pd-I averaged bond distances, 2.098(13) and 2.596(7) Å respectively, are similar to those reported for other PdI_2 complexes supported by diamine ligands.[33]
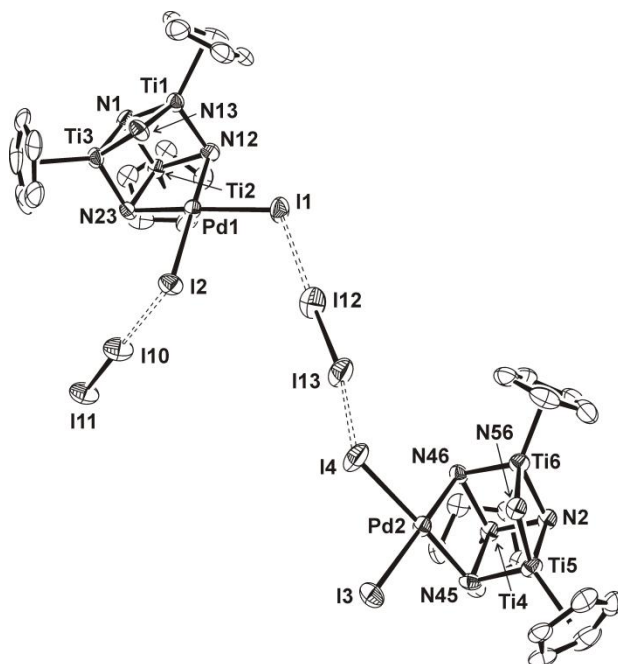
Fig. 2. Perspective view of **8** with thermal ellipsoids at the 50% probability level. Toluene solvent molecules, hydrogen atoms and methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity.

Table 2   Selected lengths (Å) and angles (º) for **8**.

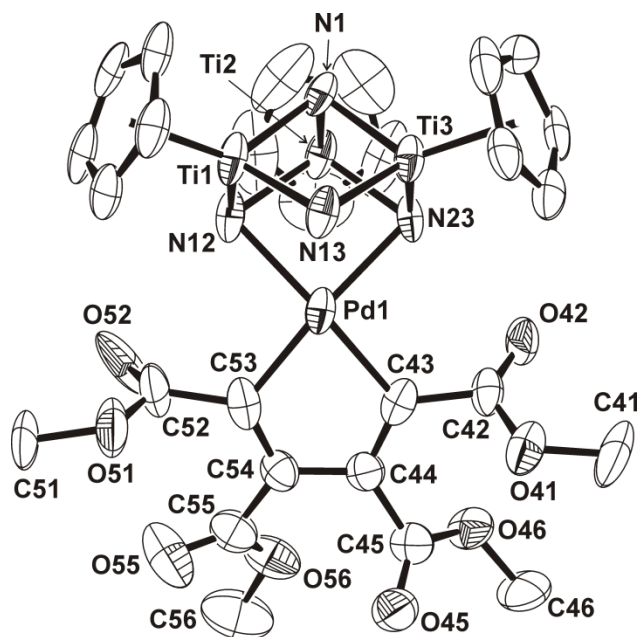| Molecule 1		Molecule 2	
Pd(1)–N(12)	2.087(6)	Pd(2)–N(45)	2.098(6)
Pd(1)–N(23)	2.118(6)	Pd(2)–N(46)	2.087(5)
Pd(1)···N(13)	2.958(6)	Pd(2)···N(56)	2.901(6)
Pd(1)–I(1)	2.608(1)	Pd(2)–I(3)	2.591(1)
Pd(1)–I(2)	2.593(1)	Pd(2)–I(4)	2.590(1)
Ti(1)–N(12)	2.034(6)	Ti(4)–N(45)	1.949(5)
Ti(1)–N(13)	1.911(6)	Ti(4)–N(46)	1.958(6)
Ti(2)–N(12)	1.962(6)	Ti(5)–N(45)	2.036(6)
Ti(2)–N(23)	1.954(6)	Ti(5)–N(56)	1.913(6)
Ti(3)–N(23)	2.020(6)	Ti(6)–N(46)	2.034(6)
Ti(3)–N(13)	1.911(6)	Ti(6)–N(56)	1.917(6)
Ti–N(1)[a]	1.921(7)	Ti–N(2)[a]	1.925(9)
Pd(1)···Ti(1)	3.083(2)	Pd(2)···Ti(4)	2.779(1)
Pd(1)···Ti(2)	2.779(2)	Pd(2)···Ti(5)	3.089(1)
Pd(1)···Ti(3)	3.120(1)	Pd(2)···Ti(6)	3.054(2)
N(12)–Pd(1)–N(23)	88.0(2)	N(45)–Pd(2)–N(46)	88.1(2)
I(1)–Pd(1)–I(2)	92.5(3)	I(3)–Pd(2)–I(4)	89.9(1)
N(12)–Pd(1)–I(1)	88.0(2)	N(45)–Pd(2)–I(3)	91.2(2)
N(12)–Pd(1)–I(2)	176.4(2)	N(45)–Pd(2)–I(4)	173.2(2)
N(23)–Pd(1)–I(1)	171.1(2)	N(46)–Pd(2)–I(3)	176.2(2)
N(23)–Pd(1)–I(2)	91.0(2)	N(46)–Pd(2)–I(4)	90.4(2)

[a] Averaged values.

IR spectra (KBr) of complexes **7** and **8** show two ν_{NH} vibrations, between 3354 and 3330 cm^{-1}, in a similar range to the value determined for **1** (3352 cm^{-1}).[18] The ^{1}H NMR spectra of complexes **7** and **8** in chloroform-d$_1$ at room temperature reveal resonance signals for equivalent NH and η^5-C$_5$Me$_5$ groups. The resonances for the η^5-C$_5$Me$_5$ ligands

are sharp indicating that the three NH ligands of the metalloligand are rapidly exchanging on the NMR timescale.

The dba ligand in **6** is strongly bonded to the palladium atom and, in NMR experiments performed in benzene-d_6 solutions, complex **6** did not show any reaction with diphenylacetylene or *trans*-stilbene. Furthermore, addition of triphenylphosphane to compound **6** revealed the immediate displacement of the metalloligand **1** while the dba ligand remained coordinated to the palladium center according to NMR spectroscopy. In contrast, the treatment of **6** with two equivalents of dimethylacetylenedicarboxylate (dmad) gave cleanly the metallacyclo-2,4-pentadiene complex [{(MeOOC)$_4$C$_4$}Pd{(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] (**9**) and free dba (Scheme 2). The formation of **9** with this alkyne substituted with electron-withdrawing groups was instantaneous and no intermediates could be detected monitoring the reaction course by NMR spectroscopy. In addition, the treatment of **6** with one equivalent of dmad gave a 1:1:1 mixture of **9**, the starting material **6** and free dba.

Complex **9** was isolated as an orange solid in 33% yield upon reaction of **6** with two equivalents of MeOOCC≡CCOOMe in toluene and subsequent crystallization to remove the DBA byproduct. Compound **9** was characterized by spectral and analytical techniques, as well as by an X-ray crystallographic determination for crystals of **9**·2C$_7$H$_8$ obtained in toluene at -35 ºC. The solid-state structure is presented in Fig. 3, while selected lengths and angles are given in Table 3. Similarly to **8**, the molecular structure of **9** shows the chelating bidentate coordination of the metalloligand [{(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] to palladium with the third NH group clearly not coordinated (distance Pd(1)···N(13) 3.085(1) Å). In addition, palladium is bonded to two carbon atoms of the C$_4$(COOMe)$_4$ fragment to give a distorted square-planar geometry (τ_4 = 0.17)[32] with N-Pd-N, C-Pd-C and N-Pd-C

(*cis*) angles between 78.9(3) and 96.5(3)º. The Pd-N (2.161(6) and 2.129(5) Å) and Pd-C

(2.030(8) and 2.031(7) Å) bond lengths are similar to those reported for other

$[Pd\{C_4(COOMe)_4\}]$ complexes supported by bidentate nitrogen ligands.[34]

Fig. 3.   Perspective view with thermal ellipsoids at the 50% probability level of complex **9**. Toluene molecules, hydrogen atoms and methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity.

Table 3   Selected lengths (Å) and angles (º) for complex **9**.

Pd(1)–N(12)	2.161(6)	Pd(1)–N(23)	2.129(5)
Pd(1)···N(13)	3.085(1)	Pd(1)–C(43)	2.031(7)
Pd(1)–C(53)	2.030(8)	C(43)–C(44)	1.360(10)
C(44)–C(54)	1.440(10)	C(53)–C(54)	1.349(11)
Ti(1)–N(12)	1.990(6)	Ti(1)–N(13)	1.915(6)
Ti(2)–N(12)	1.952(6)	Ti(2)–N(23)	1.963(6)
Ti(3)–N(23)	1.997(6)	Ti(3)–N(13)	1.886(6)
Ti–N(1)^a	1.924(3)	Pd(1)···Ti(1)	3.268(2)

Pd(1)···Ti(2)	2.728(2)	Pd(1)···Ti(3)	3.270(2)
N(12)–Pd(1)–N(23)	87.7(2)	C(43)–Pd(1)–C(53)	78.9(3)
N(12)–Pd(1)–C(43)	168.4(2)	N(12)–Pd(1)–C(53)	96.5(3)
N(23)–Pd(1)–C(43)	94.6(3)	N(23)–Pd(1)–C(53)	167.6(3)
N(12)–Ti(2)–N(23)	98.7(2)	N(12)–Ti(1)–N(13)	107.2(2)
N(13)–Ti(3)–N(23)	106.5(2)	N–Ti–N(1)[a]	85.9(6)
Pd(1)–C(43)–C(44)	115.6(5)	Pd(1)–C(53)–C(54)	115.1(6)
C(43)–C(44)–C(54)	114.2(7)	C(53)–C(54)–C(44)	115.7(7)
Pd(1)–N(12)–Ti(2)	82.9(2)	Pd(1)–N(23)–Ti(2)	83.5(2)
Pd(1)–N(12)–Ti(1)	103.8(2)	Pd(1)–N(23)–Ti(3)	104.8(2)
Ti–N(1)–Ti[b]	92.7(2)–96.0(3)	Ti–N–Ti[a]	93.1(9)

[a] Averaged values. [b] Range of values.

Complexes **8** and **9** are the first crystallographically documented examples of bidentate coordination of the metalloligand **1** to a single metal center. This mode of coordination results in a slight lengthening of the Ti-N bond lengths related with the two nitrogen atoms coordinated to palladium (range 1.949(5)-2.036(5) Å) when compared with the Ti-N distances associated with the not coordinated imido group (range 1.886(6)-1.917(6) Å).

The features of the metallacyclopentadiene part of the molecule of **9** are very similar to those found in analogous structures.[34,35] Interestingly, inspection of the crystal structure of **9** revealed that one carbonyl group of the carboxilate at the α-position (relative to palladium) is involved in a strong intramolecular hydrogen bond with one of the NH ligands coordinated to palladium (N(23)···O(42) 2.920(1) Å) (see Fig. S2 in the ESI).† Most likely, this interaction may be responsible of the three ν_{NH} vibrations at 3346, 3319, and 3282 cm^{-1} observed in the IR spectrum (KBr) instead of the two absorptions for the imido groups found in the spectra of complexes **7** and **8**. Further indication of this

interaction is the presence in the IR spectrum of **9** of three very strong bands between 1712-1682 cm^{-1} for the carbonyl units when two ν_{CO} absorptions around 1700 cm^{-1} are characteristic of the carboxylate groups in [Pd{C$_4$(COOMe)$_4$}] moieties.[35,36]

^{1}H and ^{13}C{^{1}H} NMR spectra of complex **9** in benzene-d$_6$ at room temperature reveal two and four resonance signals for the methoxycarbonyl groups, respectively. The ^{13}C{^{1}H} NMR spectrum displays also two resonances at $\delta = 165.8$ and 147.5 for the alkene carbon atoms.[34] These features are indicative of symmetry for the metallacycle fragment in solution. In addition, the ^{1}H NMR spectrum shows single resonances for the NH and η^5-C$_5$Me$_5$ ligands, likely due to a facile exchange between the free and coordinated NH groups of the metalloligand on the NMR timescale.

Platinum complexes. The treatment of **1** with one equivalent of [Pt(nbe)$_3$] (nbe = norbornene or bicyclo[2.2.1]hept-2-ene) in toluene at room temperature gave the platinum(0) complex [(nbe)Pt{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**10**) (Scheme 3). Compound **10** was isolated in 64% yield as a brown solid which exhibits a high solubility in toluene or pentane. The IR spectrum (KBr) of **10** shows two ν_{NH} vibrations at 3370 and 3350 cm^{-1}. The ^{1}H NMR spectrum in benzene-d$_6$ at room temperature reveals one single sharp resonance at $\delta = 1.97$ for the η^5-C$_5$Me$_5$ ligands and one single resonance for the NH groups at $\delta = 11.70$ with satellite peaks due to coupling with the platinum atom (^2J(H,^{195}Pt) = 33.9 Hz). The resonance for the *ipso* carbon of the C$_5$Me$_5$ groups ($\delta = 117.6$) in the ^{13}C{^{1}H} NMR spectrum is only slightly shifted downfield with respect to that found for **1** ($\delta = 117.1$),[18] thereby indicating a decreased electron density at the titanium centers upon coordination. The sharing of electron density of the Group 10 metal with the Ti$_3$ core in

complex **10** appears to be higher than that observed in the palladium complex **6** but lower than those cited above for the nickel compounds **2**-**4**.

^{1}H and ^{13}C{^{1}H} NMR spectra of complex **10** reveal well-resolved resonance signals for the coordinated norbornene ligand.[37] The olefinic protons of the nbe group in the ^{1}H NMR spectrum appears as a singlet at δ = 3.06 flanked by platinum satellites with a coupling constant ^2J(H,^{195}Pt) of 90.6 Hz. The ^{13}C{^{1}H} NMR spectrum shows one resonance for the olefinic carbons of coordinated nbe at δ = 45.5 (^1J(C,^{195}Pt) = 523.9 Hz) which is 90 ppm upfield relative to that of free norbornene.[37a]
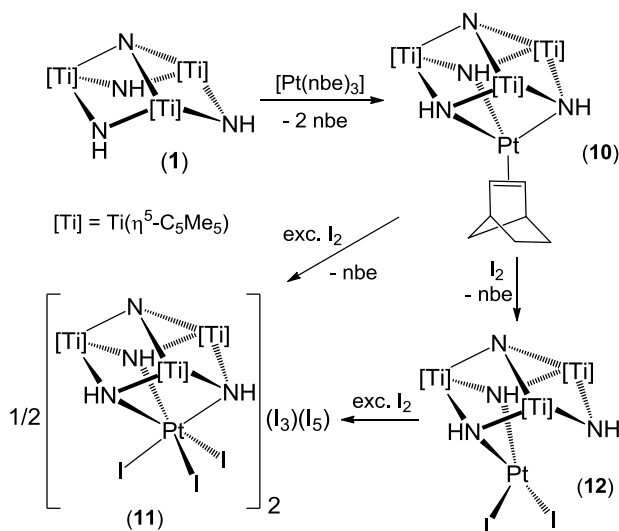
Scheme 3. Synthesis of platinum complexes.

In NMR tube experiments, complex **10** in benzene-d$_6$ did not react with diphenylacetylene, while addition of triphenylphosphane revealed the immediate displacement of the metalloligand **1**. However, slow diffusion of a benzene solution of iodine into a benzene solution of **10** afforded black crystals of the platinum(IV) ionic derivative [I$_3$Pt{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$(I$_3$)(I$_5$)·6.5C$_6$H$_6$ (**11**·6.5C$_6$H$_6$) suitable for an X-ray crystal structure determination. The asymmetric unit contains two cube-type [I$_3$Pt{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] cations, one triiodide and one pentaiodide anions,

and 6.5 benzene molecules. The I_3^- and I_5^- ions in **11** show linear and V-shaped geometries respectively, similar to those determined in many other crystalline structures with such anions.[38] There are no substantial differences between the two cations, and the structure of one of them is shown as example in Fig. 4. Selected averaged distances and angles for both cationic fragments are given in Table 4. The cations show ligands $[\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ coordinating in a tripodal fashion to the platinum atoms. In addition, the Group 10 metals are bonded to three iodine atoms to give a slightly distorted octahedral geometry for the platinum centers (average twist angle $\phi = 59(1)°$).[39] The Pt-I bond lengths of averaged 2.624(4) Å compare well with those found in the cationic complex $[I_3\text{Pt}\{(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NMe}\}]^+$.[40] However, the Pt-N bond lengths in **11** of averaged 2.187(9) Å are *ca.* 0.1 Å longer than those found in that cation containing a more flexible *fac*-coordinating trinitrogen ligand.
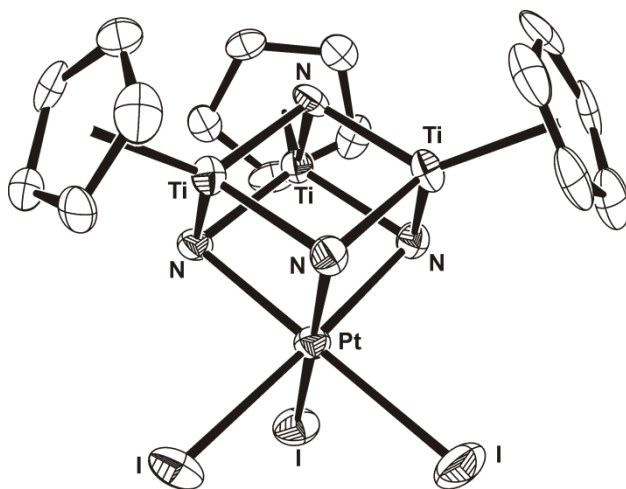
Fig. 4. Perspective view with thermal ellipsoids at the 50% probability level for one of the cationic fragments of complex **11**. Hydrogen atoms and methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity.

Table 4   Selected averaged lengths (Å) and angles (°) for the cationic fragments of **11**.

Pt–N$_{imido}$	2.187(9)	Pt–I	2.624(4)
Ti–N$_{nitrido}$	1.916(8)	Ti–N$_{imido}$	1.990(6)
Pt···Ti	2.863(12)		
N$_{imido}$–Pt–N$_{imido}$	87.8(4)	I–Pt–I	90.4(7)
N$_{imido}$–Pt–I (*cis*)	91(1)	N$_{imido}$–Pt–I (*trans*)	177.5(4)
N$_{nitrido}$–Ti–N$_{imido}$	85.0(3)	N$_{imido}$–Ti–N$_{imido}$	99.3(6)
Pt–N$_{imido}$–Ti	86.4(5)	Ti–N$_{nitrido}$–Ti	97.4(3)
Ti–N$_{imido}$–Ti	92.7(3)		

In a preparative scale reaction, a benzene solution of **10** was layered with a solution containing 3.5 equivalents of iodine in benzene to afford **11**·C$_6$H$_6$ as a black crystalline solid in 57% yield. Compound **11** is not soluble in hydrocarbon solvents and only exhibits a poor solubility in chloroform-d$_1$. Furthermore, it reacts completely with this solvent within hours precluding its characterization by ^{13}C{^{1}H} NMR spectroscopy. The ^{1}H NMR spectrum of **11** shows single resonances for the NH and η^5-C$_5$Me$_5$ ligands in accord with a C_{3v} symmetric structure in solution.

The reaction of **10** with iodine in benzene-d$_6$ was monitored by NMR spectroscopy. Upon addition of one equivalent of I$_2$, the initial brown solution turned to a red color and the platinum(II) derivative [I$_2$Pt{(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ$_3$-N)}] (**12**) was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Treatment of this red solution with an excess of iodine gave immediately a dark solution and black crystals of **11** were deposited at the bottom of the NMR tube. Despite many attempts, complex **12** could not be obtained in a pure form. However, NMR data of **12** are consistent with a structure similar to that determined in the palladium analogue [I$_2$Pd{(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ$_3$-N)}] (**8**). Interestingly, complex **8** in benzene-d$_6$ did not show any reaction with excess iodine at

temperatures below 60 ºC, while an extensive decomposition of the starting material was determined by ^{1}H NMR spectroscopy at higher temperatures.

Conclusions

A series of heterometallic complexes containing [MTi$_3$N$_4$] cube-type cores have been prepared by incorporation of Group 10 metals into the incomplete cube-type structure of [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**). The synthetic procedure involves the reaction of **1** with homoleptic Group 10 metal(0) alkene complexes at ambient temperature for palladium and platinum metals or the thermal decomposition of the [Ni(cod)$_2$] precursor and subsequent addition of donor molecules for nickel. The zerovalent Group 10 metals in the resultant [LM{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (M = Ni, Pd) complexes readily undergo oxidative addition reactions to give M^{II} (d^8) derivatives with the titanium metalloligand coordinating in a tridentate (M = Ni) or bidentate (M = Pd) chelate fashion. The oxidation of the analogue platinum(0) species [(nbe)Pt{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] with excess iodine leads to a cationic complex with the Pt^{IV} (d^6) center stabilized by a *fac*-coordinating metalloligand **1**.

Experimental section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Toluene, benzene, hexane and pentane were distilled from Na/K alloy just before use. Acetonitrile was dried with CaH_2 and distilled prior to use. Diethyl ether was distilled from a purple solution of sodium/benzophenone ketyl immediately prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (*ca.* 1×10^{-3} Torr) and subsequently filled with inert gas. [Ni(cod)$_2$], [Pd(dba)$_2$], [Pd$_2$(dba)$_3$], *trans*-stilbene (96%) and dimethylacetylenedicarboxylate were purchased from Aldrich and used as received. [PdCl$_2$(cod)] was purchased from Strem and used as received. Diphenylacetylene and triphenylphosphane were purchased from Aldrich and sublimed under vacuum prior to use. Iodine was purchased from Panreac and sublimed under vacuum prior to use. [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)][18] (**1**) and [Pt(nbe)$_3$][41] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Unity-300 and/or Mercury-300 spectrometers. Chemical shifts (δ) in the ^{1}H and ^{13}C{^{1}H} NMR spectra are given relative to residual protons or to carbon of the solvent, C_6D_6 (^{1}H: $\delta = 7.15$; ^{13}C: $\delta = 128.0$) or $CDCl_3$ (^{1}H: $\delta = 7.24$; ^{13}C: $\delta = 77.0$). Chemical shifts (δ) in the ^{31}P{^{1}H} NMR spectra are given relative to H_3PO_4 as external reference ($\delta = 0.0$). Microanalyses (C, H, N) were performed in a Leco CHNS-932 microanalyzer.

Synthesis of [(PhCCPh)Ni{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (2). A 100 mL ampule (Teflon stopcock) was charged with **1** (0.21 g, 0.35 mmol), [Ni(cod)$_2$] (0.090 g, 0.33

mmol), and toluene (30 mL). The reaction mixture was stirred at 60 ℃ for 24 h and at 80 ℃ for 3 days to give a brown solution. The solution was filtered and PhC≡CPh (0.058 g, 0.33 mmol) was added. After stirring for 16 hours at room temperature, the reaction mixture was filtered and the volatile components were removed under reduced pressure to give a red solid. The solid was washed with pentane (5 mL) and vacuum-dried to afford **2** as a red-brown powder (0.17 g, 61%). A sample suitable for elemental analysis of **2**·C_7H_8 (0.060 g, 19%) was obtained by recrystallization from toluene at -20 ℃. IR (KBr, cm^{-1}): $\tilde{v}$ 3337 (w), 3067 (w), 3051 (w), 3017 (w), 2905 (s), 2854 (s), 2721 (w), 1897 (s broad), 1588 (s), 1488 (s), 1437 (s), 1374 (s), 1273 (m), 1171 (w), 1066 (w), 1025 (m), 902 (w), 801 (w), 754 (s), 711(s), 670 (m), 631 (m), 610 (vs), 539 (m), 497 (s), 419 (m), 396 (m). ^{1}H NMR (300 MHz, C_6D_6, 20 ℃): δ 10.38 (s br, 3H; NH), 7.55-7.19 (m, 10H; C_6H_5), 1.90 (s, 45H; C_5Me_5). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 ℃): δ 134.8, 131.9, 128.5, 125.0 (C_6H_5), 116.9 (C_5Me_5), 110.4 (C≡C), 11.7 (C_5Me_5). Anal. Calcd for $C_{51}H_{66}N_4NiTi_3$ (M_w = 937.40): C 65.35, H 7.10, N 5.98. Found: C 65.03, H 6.83, N 6.01.

Synthesis of [(PhHCCHPh)Ni{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}]] (3). In a fashion similar to the preparation of **2**, PhHC=CHPh (0.090 g, 0.50 mmol) was added to the solution obtained from the heating of **1** (0.31 g, 0.51 mmol) and [Ni(cod)₂] (0.13 g, 0.47 mmol) in toluene (30 mL). After stirring for 24 h at room temperature, the volatile components were removed under reduced pressure to give a red-brown solid. The solid was washed with pentane (5 mL) and vacuum-dried to give **3** as a red-brown powder (0.32 g, 80%). IR (KBr, cm^{-1}): $\tilde{v}$ 3327 (w), 3058 (w), 3008 (w), 2905 (s), 2854 (s), 1593 (s), 1572 (m), 1502 (s), 1489 (s), 1447 (s), 1430 (s), 1374 (s), 1237 (s), 1172 (w), 1069 (m), 1027 (m), 997 (w), 802 (m), 757 (s), 736 (s), 695 (s), 668 (m), 631 (m), 606 (vs), 553 (w), 530 (s), 499 (s), 421 (s), 391 (m). ^{1}H NMR (300 MHz, C_6D_6, 20 ℃): δ 9.17 (s br, 3H; NH), 7.18-6.99 (m, 10H;

C_6H_5), 5.53 (s, 2H; HC=CH), 1.80 (s, 45H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C): δ 147.1, 128.8, 125.4, 122.7 (C_6H_5), 116.7 (C_5Me_5), 63.3 (CH=CH), 11.6 (C_5Me_5). Anal. Calcd for $C_{44}H_{60}N_4NiTi_3$ (M_w = 847.28): C 62.37, H 7.14, N 6.61. Found: C 62.10, H 7.25, N 6.88.

Synthesis of [(Ph₃P)Ni{(µ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(µ₃-N)}] (4). In a fashion similar to the preparation of **2**, PPh₃ (0.085 g, 0.32 mmol) was added to the solution obtained from the heating of **1** (0.20 g, 0.33 mmol) and [Ni(cod)₂] (0.090 g, 0.33 mmol) in toluene (30 mL). After stirring for 16 h at room temperature, the volatile components were removed under reduced pressure to give a red-brown solid. The solid was washed with pentane (5 mL) and vacuum-dried to afford **4** as a red-brown powder (0.13 g, 43%). IR (KBr, cm⁻¹): $\tilde{\nu}$ 3335 (w), 3068 (w), 3050 (w), 2907 (vs), 2855 (s), 2720 (w), 1585 (w), 1571 (w), 1478 (m), 1433 (vs), 1373 (s), 1261 (w), 1178 (m), 1089 (s), 1065 (m), 1026 (m), 801 (m), 742 (m), 728 (m), 694 (vs), 666 (m), 625 (m), 596 (vs), 586 (vs), 520 (vs), 509 (s), 487 (vs), 418 (s), 393 (m). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 9.70 (s br, 3H; NH), 7.55-7.48 (m, 6H; C_6H_5), 7.18-7.05 (m, 9H; C_6H_5), 1.91 (s, 45H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C): δ 139.8 (d, ^1J(C,P) = 27.8 Hz; *ipso*-C_6H_5), 133.5 (d, ^2J(C,P) = 15.4 Hz; *o*-C_6H_5), 115.3 (C_5Me_5), 11.6 (C_5Me_5), the *p*- and *m*-C_6H_5 resonances were not determined because of coincidence with that of the solvent. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 22.3 (s, PPh₃). Anal. Calcd for $C_{48}H_{63}N_4NiPTi_3$ (M_w = 929.32): C 62.04, H 6.83, N 6.03. Found: C 62.11, H 6.57, N 5.36.

Synthesis of [I₂Ni{(µ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(µ₃-N)}] (5). A solution of I₂ (0.12 g, 0.47 mmol) in toluene (10 mL) was added to the solution obtained from the heating of **1** (0.31 g, 0.51 mmol) and [Ni(cod)₂] (0.14 g, 0.51 mmol) at 60-80 °C in toluene (40 mL). After stirring for 30 min at room temperature, the volatile components were removed under

reduced pressure to give a brown solid. This solid was washed with toluene (5 mL) and hexane (10 mL) to give **5** as a brown powder (0.27 g, 63%). IR (KBr, cm^{-1}): $\tilde{v}$ 3328 (m), 2945 (m), 2910 (s), 2857 (m), 1486 (m), 1426 (m), 1377 (s), 1067 (w), 1023 (m), 802 (w), 776 (m), 735 (s), 698 (s), 645 (vs), 621 (vs), 526 (m), 480 (w), 470 (w), 455 (w), 430 (m), 404 (m). ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ 2.80 (s br, $\Delta v_{1/2}$ = 12 Hz, 45H; C$_5$Me$_5$), the NH resonance signal was not observed. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 °C): δ 124.6 (*C*$_5$Me$_5$), 23.4 (C$_5$*Me*$_5$). Anal. Calcd for C$_{30}$H$_{48}$I$_2$N$_4$NiTi$_3$ (M_w = 920.83): C 39.13, H 5.25, N 6.08. Found: C 38.76, H 5.48, N 6.21. The effective magnetic moment of **5** was determined to be 2.47 μ_B (based on a unit formula of C$_{30}$H$_{48}$I$_2$N$_4$NiTi$_3$) by the Evans NMR method on a CDCl$_3$ solution at 293 K (using a 300 MHz instrument with a field strength of 7.05 Tesla).[24]

Synthesis of [(dba)Pd{(μ$_3$-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (6). A 100 mL Schlenk flask was charged with **1** (0.50 g, 0.82 mmol), [Pd(dba)$_2$] (0.47 g, 0.82 mmol), and toluene (50 mL). The reaction mixture was stirred at room temperature for 4 days to give a dark red solution. After filtration, the volatile components were removed under reduced pressure to afford a red solid. The solid was washed with diethyl ether (3 × 10 mL) and vacuum-dried to give **6** as a red powder (0.43 g, 55%). IR (KBr, cm^{-1}): $\tilde{v}$ 3352 (m), 3056 (w), 2906 (s), 2855 (m), 2720 (w), 1640 (s), 1583 (s), 1573 (s), 1494 (m), 1429 (m), 1375 (m), 1329 (m), 1310 (w), 1280 (w), 1219 (w), 1069 (w), 1025 (w), 972 (w), 921 (w), 860 (w), 845 (w), 788 (w), 766 (m), 729 (s), 699 (s), 639 (vs), 565 (w), 538 (w), 523 (w), 508 (m), 486 (w), 471 (w), 420 (m), 395 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 11.55 (s br, 3H; NH), 7.96 (d, ^{3}*J*(H,H) = 15.9 Hz, 1H; CH=CH not coordinated), 7.47 (m, ^{3}*J*(H,H) = 7.2 Hz, 2H; *o*-C$_6$H$_5$), 7.26 (m, ^{3}*J*(H,H) = 7.2 Hz, 2H; *o*-C$_6$H$_5$), 7.13-6.98 (m, 6H; *p*- and *m*-C$_6$H$_5$), 6.94 (d, ^{3}*J*(H,H) = 15.9 Hz, 1H; CH=CH not coordinated), 5.28 (d, ^{3}*J*(H,H) = 10.5 Hz, 1H; CH=CH coordinated),

5.16 (d, ^3J(H,H) = 10.5 Hz, 1H; CH=CH coordinated), 1.87 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): δ 184.2 (C=O), 146.4, 142.7 (CH=CH not coordinated), 137.4, 136.4 128.9, 128.6, 128.5, 127.9, 126.4, 124.1 (C$_6$H$_5$), 118.5 (*C*$_5$Me$_5$), 68.8, 60.8 (CH=CH coordinated), 11.7 (C$_5$*Me*$_5$). Anal. Calcd for C$_{47}$H$_{62}$N$_4$OPdTi$_3$ (M_w = 949.05): C 59.48, H 6.58, N 5.90. Found: C 59.82, H 6.54, N 5.14. This compound is inevitably contaminated by free dba ($\leq$ 5% by ^{1}H NMR spectroscopy) even after repeatedly washing with diethyl ether or acetonitrile and hence satisfactory elemental analysis could not be obtained.

Synthesis of [Cl$_2$Pd{(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] (7). A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [PdCl$_2$(cod)] (0.14 g, 0.49 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 20 h. The volatile components were removed under reduced pressure to give a brown solid. The solid was washed with hexane (15 mL) and vacuum-dried to give **7** as a brown powder (0.32 g, 84%). IR (KBr, cm^{-1}): $\tilde{v}$ 3354 (m), 3330 (m), 2909 (s), 2857 (m), 1488 (m), 1427 (s), 1377 (s), 1136 (w), 1067 (w), 1025 (m), 930 (m), 842 (m), 748 (s), 730 (s), 686 (m), 662 (vs), 635 (vs), 541(m), 468 (m), 427 (m), 404 (m). ^{1}H NMR (300 MHz, CDCl$_3$, 20 ºC): δ 11.07 (s br, 3H; NH), 2.10 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 ºC): δ 122.6 (*C*$_5$Me$_5$), 12.1 (C$_5$*Me*$_5$). Anal. Calcd for C$_{30}$H$_{48}$Cl$_2$N$_4$PdTi$_3$ (M_w = 785.66): C 45.86, H 6.16, N 7.13. Found: C 45.61, H 6.15, N 7.11.

Synthesis of [I$_2$Pd{(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] (8). A 100 mL Schlenk flask was charged with **1** (0.20 g, 0.33 mmol), [Pd(dba)$_2$] (0.19 g, 0.33 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 3 days to give a dark red solution. After filtration, a solution of I$_2$ (0.083 g, 0.33 mmol) in toluene (5 mL) was added. The resultant solution was stirred at room temperature for 3 h and the volatile components

were removed under reduced pressure to afford a brown-red solid. This solid was washed with toluene (3×5 mL) and hexane (5 mL) to give **8** as a brown powder (0.14 g, 44%). IR (KBr, cm^{-1}): $\tilde{v}$ 3350 (m), 3322 (m), 2941 (m), 2909 (s), 2855 (m), 1485 (m), 1426 (m), 1377 (s), 1067 (w), 1023 (m), 802 (m), 751 (s), 731 (m), 710 (m), 665 (vs), 653 (vs), 632 (vs), 541 (m), 519 (m), 478 (m), 466 (m), 421(m), 401 (m). ^{1}H NMR (300 MHz, CDCl$_3$, 20 ºC): δ 11.55 (s br, 3H; NH), 2.12 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 ºC): δ 122.2 (*C*$_5$Me$_5$), 12.5 (C$_5$*Me*$_5$). Anal. Calcd for C$_{30}$H$_{48}$I$_2$N$_4$PdTi$_3$ (M_w = 968.56): C 37.20, H 4.99, N 5.78. Found: C 37.09, H 4.80, N 5.67.

Synthesis of [{(MeOOC)$_4$C$_4$}Pd{(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ$_3$-N)}] (9). A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [Pd$_2$(dba)$_3$] (0.23 g, 0.25 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 4 days to give a dark red solution. MeOOCC≡CCOOMe (0.14 g, 0.99 mmol) was added to this solution, and the reaction mixture was stirred at room temperature for 1.5 h. The resultant solution was concentrated under reduced pressure to *ca.* 25 mL and was filtered through a glass frit. After cooling at -35 ºC for 3 days, compound **9** was isolated by filtration as an orange solid (0.16 g, 33%). IR (KBr, cm^{-1}): $\tilde{v}$ 3346 (w), 3319 (m), 3282 (m), 2945 (s), 2909 (s), 2860 (m), 1712 (vs), 1695 (vs), 1682 (vs), 1619 (w), 1576 (w), 1545 (m), 1526 (m), 1494 (m), 1431 (s), 1379 (m), 1336 (s), 1248 (s), 1201 (vs), 1162 (s), 1063 (m), 1010 (m), 931 (w), 895 (w), 786 (s), 774 (s), 714 (m), 660 (vs), 550 (w), 524 (w), 478 (w), 445 (w), 418 (w). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): δ 12.25 (s br, 3H; NH), 3.69 (s, 6H; COOMe), 3.42 (s, 6H; COOMe), 1.96 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): δ 174.7, 165.13 (*C*OOMe), 165.08, 147.5 (C=C), 121.0 (*C*$_5$Me$_5$), 51.2, 50.9 (COO*Me*), 11.9 (C$_5$*Me*$_5$). Anal. Calcd for C$_{42}$H$_{60}$N$_4$O$_8$PdTi$_3$ (M_w = 998.98): C 50.50, H 6.05, N 5.61. Found: C 50.98, H 5.64, N 5.97.

Synthesis of [(nbe)Pt{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (10). A 100 mL Schlenk flask was charged with **1** (0.31 g, 0.51 mmol), [Pt(nbe)₃] (0.24 g, 0.50 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 20 h. The volatile components were removed under reduced pressure and the resultant brown solid was extracted with pentane (15 mL). Filtration of the pentane extract through a coarse glass frit gave a brown solution. The volatile components of this solution were removed under reduced pressure to afford **10** as a brown powder (0.29 g, 64%). IR (KBr, cm⁻¹): $\tilde{v}$ 3370 (m), 3350 (m), 2942 (vs), 2905 (vs), 2856 (vs), 2721 (w), 1490 (m), 1430 (s), 1375 (s), 1329 (w), 1295 (w), 1243 (m), 1171 (w), 1154 (w), 1117 (m), 1034 (m), 995 (w), 948 (w), 929 (w), 903 (s), 874 (m), 843 (w), 790 (m), 753 (m), 715 (s), 673 (m), 656 (vs), 641 (vs), 621 (vs), 588 (s), 514 (m), 464 (w), 446 (w), 390 (s). ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 11.70 (s br, ^2J(H,^{195}Pt) = 33.9 Hz, 3H; NH), 3.06 (s, ^2J(H,^{195}Pt) = 90.6 Hz, 2H; CH=CH nbe), 2.72 (s, ^3J(H,^{195}Pt) = 18.9 Hz, 2H; nbe), 1.97 (s, 45H; C₅Me₅), 1.82 (m, 1H; nbe), 1.45 (m, 4H; nbe), 0.44 (d, ^2J(H,H) = 7.5 Hz, 1H; nbe). ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C): δ 117.6 (C₅Me₅), 45.5 (^1J(C,^{195}Pt) = 523.9 Hz; CH=CH nbe), 44.0 (J(C,^{195}Pt) = 17.5 Hz; nbe), 39.6 (J(C,^{195}Pt) = 56.1 Hz; nbe), 30.4 (J(C,^{195}Pt) = 94.9 Hz; nbe), 11.8 (C₅Me₅). Anal. Calcd for C₃₇H₅₈N₄PtTi₃ (M_w = 897.57): C 49.51, H 6.51, N 6.24. Found: C 49.73, H 6.63, N 5.51.

Synthesis of [I₃Pt{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}]₂(I₃)(I₅) (11). A solution of I₂ (0.049 g, 0.19 mmol) in benzene (5 mL) was carefully added to a solution of compound **10** (0.050 g, 0.056 mmol) in benzene (5 mL). The system was allowed to react at room temperature without any stirring. After 3 days, **11**·C₆H₆ was isolated as a black crystalline solid (0.053 g, 57%). IR (KBr, cm⁻¹): $\tilde{v}$ 3320 (w), 3249 (w), 3215 (w), 2943 (w), 2906 (m), 2851 (w), 1477 (m), 1423 (s), 1376 (s), 1261 (w), 1018 (m), 852 (w), 799 (m), 710 (s), 682 (s), 628 (vs), 607 (vs), 509 (s), 469 (m), 424 (s). ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 11.13 (s br,

3H; NH), 2.20 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR data for **11** could not be obtained because of the low solubility and instability of the compound in CDCl$_3$. Anal. Calcd for C$_{66}$H$_{102}$I$_{14}$N$_8$Pt$_2$Ti$_6$ (M_w = 3461.55): C 22.90, H 2.97, N 3.24. Found: C 23.41, H 3.07, N 3.66.

Oxidation reaction of 10 with one equivalent of iodine. A 5-mm valved NMR tube was charged with **10** (0.008 g, 0.009 mmol), I$_2$ (0.002 g, 0.008 mmol) and benzene-d$_6$ (1.00 mL). The course of the reaction was monitored by ^{1}H NMR spectroscopy. After 10 min at room temperature the spectrum of the resultant red solution showed consumption of **10** and complex [I$_2$Pt{(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] (**12**) was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. NMR data for [I$_2$Pt{(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}] (**12**): ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): δ 11.55 (s br, 3H; NH), 2.12 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): δ 122.2 (*C*$_5$Me$_5$), 12.5 (C$_5$*Me*$_5$).

X-ray structure determination of 5, 8, 9 and 11. Crystals of complex **5**·1/2C$_7$H$_8$ were grown by slow diffusion of a toluene solution of I$_2$ into the toluene solution obtained from heating a 1:1 mixture of **1** and [Ni(cod)$_2$]. Crystals of complex **8**·I$_2$·3/4C$_7$H$_8$ were grown by slow diffusion of a toluene solution of I$_2$ into the toluene solution obtained from the reaction of **1** and [Pd(dba)$_2$] at room temperature. Orange crystals of compound **9**·2C$_7$H$_8$ were grown from a toluene solution at -35 ºC. Black crystals of **11**·6.5C$_6$H$_6$ were grown by slow diffusion of a benzene solution of I$_2$ into a benzene solution of compound **10** in an NMR tube. The crystals were removed from the Schlenk flasks or the NMR tube and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford

Cryostream 700 unit. The molybdenum radiation was used in all cases, graphite monochromated, and enhanced with a MIRACOL collimator. Crystallographic data for all the complexes are presented in Table 5 (see page 39).

The structures were solved, using the WINGX package,[42] by Patterson (**5**) or direct (**8**, **9** and **11**) methods (SHELXS-97 or SHELXS-2013) and refined by least-squares against F^2 (SHELXL-97 or SHELXL-2014/7).[43] Compound **5** crystallized with half a molecule of toluene, which was found in the Fourier map, but it was not possible to get a chemical sensible model for it, so Squeeze[44] procedure was used to remove their contribution to the structure factors. This treatment was also employed for the molecules of solvent in the crystallographic studies of the rest of the complexes.

Crystals of **8** contained two independent molecules in the asymmetric unit, and there were no significant differences between them. This compound crystallized with two iodine molecules and one molecule and a half of toluene per asymmetric unit. The solvent molecules showed severe disorder, so Squeeze[44] procedure was used. Moreover DELU restraints were applied for the carbon atoms C(11)-C(20) and C(31)-C(40) of the pentamethylcyclopentadienyl ligands linked to Ti(1) and Ti(3) respectively. Additionally SIMU restraints were also used for C(31)-C(40).

On the other hand, complex **9** crystallized with two molecules of toluene. Several attempts to obtain chemically sensible models for these molecules of solvent failed, so Squeeze[44] procedure was employed. Simultaneously, these crystals presented disorder for the atoms C(51), O(51) and O(52) of one of the groups COOMe. This disorder was treated conventionally by using the PART tool and allowing free refinement of the occupancy factors with the FVAR command. The final values for the occupancy factors were 52 and 48% for each position. Furthermore this disordered fragment was constrained with DFIX instructions, and DELU and SIMU restraints were used for the atoms C(51), O(51), O(52),

30

C(51)', O(51)' and O(52)'. Moreover the ring linked to Ti(2) was constrained to be an idealized pentamethylcyclopentadienyl ligand, and the carbon atoms C(21)-C(30) were treated with DELU and SIMU instructions. DELU restraints were also used for the carbon atoms C(11)-C(20) of the pentamethylcyclopentadienyl group linked to Ti(1).

Finally, compound **11** crystallized with six and a half benzene molecules. Whereas it was not possible to get a chemical sensible model for one and a half of them (and Squeeze[44] procedure was applied), the rest of molecules of benzene were properly refined by using DFIX instructions. DELU restraints were also employed for the carbon atoms C(130)-C(135) and C(150)-C(155) of benzene molecules. The highest peak found in the Fourier map of 2.41 e Å^{-3} is located close to I(15) (1.03 Å).

In the crystallographic study of all the complexes, non-hydrogen atoms were anisotropically refined, while the hydrogen atoms were positioned geometrically and refined by using a riding model.

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Table 5   Experimental data for the X-ray diffraction studies on **5**, **8**, **9** and **11**.

formula	$C_{33.5}H_{52}I_2N_4NiTi_3$	$C_{35.25}H_{54}I_4N_4PdTi_3$	$C_{56}H_{76}N_4O_8PdTi_3$	$C_{99}H_{135}I_{14}N_8Pt_2Ti_6$
	($\mathbf{5}\cdot0.5C_7H_8$)	($\mathbf{8}\cdot I_2\cdot0.75C_7H_8$)	($\mathbf{9}\cdot2C_7H_8$)	($\mathbf{11}\cdot6.5C_6H_6$)
M_r	967.00	1291.52	1183.31	3891.32
T [K]	200(2)	200(2)	200(2)	200(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P{-}1$	$P2_1/c$	$P2_1/n$	$P{-}1$
a [Å]; α [deg]	10.614(1); 90.77(1)	19.257(5)	18.795(6)	14.122(1); 84.31(1)
b [Å]; β [deg]	10.970(2); 99.33(1)	21.230(2); 101.86(3)	11.323(3); 105.25(2)	20.259(2); 77.97(1)
c [Å]; γ [deg]	19.142(2); 117.47(1)	22.053(8)	27.184(6)	22.173(3); 77.46(1)
V [Å^3]	1941.6(5)	8823(4)	5581(3)	6047(1)
Z	2	8	4	2
ρ_{calcd} [g cm^{-3}]	1.654	1.944	1.408	2.137
$\mu_{MoK\alpha}$ [mm^{-1}]	2.689	3.752	0.786	6.296
$F(000)$	962	4940	2464	3630
cryst size [mm^3]	$0.34 \times 0.34 \times 0.15$	$0.29 \times 0.24 \times 0.24$	$0.24 \times 0.14 \times 0.12$	$0.33 \times 0.25 \times 0.12$
θ range [deg]	3.17 to 27.50°	3.03 to 25.24°	3.05 to 25.24°	3.01 to 25.24°
index ranges	−13 to 13, −14 to 14, −22 to 24	−23 to 23, −25 to 25, −26 to 26	−22 to 21, −13 to 13, 0 to 32	−16 to 16, −24 to 24, −26 to 26
reflns collected	41739	258793	98028	126471
unique data	8895 [R_{int} = 0.086]	15933 [R_{int} = 0.128]	10099 [R_{int} = 0.093]	21834 [R_{int} = 0.158]
obsd data [I>2σ(I)]	6246	11268	5109	16075
Goodness–of–fit on F^2	1.085	1.113	0.948	1.052
final R^a indices [I>2σ(I)]	R1 = 0.058, wR2 = 0.155	R1 = 0.043, wR2 = 0.091	R1 = 0.079, wR2 = 0.195	R1 = 0.052, wR2 = 0.117
R^a indices (all data)	R1 = 0.088, wR2 = 0.171	R1 = 0.079, wR2 = 0.115	R1 = 0.158, wR2 = 0.224	R1 = 0.080, wR2 = 0.136
largest diff. peak/hole [e Å^{-3}]	1.874/−2.190	1.408/−1.459	0.780/−0.543	2.406/−1.880

[a] $R1 = \Sigma||F_0|-|F_c||/[\Sigma|F_0|]$ $wR2 = \{[\Sigma w(F_0^2-F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$