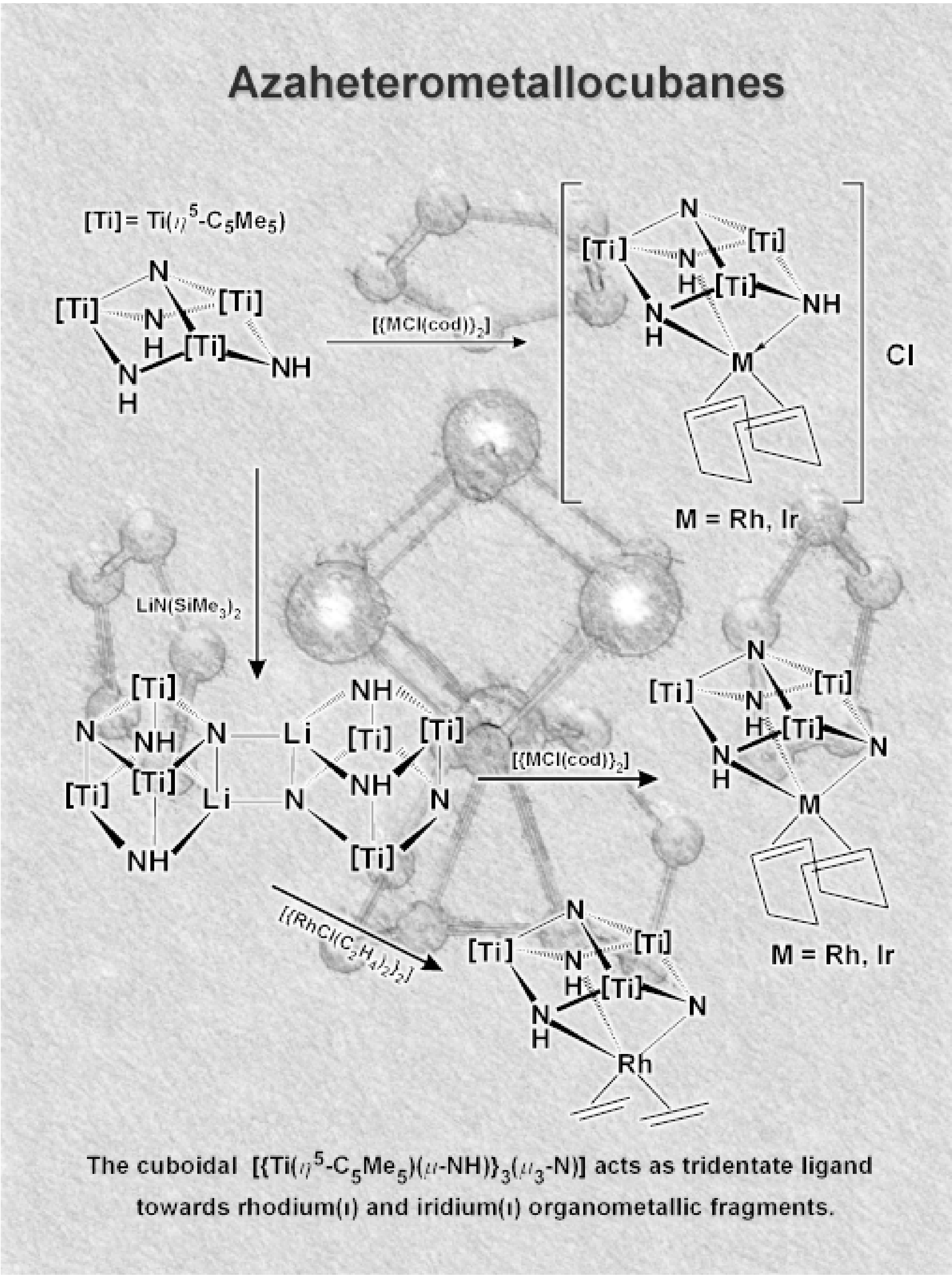
Azaheterometallocubanes
[Ti] = Ti(η5-C5Me5)
[{MCl(cod)}2]
Cl
M = Rh, Ir
LiN(SiMe3)2
[{MCl(cod)}2]
[{RhCl(C2H4)2}2]
M = Rh, Ir
The cuboidal [{Ti(η5-C5Me5)(μ-NH)}3(μ3-N)] acts as tridentate ligand
towards rhodium(I) and iridium(I) organometallic fragments.

Rhodium/Iridium-Titanium Azaheterometallocubanes

Katrin Freitag,[a] José Gracia,[b] Avelino Martín,[a] Miguel Mena,*[a] Josep-M. Poblet,[b] José P. Sarasa,[c] and Carlos Yélamos[a]

Abstract: Treatment of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) with the diolefin complexes [{MCl(cod)}$_2$] (M = Rh, Ir; cod = 1,5-cyclooctadiene) in toluene afforded the ionic complexes [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)]Cl [M = Rh (**2**), Ir (**3**)]. Reaction of complexes **2** and **3** with [Ag(BPh$_4$)] in dichloromethane leads to anion metathesis and formation of the analogous ionic derivatives [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)][BPh$_4$] [M = Rh (**4**), Ir (**5**)]. An X-ray crystal structure determination for **5** reveals a cube-type core [IrTi$_3$N$_4$] for the cationic fragment, in which **1** coordinates in a tripodal fashion to the iridium atom. Reaction of the diolefin complexes [{MCl(cod)}$_2$] (M = Rh, Ir) and [{RhCl(C_2H_4)$_2$}$_2$] with the lithium derivative [{Li(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}$_2$]·C_7H_8 (**6**·C_7H_8) in toluene gave the neutral cube-type complexes [M(cod)(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)] [M = Rh (**7**), Ir (**8**)] and [Rh(C_2H_4)$_2$(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)] (**9**), respectively. Density functional theory calculations have been carried out on the ionic and neutral azaheterometallocubane complexes to understand their electronic structures.

Keywords: cubanes · density functional calculations · iridium · nitrido complexes · rhodium · titanium

Introduction

An extensive coordination chemistry of rhodium and iridium has been developed with tridentate nitrogen-based ligands. Representative examples are tris(pyrazolyl)borates,[1] tris(pyrazolyl)methane,[2] and triazacyclononanes,[3] as well as many others,[4] because of their ability to serve as facially coordinating six-electron donors. Moreover, the hydridotris(pyrazolyl)borate (Tp) and its substituted derivatives (Tp^{R_2}) have been claimed as monoanionic cyclopentadienyl (Cp) analogues, although the electron-donating ability[5] and the steric profile of such ligands are very different.[6] The electronic and especially the steric properties of tris(pyrazolyl)borates have given different reactivity patterns, frequently permitting the isolation of species whose cyclopentadienyl relatives are highly reactive.[1]

On the other hand, the imido-nitrido complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**)[7, 8] can also be seen as a sophisticated, preorganized, tridentate ligand that shows an incomplete cube-type structure with three NH electron-donor imido groups in the base (Figure 1).[9] Indeed, compound **1** is prone to the incorporation of different metal complex fragments to produce cube-type derivatives.[8, 10–12] In those studies, we have noticed that this trinuclear titanium system is capable of acting as a neutral, monoanionic, dianionic, and even as a trianionic polydentate ligand to the metal centers through the basal nitrogen atoms. Herein we report the incorporation of rhodium(I) and iridium(I) diolefin fragments to give azaheterometallocubane complexes that contain imido and/or nitrido groups bridging the d^0 and d^8 transition metal centers. The coordination of the tripodal organometallic ligand **1** and its monoanionic derivative [Ti$_3$(μ_3-NH)$_2$(μ_3-N)(η^5-C_5Me_5)$_3$(μ_3-N)]$^-$ to rhodium and iridium is compared with the already mentioned "non-organometallic" ligands. Density functional theory (DFT) calculations have been carried out on the rhodium/iridium-titanium azaheterometallocubane complexes with the aim of comparing their energies and electronic structures.

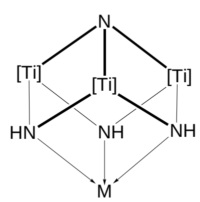

Figure 1. Simplified view of the incomplete Ti cube coordinated to a metal (M).

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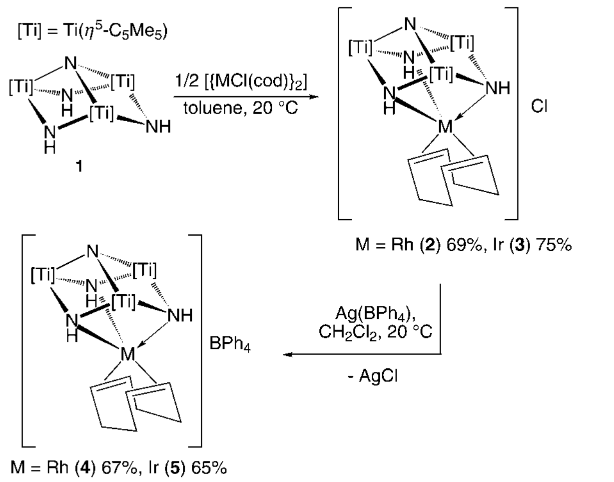
Results and Discussion

Treatment of the diolefin complexes [{MCl(cod)}$_2$] (M = Rh,[13] Ir;[14] cod = 1,5-cyclooctadiene) with **1** (2 equiv) in toluene at room temperature leads to the precipitation of [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)]Cl [M = Rh (**2**) 69 %, Ir (**3**) 75 %] as red solids (Scheme 1). Complexes **2** and **3** are only soluble in polar organic solvents, suggesting an ionic character. In the IR spectra, the three NH groups of these compounds give rise to two of the three expected bands for C_s symmetry (2A′, 1A″) between 3351 and 3327 cm^{-1}. Complexes **2** and **3** show, at room temperature, equivalent NH and η^5-C$_5$Me$_5$ groups on the NMR timescale. The NMR data are consistent with the complexes being fluxional in solution. Treatment of **2** and **3** with [Ag(BPh$_4$)] in dichloromethane at room temperature leads to anion metathesis and formation of the analogous ionic derivatives [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)][BPh$_4$] [M = Rh (**4**) 67 %, Ir (**5**) 65 %]. Not surprisingly, spectral data for complexes **4** and **5** are similar to the chloride salts **2** and **3**.



Scheme 1. Synthesis of the ionic azaheterometallocubane complexes **2**–**5**.

In order to establish unambiguously the ionic nature of the complexes and the coordination geometry for the Group 9 elements, an X-ray crystal structure determination was undertaken for complex **5**. The structure reveals a cube-type core for the cationic fragment (Figure 2). The geometry around the iridium atom is a distorted trigonal bipyramid in which the neutral ligand [(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] coordinates in a tripodal fashion, occupying one axial and two equatorial coordination sites, in a similar way to that shown by other triazaderivatives linked to Group 9 metals such as 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn*)[3c] and hydridotris(pyrazolyl)borates (Tp).[15] The angles and bond lengths around the iridium center compare well with those determined for the analogous triazaderivatives as can be seen in Table 1. The nitrogen-iridium-nitrogen angles span 83.7(3)–

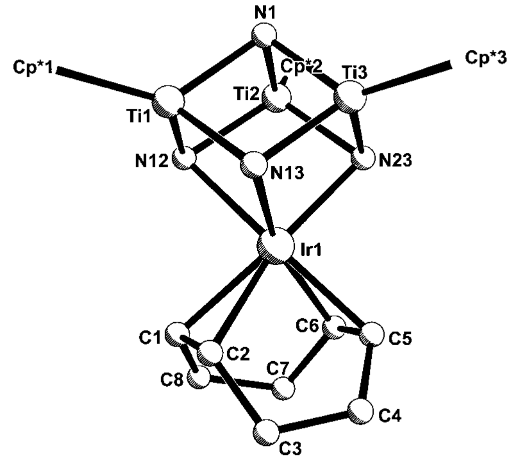


Figure 2. Simplified view of the cationic fragment of **5**. The pentamethylcyclopentadienyl ligands are not shown for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for different triazaderivatives of Group 9 metals.[a]

	5	[Ir(η^3-Tp)(cod)][15a]	[Rh(Cn*)(cod)][BPh$_4$][3c]
M–N$_{ax}$	2.106(9)	2.086(9)	2.198(2)
M–N$_{eq}$	2.299(8)	2.218(9)	2.339(2)
	2.306(8)	2.242(9)	2.335(2)
M–C$_{ax}$	2.186(12)	2.13(1)	2.158(3)
	2.171(12)	2.12(1)	2.169(3)
M–C$_{eq}$	2.097(12)	2.03(1)	2.083(3)
	2.107(13)	2.06(1)	2.076(3)
M–Cm$_{ax}$	2.065	2.01(1)	2.05
M–Cm$_{eq}$	1.976	1.92(1)	1.952
N$_{eq}$-M-N$_{eq}$	83.7(3)	80.6(3)	76.8(1)
N$_{ax}$-M-N$_{eq}$	86.4(3)	83.7(3)	80.1(1)
	85.4(3)	83.1(3)	78.9(1)
N$_{eq}$-M-Cm$_{eq}$	140.7	138.2(2)	135.9
	134.8	140.0(2)	145.1
N$_{ax}$-M-Cm$_{eq}$	89.2	90.5(2)	93.2
N$_{eq}$-M-Cm$_{ax}$	100.0	98.1(2)	102.7
	97.0	98.9(3)	100.1
N$_{ax}$-M-Cm$_{ax}$	173.3	177.2(2)	178.4

[a] Cp* = pentamethylcyclopentadienyl, Tp = hydridotris(pyrazolyl)borate, Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane, Cm = centroid of the olefin groups.

Abstract in Spanish: *El complejo [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) reacciona con los derivados [{MCl(cod)}$_2$] (M = Rh, Ir; cod = 1,5-ciclooctadieno) para dar las especies iónicas [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)]Cl [M = Rh (**2**), Ir (**3**)]. El tratamiento de los compuestos **2** y **3** con [Ag(BPh$_4$)] conduce a los análogos [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)]-[BPh$_4$] [M = Rh (**4**), Ir (**5**)]. La estructura cristalina del derivado **5** pone de manifiesto la coordinación tridentada del complejo **1** al átomo de iridio, originando un cubo [IrTi$_3$N$_4$] como unidad central en el fragmento catiónico. La reacción del derivado de litio [{Li(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] · C$_7$H$_8$ (**6** · C$_7$H$_8$) con los complejos [{MCl(cod)}$_2$] (M = Rh, Ir) y [{RhCl(C$_2$H$_4$)$_2$}$_2$] da lugar a los azaheterometalocubanos neutros [M(cod)(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] [M = Rh (**7**), Ir (**8**)] y [Rh(C$_2$H$_4$)$_2$(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$-(μ_3-N)] (**9**). El estudio teórico basado en cálculos de DFT realizados sobre los complejos azaheterometalocubanos iónicos y neutros permite describir adecuadamente su estructura electrónica.*

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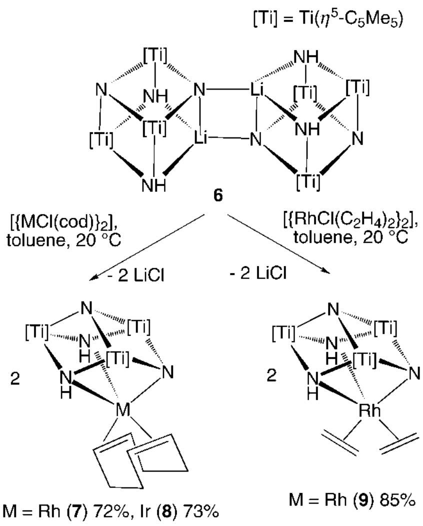
86.4(3)°, whereas that formed by the centroids of the olefinic groups with the iridium is 84.9°. The iridium–nitrogen axial bond length (2.106(9) Å) is shorter than those to the equatorial ligands (2.299(8) and 2.306(8) Å), as predicted by Hoffmann and Rossi for complexes with this geometry.[16] The value of the cone angleproduced by the [(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] ligand, which lies between those of Tp and Tp^{Me_2}, and close to Cn*, is given in Table 2. This value of the cone angle might be a good point of view from which to explain the similarity of the compared compounds with such different ligands.

Table 2. Cone angles produced by different triazaligands linked to Group 9 metals.[a]

	1 (ligand)	Tp^{R_2}	Cn*
5	220°		
[Ir(η^3-Tp)(cod)][15a]		R = H 212°	
[Ir(η^3-Tp^{Me_2})(H$_2$C = CH$_2$)$_2$][15b]		R = Me 255°	
[Rh(Cn*)(cod)][BPh$_4$][3c]			220°

[a] Tp^{Me_2} = hydridotris(3,5-dimethylpirazolyl)borate, Tp = hydridotris(pyrazolyl)borate, Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane.

Neutral rhodium-titanium and iridium-titanium cube-type complexes were obtained upon treatment of the diolefin complexes [{MCl(cod)}$_2$] (M = Rh,[13] Ir[14]) and [{RhCl(C$_2$H$_4$)$_2$}$_2$][17] with the lithium derivative [{Li(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$-(μ_3-N)}$_2$] · C$_7$H$_8$[12] (6 · C$_7$H$_8$) (Scheme 2). The reactions were performed in toluene at room temperature to give the complexes [M(cod)(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] (M = Rh (**7**) 72 %, Ir (**8**) 73 %) and [Rh(C$_2$H$_4$)$_2$(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] (**9**, 85 %) as red or brown solids after work-up. Complexes **7**–**9** are soluble in aromatic solvents; this suggests that they have a molecular nature. IR spectra show two absorptions in the range 3351–3324 cm^{-1} for the NH groups. NMR spectra reveal resonances for two nonequivalent C$_5$Me$_5$ ligands in a 2:1 ratio and two equivalent NH groups. The spectral data are consistent with a trigonal bipyramidal geometry about the Group 9 metal, where the [(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] organometallic ligand coordinates in a tripodal fashion, the nitrido group occupying one axial and the NH ligands two equatorial positions.



Scheme 2. Synthesis of the neutral azaheterometallocubanes **7**–**9**.

Complexes **7** and **8** are thermally stable in [D$_6$]benzene at temperatures below 190 °C.[18] The bis(ethene) derivative **9** exhibits a lower thermal stability in [D$_6$]benzene solutions and decomposes slowly at room temperature. The decomposition process is complete in minutes at 50 °C to give ethene as the only identified product in the NMR spectra.

In preliminary NMR experiments, rhodium complexes **2** and **7** were found to be efficient catalysts for highly stereoregular polymerization of phenylacetylene, whereas the iridium derivatives **3** and **8** were inactive. A similar behavior has been observed for analogous Group 9 metal complexes, in which the the κ^3–κ^2 isomerism of the polydentate nitrogen ligands has been postulated to explain the different reactivities observed toward phenylacetylene.[19, 4a] Our results are consistent with the existence of κ^3–κ^2 isomerism in solution, and reflect the preference of iridium for five-coordinate geometry.

Theoretical study of the rhodium/iridium-titanium azaheterometallocubane complexes: To understand the electronic structures of these azaheterometallocubane complexes, DFT calculations were carried out. Optimized geometries were calculated for the ionic [M(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$H$_5$)$_3$(μ_3-N)]$^+$ [M = Rh (**4′**) and M = Ir (**5′**)] and neutral [M(cod)(μ_3-NH)$_2$(μ_3-N){Ti(η^5-C$_5$H$_5$)}$_3$(μ_3-N)] [M = Rh (**7′**) and M = Ir (**8′**)] model compounds. The C_s symmetry was imposed for all calculated structures.

The DFT calculation on model **5′** reproduces the experimental geometry very well, since the difference between X-ray and DFT bond lengths is about 0.02 Å. As in the X-ray structure determination, the central core is cube-type. This result is similar for all studied compounds, with a small contraction for the neutral ones that must be attributed to the higher electrostatic interaction between the positive charge localized on {M(cod)}$^+$ and the negative charge delocalized on the preorganized incomplete-cube ligand. The analysis of the molecular orbitals shows that all these clusters have eight metallic electrons localized on the Group 9 element. As in the previously studied hetero-[10] and homometallocubanes[20] the LUMO is a bonding combination of titanium d orbitals, stressing that the formation of the azametallocubane is not accompanied by an oxidation of the Group 9 element. However, the molecular orbital (MO) composition given in Table 3 shows that there is a non-negligible mixing between rhodium (or iridium) and titanium d orbitals. In complex **4′** the HOMO may be described as a bonding combination between the d$_{z^2}$ rhodium orbital (63 %) and titanium d orbitals (12 %) with other smaller contributions. The other three orbitals reported in Table 3 also show mixing between the rhodium and the Ti$_3$ core orbitals, but of minor extension. By means of these orbital combinations, the rhodium atom shares

Table 3. Description of HOMO, LUMO, and some occupied molecular orbitals with important mixings between d^8 metal and Ti_3 d orbitals in clusters **4′** and **5′**. The highest MO with an important participation of $d_{x^2-y^2}$ rhodium (or iridium) orbital is also included.[a]

Complex	Orbital	E [eV]	$\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-N})\}$ Ti(d)	N(p)	C(p)	{M(cod)} M(d_{z^2})	M(d_{xz})	M(d_{yz})	M($d_{x^2-y^2}$)	C(p)
4′	57 a′ (LUMO)	− 6.12	82							
	56 a′ (HOMO)	− 8.04	12.2			62.7				
	41 a″	− 8.16	7.5	19.6			11.6	18.7		18.1
	55 a′	− 8.65		9.7	27.9				36.4	
	40 a″	− 8.80	7.8	14.4		39.4	16.4			8.4
5′	61 a′ (LUMO)	− 6.08	81.9							
	60 a′ (HOMO)	− 8.04	16.1			57.7				
	44 a″	− 8.22	10.6	17.9			11.5	15.4		21.0
	59 a′	− 8.64		10.0	20.7				49.6	
	43 a″	− 8.85	8.8	15.4			33.3	13.2		10.6

[a] The atomic d_{xy} orbitals for Rh and Ir do not appear in the occupied molecular orbitals stressing the d^8 nature of the complexes. Non-negligible percentage of d_{xz}, d_{yz}, and $d_{x^2-y^2}$ Rh and Ir orbitals appear in lower molecular occupied orbitals which are not included in this table. Only contributions > 7 % are reported.

its d electrons with the Ti_3 core. A similar situation has already been reported for the series of heterometallocubanes $[M(CO)_3(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-N})]$ [M = Cr, Mo, and W][10] and $[MMo_3S_4]$ (M = Ni, Pd, Co).[21] For the analogous iridium complex **5′** there is a greater mixing and, therefore, the delocalization of iridium d electrons is somewhat larger. Hence, the Mulliken analysis assigns a total population for rhodium d orbitals of 7.64 e in **4′**, while in **5′** the population for the iridium d orbitals is 7.34 e. For the neutral compounds **7′** and **8′** the situation is basically equivalent to the charged clusters, with a slightly greater delocalization of the Group 9 metal electrons. The transfer of charge associated with the occupied metal orbitals described in Table 3 was calculated to be 0.55 and 0.72 e for the cationic rhodium and iridium complexes, while that for the isoelectronic neutral systems is 0.69 and 0.82 e, respectively.

In agreement with the electronic sharing for larger metals in the iridium complexes, the dissociation energy to give the {M(cod)} + incomplete-cube fragments is computed to be 444.7 kJ mol^{-1} for **5′**, 66 kJ mol^{-1} above that of **4′**. These values are not very different from those computed for d^0–d^6 complexes,[10] which range between 350–445 kJ mol^{-1}.

In the neutral molecules **7′** and **8′** the process is manifestly more energetic and the dissociation energies were computed as 719.4 kJ mol^{-1} and 785.8 kJ mol^{-1}, respectively. The significant difference in these dissociation energies is mainly related to the charge separation in the neutral complexes, which may be formally seen as the interaction of the two charged fragments: $\{M(cod)\}^+$ and $\{(\mu_3\text{-NH})_2(\mu_3\text{-N})Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-N})\}^-$. For example, for the rhodium complex **7′** the Mulliken analysis estimates net charges of + 0.66 e for {M(cod)} and − 0.66 e for the incomplete-cube. In the parent cationic complex **5′** the charges for the corresponding fragments are + 0.90 and + 0.10 e.

To confirm the electrostatic interaction as the origin of the increase in the dissociation energy, we have carried out a decomposition of the interaction energy between the two fragments (*fragment interaction energy*, FIE); this is an extension of the well-known decomposition scheme of Morokuma[22] and developed by Ziegler and Rouk.[23]

The FIE can be decomposed into two terms: FIE = SR + OI, in which SR, known as the steric repulsion term, consists of two components: the classical *electrostatic* interaction (EI) between two unperturbed charge distributions of the two interacting fragments, and the so-called exchange repulsion or Pauli repulsion (PR). The latter term is composed of the four-electron destabilizing interactions between occupied orbitals in the fragments and is responsible for the steric repulsion. In addition to the steric repulsions, there are orbital interactions (OI). This term represents the stabilization produced when the electron densities are allowed to relax and accounts for charge transfer between fragments and mutual polarization of each fragment. These contributions are displayed in Table 4.

Table 4. Decomposition of the interaction energies for complexes **4′**, **5′**, **7′**, and **8′** [in kJ mol^{-1}].

	Rh (**4′**)	Ir (**5′**)	Rh (**7′**)	Ir (**8′**)
PR[a]	942.4	1267.8	1000.2	1341.9
EI[b]	− 767.4	− 999.4	− 1100.7	− 1341.0
SR[c]	+ 175.0	+ 286.4	− 100.5	+ 0.9
OI[d]	− 586.2	− 756.1	− 656.5	− 835.3
FIE[e]	− 411.2	− 487.7	− 757.0	− 834.4

[a] PR = Pauli repulsion. [b] EI = electrostatic interaction. [c] SR = steric repulsion (PR + EI). [d] OI = orbital interaction. [e] FIE = fragment interaction energy.

Let us consider first the rhodium complexes. In the cationic complex **4′** the Pauli repulsion is larger than the electrostatic contribution and, therefore, the SR term is repulsive (+ 175 kJ mol^{-1}). The other contribution to FIE, the OI term, largely overcomes the destabilizing steric term and is the main contribution to the bond (− 586 kJ mol^{-1}). When a proton is removed from the $\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-N})\}$ moiety in **7′**, the situation is quite different since the electrostatic contribution (EI) increases by 333 kJ mol^{-1}, and as a consequence of this fact, the SR term becomes attractive (− 100 kJ mol^{-1}). It is worth noting that the change in the EI energy almost coincides with the variation in the total FIE, + 346.8 kJ mol^{-1}. For the **5′** and **8′** iridium complexes the variations in the EI and FIE terms are also very similar. These results entirely confirm the importance of the *electrostatic interaction* in the neutral complexes.

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The values given in Table 4 also corroborate the above qualitative MO discussion about the distinct behavior of rhodium and iridium in these azaheterometallocubane complexes, since the OI term, which accounts for the orbital mixing between the incomplete-cube and {M(cod)} moieties, is considerably larger when M = Ir. This difference is about 170 kJ mol^{-1} in both cationic and neutral complexes. Finally, we should comment that the FIE term is not exactly equal to the binding energy (BE) of the complex formation from {(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$H$_5$)$_3$(μ_3-N)} and {M(cod)}, since BE = FIE + DE. Here DE is the deformation energy necessary to transform the fragments from their optimal structure to the geometry they adopt in the cluster. For M = Rh, DE is ~35 kJ mol^{-1}, whereas for the Ir it is ~10 kJ mol^{-1} greater. The DE term has also been denominated as the preparation energy.[23] A deeper discussion on the decomposition energy used here and its ability for describing the metal–ligand interaction in organometallic complexes can be found in the review of Ziegler[24] and in the works of Branchadell and coworkers.[25] This methodology has also been used in the study of more complicated complexes.[26]

Conclusion

Here we have demonstrated that complex **1** and its monoanionic derivative [(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)]$^-$ are able to act as tridentate tripodal ligands with Group 9 metals. Their coordination modes have a strong resemblance to the well-established "non-organometallic" triazacyclononane and tris(pyrazolyl)borate ligands. DFT calculations performed on a series of rhodium/iridium-titanium azaheterometallocubane model complexes have shown that the formation of the complex is not accompanied by the oxidation of the Group 9 element, but there is a sharing of the charge density between the d^8 metals and the Ti$_3$ core by means of metal–metal couplings. Calculations also showed that in the neutral complexes there are strong electrostatic interactions between the two charged {M(cod)}$^+$ and {(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$H$_5$)$_3$(μ_3-N)}$^-$ moieties.

Experimental Section

General considerations: All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K amalgam and toluene was distilled over sodium prior to use. Dichloromethane and chloroform were distilled from P$_2$O$_5$. NMR solvents were dried with P$_2$O$_5$ (CDCl$_3$) or Na/K amalgam (C$_6$D$_6$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Phenylacetylene was purchased from Aldrich and used as received. [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**),[7] [{Li(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] · C$_7$H$_8$ (**6** · C$_7$H$_8$),[12] [{MCl(cod)}$_2$] (M = Rh,[13] Ir[14]) and [{RhCl(C$_2$H$_4$)}$_2$][17] were prepared according to published procedures.

Infrared spectra were recorded by using Nujol mulls on CsI plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts (δ) are given relative to the residual protons or carbon of the solvent. Electron-impact mass spectra were obtained at 70 eV. Microanalysis (C, H, N) were performed in a Heraeus CHN-O-Rapid microanalyzer.

Synthesis of [Rh(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)]Cl (2): A 100 mL Schlenk flask was charged with **1** (0.27 g, 0.44 mmol), [{RhCl(cod)}$_2$] (0.109 g, 0.22 mmol), and toluene (40 mL). The reaction mixture was stirred at room temperature for 15 h to give a red solution and a brick red solid. The solution was decanted, and the solid was washed with hexane (20 mL) and vacuum dried to afford **2** (0.26 g, 69 %). Crystallization from a 1:3 mixture of dichloromethane/hexane produced large red crystals of **2** · CH$_2$Cl$_2$, which were used for microanalysis. IR (Nujol): $\tilde{\nu}$ = 3347 (w), 3331 (w), 2724 (w), 1616 (m), 1262 (w), 1158 (w), 1026 (m), 970 (w), 871 (w), 821 (m), 778 (m), 731 (s), 669 (m), 642 (vs), 623 (s), 550 (w), 519 (m), 465 (w), 435 cm^{-1} (s) ; ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C, TMS): δ = 11.77 (br s, 3 H; NH), 3.61 (m, 4 H; cod), 2.34–1.70 (m, 8 H; cod), 2.10 (s, 45 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 °C, TMS): δ = 121.1 (*C*$_5$Me$_5$), 75.4 (d, ^1J(C,Rh) = 11.6 Hz; cod), 31.4 (cod), 12.1 (C$_5$*Me*$_5$); MS (70 eV, EI): *m*/*z* (%): 819 (1) [*M* – Cl]$^+$, 711 (5) [*M* – Cl – cod]$^+$; elemental analysis calcd (%) for C$_{39}$H$_{62}$N$_4$Cl$_3$RhTi$_3$: C 49.84, H 6.65, N 5.96; found C 50.39, H 6.69, N 5.33.

Synthesis of [Ir(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)]Cl (3): In a fashion similar to the preparation of **2**, compound **1** (0.30 g, 0.49 mmol) and [{IrCl(cod)}$_2$] (0.166 g, 0.25 mmol) were allowed to react in toluene (50 mL) to afford **3** (0.35 g, 75 %). Red crystals of **3** were obtained by crystallization in chloroform at –10 °C. IR (Nujol): $\tilde{\nu}$ = 3351 (w), 3327(w), 2737 (w), 1659 (m), 1323 (w), 1294 (w), 1262 (w), 1206 (w), 1159 (m), 1090 (w), 1068 (w), 1026 (s), 970 (w), 919 (w), 906 (w), 878 (w), 860 (w), 841 (w), 803 (w), 786 (w), 737 (s), 675 (m), 638 (vs), 550 (w), 517 (s), 488 (w), 471 (m), 426 cm^{-1} (s); ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C, TMS): δ = 11.64 (br s, 3 H; NH), 3.41 (m, 4 H; cod), 2.33–1.88 (m, 8 H; cod), 2.10 (s, 45 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 °C, TMS): δ = 121.2 (*C*$_5$Me$_5$), 61.0 (cod), 32.7 (cod), 12.1 (C$_5$*Me*$_5$); MS (70 eV, EI): *m*/*z* (%): 801 (16) [*M* – Cl – cod]$^+$; elemental analysis calcd (%) for C$_{38}$H$_{60}$N$_4$ClIrTi$_3$: C 48.34, H 6.40, N 5.93; found C 48.08, H 6.31, N 4.69.

Synthesis of [Rh(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)][BPh$_4$] (4): A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.35 mmol), [AgBPh$_4$] (0.15 g, 0.35 mmol), and dichloromethane (50 mL). The reaction mixture was stirred at room temperature for 16 h. A red solution was separated from a dark orange solid by filtration. The volatile components were then removed under reduced pressure to give **4** as a dark orange crystalline solid (0.27 g, 67 %). IR (Nujol): $\tilde{\nu}$ = 3339 (w), 3330 (w), 2727 (w), 1579 (m), 1426 (m), 1331 (w), 1303 (w), 1262 (w), 1180 (w), 1153 (w), 1065 (w), 1031 (m), 970 (w), 870 (m), 843 (m), 788 (s), 731 (vs), 703 (s), 667 (m), 637 (vs), 613 (s), 548 (w), 520 (m), 467 (m), 430 cm^{-1} (s); ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C, TMS): δ = 11.13 (br s, 3 H; NH), 7.43 (br m, 8 H; Ph), 7.04 (m, 8 H; Ph), 6.88 (m, 4 H; Ph), 3.39 (m, 4 H; cod), 2.38–1.80 (m, 8 H; cod), 2.03 (s, 45 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 °C, TMS): δ = 165.0, 136.2, 125.5, 121.6 (Ph), 121.4 (*C*$_5$Me$_5$), 75.1 (d, ^1J(C,Rh) = 12.2 Hz; cod), 31.3 (cod), 12.1 (C$_5$*Me*$_5$); elemental analysis calcd (%) for C$_{62}$H$_{80}$N$_4$BRhTi$_3$: C 65.39, H 7.08, N 4.92; found C 64.96, H 7.19, N 4.68.

Synthesis of [Ir(cod)(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)][BPh$_4$] (5): In a fashion similar to the preparation of **4**, compound **3** (0.27 g, 0.29 mmol) and [AgBPh$_4$] (0.12 g, 0.29 mmol) were allowed to react in dichloromethane (50 mL) to yield **5** as a dark red crystalline solid (0.23 g, 65 %). Suitable single crystals for X-ray diffraction analysis were obtained by careful layering of a dichloromethane solution (20 mL) with hexane (40 mL). IR (Nujol): $\tilde{\nu}$ = 3341 (m), 3328 (m), 2728 (w), 1579 (m), 1424 (m), 1329 (w), 1301 (w), 1262 (w), 1243 (w), 1207 (w), 1179 (w), 1153 (w), 1133 (w), 1065 (w), 1030 (w), 1021 (m), 968 (w), 980 (m), 869 (w), 842 (m), 802 (w), 783 (w), 770 (w), 734 (vs), 707 (s), 671 (m), 641 (vs), 624 (vs), 612 (s), 549 (w), 519 (m), 472 (m), 432 (s), 406 cm^{-1} (m); ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C, TMS): δ = 11.14 (br s, 3 H; NH), 7.42 (br m, 8 H; Ph), 7.04 (m, 8 H; Ph), 6.88 (m, 4 H; Ph), 3.24 (m, 4 H; cod), 2.34–1.84 (m, 8 H; cod), 2.05 (s, 45 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 °C, TMS): 165.0, 136.4, 125.4, 121.6 (Ph), 121.5 (*C*$_5$Me$_5$), 60.7 (cod), 32.7 (cod), 12.1 (C$_5$*Me*$_5$); elemental analysis calcd (%) for C$_{62}$H$_{80}$N$_4$BIrTi$_3$: C 60.64, H 6.57, N 4.56; found C 59.54, H 6.55, N 4.13.

Synthesis of [Rh(cod)(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] (7): A 100 mL Schlenk flask was charged with **6** · C$_7$H$_8$ (0.28 g, 0.21 mmol), [{RhCl(cod)}$_2$] (0.11 g, 0.21 mmol), and toluene (40 mL). The reaction mixture was stirred at room temperature for 20 h to yield a dark red solution and a fine white powder. The solution was filtered, and the volatile components removed under reduced pressure. The red solid obtained was washed with toluene (5 mL) and dried in vacuo to give **7** (0.25 g, 72 %). IR (Nujol): $\tilde{\nu}$ = 3351 (m), 3329 (w), 2721 (w), 1325 (w), 1262 (w), 1242 (w), 1209 (w), 1173 (w), 1152 (w), 1075 (w), 1024 (m), 960 (w), 865 (m), 794 (m), 727 (vs), 714 (vs), 613 (s), 523 (m), 482 (w), 464 (w), 419 cm^{-1} (s); ^1H NMR (300 MHz, C_6D_6, 20°C, TMS): $\delta = 10.06$ (br s, 2H; NH), 3.49 (m, 4H; cod), 2.36 – 1.85 (m, 8H; cod), 2.10 (s, 30H; C_5Me_5), 1.95 (s, 15H; C_5Me_5); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20°C, TMS): $\delta = 116.7$ (C_5Me$_5$), 115.9 (C_5Me$_5$), 70.8 (d, ^1J(C,Rh) = 11.7 Hz; cod), 32.2 (cod), 12.0 (C_5Me_5), 11.9 (C_5Me_5); MS (70 eV, EI): m/z (%): 819 (2) $[M]^+$, 711 (9) $[M - cod]^+$; elemental analysis calcd (%) for $C_{38}H_{59}N_4RhTi_3$: C 55.76, H 7.27, N 6.84; found C 56.32, H 7.37, N 6.10.

Synthesis of [Ir(cod)(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] (8): In a similar fashion to the preparation of **7**, compound **6** · C_7H_8 (0.28 g, 0.21 mmol) was treated with [{IrCl(cod)}$_2$] (0.14 g, 0.21 mmol) in toluene (40 mL) to give **8** as a red solid (0.28 g, 73 %). IR (Nujol): $\tilde{\nu} = 3351$ (m), 3324 (w), 2721 (w), 1605 (w), 1319 (w), 1262 (w), 1238 (w), 1202 (w), 1168 (w), 1152 (w), 1074 (w), 1024 (m), 980 (w), 904 (m), 860 (w), 789 (m), 728 (vs), 712 (vs), 678 (s), 667 (s), 608 (s), 523 (m), 464 (w), 422 cm^{-1} (s); ^1H NMR (300 MHz, C_6D_6, 20°C, TMS): $\delta = 10.15$ (br s, 2H; NH), 3.23 (m, 4H; cod), 2.28 – 1.86 (m, 8H; cod), 2.08 (s, 30H; C_5Me_5), 1.93 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20°C, TMS): $\delta = 116.8$ (C_5Me$_5$), 116.1 (C_5Me$_5$), 55.5 (cod), 33.6 (cod), 12.0 (C_5Me_5), 11.9 (C_5Me_5); MS (70 eV, EI): m/z (%): 800 (27) $[M - cod]^+$; elemental analysis calcd (%) for $C_{38}H_{59}N_4IrTi_3$: C 50.28, H 6.55, N 6.17; found C 51.27, H 6.61, N 4.94.

Synthesis of [Rh(C$_2$H$_4$)$_2$(μ_3-NH)$_2$(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] (9): In a fashion similar to the preparation of **7**, compound **6** · C_7H_8 (0.30 g, 0.23 mmol) and [{RhCl(C_2H_4)$_2$}$_2$] (0.09 g, 0.23 mmol) were allowed to react in toluene (40 mL) for 8 h to afford **9** as a brown solid (0.30 g, 85 %). IR (Nujol): $\tilde{\nu} = 3354$ (m), 3335 (w), 2721 (w), 1604 (w), 1262 (w), 1230 (w), 1169 (m), 1065 (w), 1025 (m), 857 (w), 802 (m), 668 (m), 613 (s), 524 (m), 482 (w), 465 (w), 420 cm^{-1} (s); ^1H NMR (300 MHz, C_6D_6, 20°C, TMS): $\delta =$ 10.37 (br s, 2H; NH), 2.24 – 2.15 (m, 8H; C_2H_4), 2.09 (s, 30H; C_5Me_5), 1.91 (s, 15H; C_5Me_5); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20°C, TMS): $\delta = 116.9$ (C_5Me$_5$), 116.2 (C_5Me$_5$), 47.4 (d, ^1J(C,Rh) = 12.5 Hz; C_2H_4), 12.03 (C_5Me_5), 11.96 (C_5Me_5); elemental analysis calcd (%) for $C_{34}H_{55}N_4RhTi_3$: C 53.28, H 7.23, N 7.31; found C 53.43, H 7.28, N 6.54.

Polymerization of phenylacetylene:

Catalyst **2**: A 5 mm NMR tube was charged with **2** (0.010 g, 0.012 mmol) and [D$_1$]chloroform (1.00 mL). Upon addition of phenylacetylene (0.046 g, 0.45 mmol) the initial red solution immediately became more viscous. The course of the reaction was monitored by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Spectra taken after 4 h showed complete consumption of phenylacetylene, with concomitant formation of poly(phenylacetylene) and complex **2**. The high stereoregularity of the polymer (head-to-tail, cis-transoidal structure) is supported by the existence of only one set of signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra, which are identical to those reported in the literature.[19] NMR data for the polymer: ^1H NMR (300 MHz, $CDCl_3$, 20°C, TMS): $\delta =$ 6.96 – 6.94 (br m; Ph), 6.65 – 6.63 (br m; Ph), 5.85 (br s; vinyl); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20°C, TMS): $\delta = 142.8$ (quaternary carbon of the main chain), 139.3 (Ph), 131.8 (vinyl) 127.8 (Ph), 127.5 (Ph), 126.7 (Ph).

Catalyst **7**: In a similar fashion to that described for **2**, the reaction of **7** (10 mg, 0.012 mmol) in [D$_6$]benzene (1.00 mL) with phenylacetylene (0.046 g, 0.45 mmol) was followed by NMR spectroscopy. Almost immediately, the reaction mixture became very viscous, and an abundant orange solid was formed. After 16 h at room temperature, the volatile components were removed under reduced pressure, and the resultant solid was dissolved in [D$_1$]chloroform. ^1H and $^{13}C\{^1H\}$ NMR spectra revealed the resonances above described for poly(phenylacetylene).

X-ray structure determination of complex 5: All data were collected on an ENRAF NONIUS CAD4 diffractometer at room temperature. Crystallographic data for complex **5** are presented in Table 5. Intensity measurements for **5** were performed by $\omega - 2\theta$ scans in the range $6° < 2\theta < 40°$. Of the 5577 measured reflections, 5251 were independent; $R1 = 0.056$ and $wR2 = 0.150$ (for 4578 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

The structure was solved, with the WINGX package,[27] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[28] All non-hydrogen atoms, except those of the pentamethylcyclopentadienyl C31 – C40 ring, which was partially disordered, were anisotropically refined. Deepest hole and highest peak (−0.82 and 2.54 e Å^{-3}) are located inside the disordered pentamethylcyclopentadienyl ring. The hydrogen atoms were positioned geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156563. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 5. Crystallographic data for complex **5**.

formula	$C_{62}H_{80}BIrN_4Ti_3$
M_r	1228.01
T [K]	293(2)
λ [Å]	0.71073
crystal system	triclinic
space group	$P\bar{1}$
a [Å]; α [°]	12.349(1); 93.08(1)
b [Å]; β [°]	15.269(2); 99.03(1)
c [Å]; γ [°]	15.376(3); 97.85(1)
V [Å^3]	2828.1(7)
Z	2
ρ_{calcd} [g cm^{-3}]	1.442
μ (Mo$_{K\alpha}$) [mm^{-1}]	2.795
F(000)	1256
crystal size [mm]	0.50 × 0.23 × 0.12
θ range	3.10 – 19.98°.
index ranges	$0 \le h \le 11$, $-14 \le k \le 14$, $-14 \le l \le 14$
reflections collected	5577
unique data	5251
observed data [$I > 2\sigma(I)$]	5478
goodness-of-fit on F^2	1.116
final R indices [$I > 2\sigma(I)$]	$R1 = 0.056$, $wR2 = 0.150$
R indices (all data)	$R1 = 0.067$, $wR2 = 0.158$
largest diff. peak/hole [e Å^{-3}]	2.540/ − 0.821

Computational details: All DFT calculations were carried out with the ADF program[29] by using triple-ζ and polarization Slater basis sets to describe the valence electrons of C and N. For titanium, a frozen core composed of the 1s, 2s, and 2p orbitals was described by double-ζ Slater functions, the 3d and 4s orbitals by triple-ζ functions, and the 4p orbital by a single orbital. Basis sets of the same quality were used for Rh and Ir. Hydrogen atoms were described by triple-ζ and polarization functions. The geometries and binding energies were calculated with gradient corrections. We used the local spin density approximation, characterized by the electron gas exchange (Xα with $\alpha = 2/3$) together with Vosko – Wilk – Nusair parametrization[30] for correlation. Becke's nonlocal corrections[31] to the exchange energy and Perdew's nonlocal corrections[32] to the correlation energy were added. Quasirelativistic corrections were employed by using the Zora formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC.[29] In the DFT calculations on complexes **4**, **5**, **7**, and **8**, the methyl groups were replaced by hydrogen atoms.

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