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Reactivity of Yttrium Quinoline–Imine–Phenoxide Complexes Towards Inter- and Intramolecular Alkyl Nucleophilic Attacks

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Keywords: Yttrium / Magnesium / Chloride complexes / Imine Ligands

Yttrium(III) chloride complexes $[YCl_2(NNO^H)]$ (**1^H**) and $[YCl_2(NNO^{Me})]$ (**1^{Me}**) {NNO^H = 2-*tert*-butyl-6-(quinolin-8-yliminomethyl)phenoxide; NNO^{Me} = 2-*tert*-butyl-6-[(2-methylquinolin-8-ylimino)methyl]phenoxide} were synthesized by treating a thf solution of YCl_3 at room temperature with the NNO^H-H and NNO^{Me}-H ligands {NNO^H-H = 2-*tert*-butyl-6-(quinolin-8-yliminomethyl)phenol; NNO^{Me}-H = 2-*tert*-butyl-6-[(2-methylquinolin-8-ylimino)methyl]phenol}, which were previously deprotonated with potassium *tert*-butoxide or thallium ethoxide. Surprisingly, reaction of **1^H** with the Grignard reagent MeMgBr to prepare the corresponding dialkyl derivative led to the formation of the tetranuclear magnesium dimer $[Mg_2BrCl\{NN(Me)O^H\}(thf)]_2$ {$NN(Me)O^H$ = 2-*tert*-butyl-6-[1-(quinolin-8-ylamido)ethyl]phenoxide} (**2**), whose structure was determined by single-crystal X-ray diffraction. By reacting the neutral ligand NNO^H-H with $Y(CH_2SiMe_3)_3$·2thf in toluene at low temperature the alkyl complex $[Y(CH_2SiMe_3)\{NN(CH_2SiMe_3)O\}(thf)]$ {$NN(CH_2SiMe_3)O$ = 2-*tert*-butyl-6-[1-(quinolin-8-ylamido)-2-trimethylsilanylethyl]phenoxide} (**3**) was isolated. The supposed reaction mechanism leading to the formation of **3** was simulated by using the PM6 Hamiltonian.

Introduction

Group 3 and lanthanide alkyl and aryl complexes are an attractive field of research, as the predominant ionic character of the Ln···C bond makes these derivatives reactive precursors towards a wide range of inorganic and catalytic reactions.[1] In particular, recent literature shows a development of new neutral and cationic alkyl complexes of group 3 and rare-earth metals as catalysts for olefin polymerization.[2] The organometallic active species in this type of reactions are often obtained in situ by reacting precatalysts such as chloride complexes with cocatalysts like MAO (methyl aluminoxane), Grignard reagents and lithium or aluminium alkyls, including also, for example, compounds able to act as carbanion sources, even if several organometallic derivatives have been isolated and characterized.

A great variety of ancillary ligands have been reported in the coordination chemistry of group 3 metals and lanthanides, mainly containing N-, O- or C-donor groups. Among all, imine–phenoxide-based ligands are usually able to strongly coordinate hard metal centers such as Ln^{III} and analogous ions to give well-defined species.[3] Free and coordinated imines are, however, susceptible to nucleophilic attack or insertion into the Ln···C bond;[4] therefore, the isolation of reactive alkyl complexes bearing imine-based ligands in their coordination sphere can be a demanding objective.

During the last years our research group has been interested in the coordination chemistry of early d- and f-block elements with polydentate imine-based ligands and in the preparation of organometallic derivatives for olefin polymerization.[5–7] It was observed that the synthesized precatalysts, once activated with alkylating agents, often showed a relatively low activity with formation of polymers with high polydispersivity index (PDI), this suggesting the formation of different catalytic sites. To better give insight into the organometallic chemistry of group 3 and lanthanides complexes with polydentate imine-based ancillary ligands, in this paper the results of inter- and intramolecular nucleophilic attacks by carbanion sources on yttrium-coordinated quinoline–imine–phenoxide ligands, leading to the isolation and characterization of unexpected products, are reported. The ionic radius of Y^{III}, 89.3 pm, intermediate among many Ln^{3+} ions, allows this element to be considered as a representative for several 4f-block metals, in particular thulium (87.0 pm), erbium (88.1 pm), holmium (89.4 pm) and dysprosium (90.8 pm).

Results and Discussion

Synthesis and Characterization of the Quinoline–Imine–Phenoxide Complexes

The neutral quinoline–imine–phenoxide yttrium chloride complexes $YCl_2(NNO^H)$ (**1^H**) and $YCl_2(NNO^{Me})$ (**1^{Me}**)

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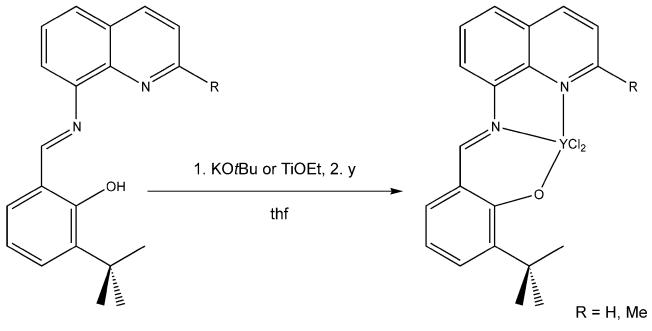
{NNO^H = 2-*tert*-butyl-6-(quinolin-8-yliminomethyl)phenoxide; NNO^{Me} = 2-*tert*-butyl-6-[(2-methylquinolin-8-ylimino)methyl]phenoxide} were prepared in good yields by reacting the YCl_3 salt with the corresponding ancillary ligands previously deprotonated with potassium *tert*-butoxide or thallium ethoxide, as depicted in Scheme 1. In the case of thallium ethoxide as base, the thallium salts $Tl(NNO^H)$ and $Tl(NNO^{Me})$ were isolated before the subsequent reaction with YCl_3. Similar synthetic approaches were already successfully applied for the preparation of group 4 chloride complexes of the type $MCl_3(NNO^H)$ (M = Ti, Zr, Hf)[6] and the scandium(III) complex $ScCl_2(NNO^H)(thf)$.[7] The neutral ligands NNO^H-H and NNO^{Me}-H were prepared on the basis of a reported procedure,[6] that is, by treating 8-aminoquinoline or 2-methyl-8-aminoquinoline with 3-*tert*-butyl-2-hydroxybenzaldehyde in refluxing methanol in the presence of anhydrous magnesium sulfate and molecular sieves. The commercially unavailable 2-methyl-8-aminoquinoline was synthesized from 2-methyl-8-nitroquinoline on the basis of a reported method.[8]



Scheme 1. Synthesis of $\mathbf{1^H}$ and $\mathbf{1^{Me}}$.

The two yttrium chloride compounds were characterized by elemental analyses, 1D and 2D ^1H NMR spectroscopic experiments and mass spectrometry. All data strongly agree with the proposed formulations. In particular, homonuclear decoupling, ^1H COSY and ^1H NOESY, experiments allowed all the resonances corresponding to the aromatic protons of the coordinated ligands to be assigned unambiguously. The most downfield signal of the ^1H NMR spectrum of $YCl_2(NNO^H)$ $\mathbf{1^H}$ is a doublet of doublets at δ = 8.97 ppm corresponding to the proton in the α position with respect to the N atom of the quinoline group. A characteristic ^1H signal of the imine group falls at 8.88 ppm (Figure 1). The coupling between this hydrogen atom and the metal center (100% ^{89}Y, I = 1/2) is diagnostic, with a $^3J_{YH}$ constant of 1.2 Hz, which is probably due to the presence of the imine π system and a favourable Karplus angle. The other aromatic protons fall in the range 7.91–7.39 ppm, with the exception of the quite strongly shielded hydrogen atom in the *para* position with respect to the oxygen atom, which corresponds to a triplet at δ = 6.69 ppm. In the aliphatic region, only a sharp singlet due to the *tert*-butyl group is observable. The complete ^1H NMR spectrum of complex $\mathbf{1^H}$ and the corresponding ^1H COSY spectrum are reported in the Supporting Information. The ^1H NMR spectrum of the $YCl_2(NNO^{Me})$ ($\mathbf{1^{Me}}$) derivative is, as expected, quite similar to the one previously described. The most downfield resonance is attributed to the imine proton, whose coupling with the metal center is identical to that of compound $\mathbf{1^H}$, that is, $^3J_{YH}$ = 1.2 Hz. The aromatic H atoms show signals between 8.05 and 6.38 ppm, and the last triplet corresponds to the proton in the *para* position with respect to oxygen atom in the phenoxide ring, as for $\mathbf{1^H}$. The aliphatic region shows, besides the *tert*-butyl singlet at δ = 1.31 ppm, the quinoline methyl group at δ = 2.77 ppm as a sharp singlet.

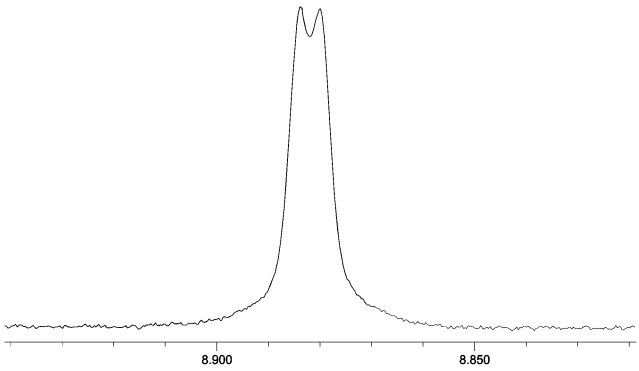


Figure 1. ^1H NMR signal of the hydrogen atom of the imine group coupled to the metal center in compound $\mathbf{1^H}$.

In both the mass spectra of $\mathbf{1^H}$ and $\mathbf{1^{Me}}$ it was possible to detect the isotopic clusters of the molecular ions at *m*/*z* = 462 and 477, respectively, in agreement with the theoretical ones. The other characterized fragments are attributable to the loss of the molecular ion of chloride and/or methyl groups: in the $\mathbf{1^H}$ spectrum the clusters at *m*/*z* = 447, 427 and 411 correspond to the $[M^{\cdot+} - CH_3]^+$, $[M^{\cdot+} - Cl]^+$ and $[M^{\cdot+} - Cl - Me]^{\cdot+}$ ions, respectively, whereas in the $\mathbf{1^{Me}}$ spectrum the $[M^{\cdot+} - Cl]^+$ and $[M^{\cdot+} - Cl - Me]^{\cdot+}$ ions show their clusters at *m*/*z* = 442 and 425, respectively.

Reaction of $\mathbf{1^H}$ with MeMgBr and X-ray Structure Determination of the Product

Once isolated and characterized, chloride complex $\mathbf{1^H}$ was allowed to react in thf at low temperature with two equivalents of methylmagnesium bromide. The objective of this reaction was to prepare a yttrium dialkyl derivative with the NNO^H ligand, that is, a species able to undergo facile cation formation by reaction with Brønsted or Lewis acids like $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, $[PhNMe_2H][B(C_6F_5)_4]$, etc., with consequent formation of a charged organometallic complex potentially active for olefin polymerization. The crude product was separated from the by-products by extraction with toluene and allowed to precipitate by addition of *n*-hexane. Two classes of reactions were potentially expected: the nucleophilic attack of the Grignard reagent on the coordinated imine group and/or the substitution of the coordinated chloride ligands by a methyl group.

The ^1H NMR spectrum of isolated product **2**, reported in the Supporting Information, shows the signals of the aro-

matic rings between 7.90 and 6.26 ppm. The corresponding $^{13}C\{^1H\}$ singlets fall in the range 142.5–102.2 ppm. The assignments of the aromatic hydrogen and carbon atoms were carried out on the basis of 2D homo- and heteronuclear experiments. The downfield region of the NMR spectra of compound **2** show the absence of signals attributable to the R-CH=N-R′ group. In the aliphatic region, besides the presence of the *tert*-butyl group and a molecule of coordinated thf, is diagnostic evidence for the presence of a ^1H quartet at δ = 4.54 ppm, which couples with a doublet at δ = 0.65 ppm ($^3J_{HH}$ = 6.6 Hz).The corresponding signals in the $^{13}C\{^1H\}$ NMR spectrum fall at δ = 59.7 and 20.2 ppm. This ^1H AB_3 spin system allowed for the assumption that nucleophilic attack of the MeMgBr reagent at the coordinated imine occurred with subsequent formation of the corresponding coordinated amido group. No signal attributable to alkyl group coordination was detected.

The formation of a complex of the type YCl[NN(Me)-O^H](thf) {NN(Me)O^H = 2-*tert*-butyl-6-[1-(quinolin-8-ylamido)ethyl]phenoxide} was therefore supposed, but elemental analysis data for compound **2** showed a strong contrast with the proposed formulation. Crystals suitable for X-ray structure analysis were thus obtained by slow cooling of saturated toluene/*n*-hexane solutions: astonishingly, compound **2** resulted to be the tetranuclear magnesium dimer $[Mg_2BrCl\{NN(Me)O^H\}(thf)]_2$ represented in Figure 2 and not the expected yttrium quinoline–amide–phenoxide complex. Compound **2** has C_2 symmetry by virtue of a twofold crystallographic axis passing in between the Mg1 cations. The structure consists of two different Mg environments. The central Mg1 cations are five-coordinate and are bridged by two μ-O1 phenoxide oxygen atoms forming a Mg1–O1–Mg1–O1 four-membered ring. They adopt a distorted trigonal bipyramidal geometry with the ligand acting in a tridentate mode where the O1 phenoxide oxygen atom and the N1 quinoline nitrogen atom are in axial positions, whereas the equatorial sites are occupied by the N2 amido nitrogen atom, the Br1 anion and the O1 phenoxide oxygen atom of the symmetry-related ligand. Conversely, each peripheral Mg2 cation displays a distorted tetrahedral coordination and is bound to Br1 and N2 bridging Mg1 and Mg2 cations, forming two four-membered Mg1–Br1–Mg2–N2 rings. The remaining coordination sites are occupied by a Cl anion and the oxygen atom of a thf molecule. The ORTEP[9] view is shown in Figure 2 and selected bond lengths and angles are given in Table 1.

Table 1. Selected bond lengths and angles.

Bond lengths [Å]			
Mg1–Br1	2.600(2)	Mg2–Br1	2.452(2)
Mg1–O1	1.996(5)	Mg2–Cl1	2.277(6)
Mg1–N1	2.200(6)	Mg2–O2	2.052(6)
Mg1–N2	2.106(6)	Mg2–N2	2.156(6)
Bond angles [°]			
Br1–Mg1–O1	100.1(2)	Br1–Mg2–Cl1	134.6(2)
Br1–Mg1–O1′	132.5(2)	Br1–Mg2–O2	95.8(2)
Br1–Mg1–N1	99.0(2)	Br1–Mg2–N2	93.2(2)
Br1–Mg1–N2	90.3(2)	Cl1–Mg2–O2	105.5(2)
O1–Mg1–O1′	78.6(2)	Cl1–Mg2–N2	115.2(2)
O1–Mg1–N1	157.4(2)	O2–Mg2–N2	110.1(2)
O1′–Mg1–N1	97.0(2)	Mg1–Br1–Mg2	78.4(1)
O1–Mg1–N2	90.1(2)	Mg1–N2–Mg2	97.1(2)
O1′–Mg1–N2	136.8(2)	Mg1–O1–Mg1′	98.0(2)
N1–Mg1–N2	77.9(2)		

The monomer unit of compound **2** is sketched in Scheme 2 for the sake of clarity. Even if the suggestion of a complete reaction mechanism for the formation of $[Mg_2BrCl\{NN(Me)O^H\}(thf)]_2$ from $\mathbf{1^H}$ is a demanding objective, it appears reasonable to consider the nucleophilic attack of one equivalent of the Grignard reagent on the coordinated imine bond of $YCl_2(NNO^H)$ and the consequent formation of the corresponding amide group as one of the key steps of the reaction pathway leading to the formation of **2**. The substitution of the yttrium center by magnesium does not find, instead, a simple explanation, especially on considering the polydentate nature of the ancillary ligand used. From the mother liquor of **2** it was impossible to separate pure yttrium compounds, and as a matter of

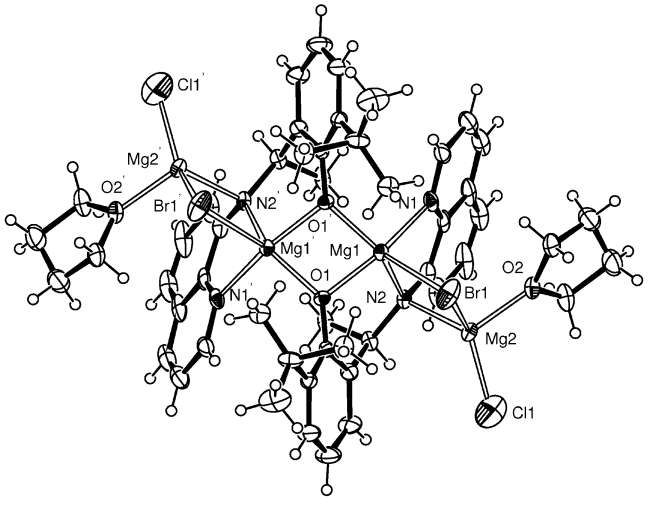
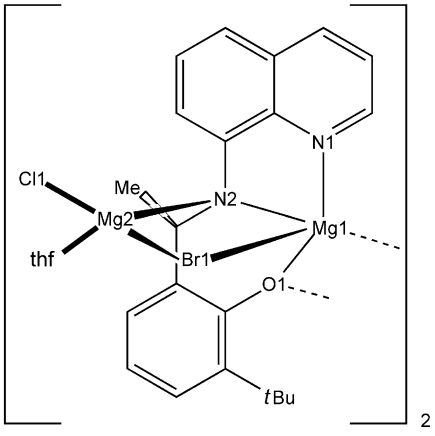


Figure 2. ORTEP view of complex **2** displaying the thermal ellipsoids at 40% probability.



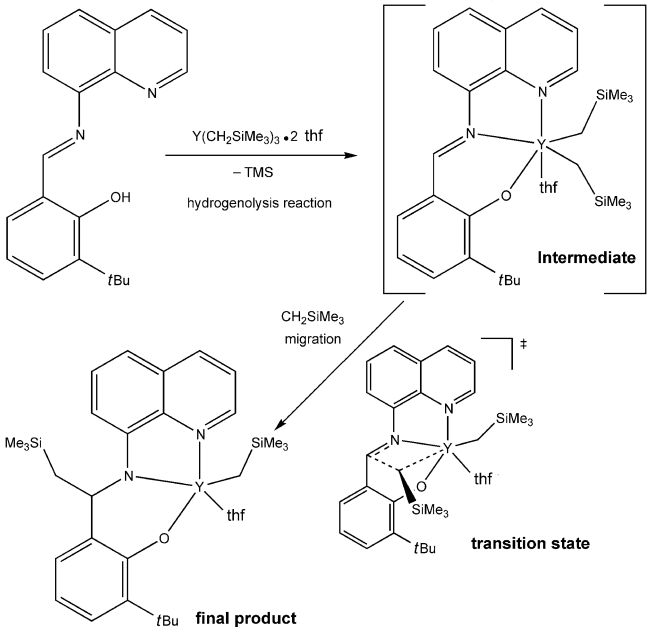
Scheme 2. Sketch of the monomer unit of complex **2**.

fact, any attempt to reduce the MeMgBr/**1**^{H} ratio from the original 2:1 led only to the formation of complex mixtures of hardly separable products.

Synthesis and Characterization of [Y(CH$_2$SiMe$_3$){NN(CH$_2$SiMe$_3$)O}(thf)] (3)

After the structural characterization of **2**, we tried to improve our knowledge about the reactivity of Y-coordinated imine groups in the presence of carbanion sources by treating the neutral ligand NNO^{H}-H with a stoichiometric amount of the organometallic precursor Y(CH$_2$SiMe$_3$)$_3$·2thf[10] in toluene.

Isolated compound **3** was characterized by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum, reported in the Supporting Information, shows the characteristic signals of the phenoxide and quinoline rings between 7.66 and 6.40 ppm, assigned on the basis of COSY and NOESY experiments. The corresponding carbon atoms were identified in the ^{13}C{^{1}H} NMR spectrum between 143.3 and 104.4 ppm by HMQC experiments. As for compound **2**, the NMR spectra of complex **3** do not show any signal in the downfield region attributable to the R-CH=N-R′ group, whereas a molecule of coordinated thf and the ancillary *tert*-butyl ligand can be detected. At 4.54 ppm falls a doublet of doublets corresponding to a ^{13}C singlet at δ = 61.4 ppm, which couples with two different hydrogen atoms at δ = 1.80 and 1.42 ppm ($^{3}J_{HH}$ = 10.0 and 4.8 Hz), as observable in the ^{1}H COSY spectrum reported in the Supporting Information. These two aliphatic protons couple each other with a $^{2}J_{HH}$ coupling constant of 13.0 Hz and give HMQC signals with a single carbon atom at δ = 31.2 ppm. The chemical shift of the most downfield resonance of the described ABC spin system is attributable to the N-bonded CH formed after nucleophilic attack at the imine carbon atom of a CH$_2$SiMe$_3$ group, whereas the B and C multiplets can be referred to the methylene group of the nucleophile. Both the yttrium-coordinated nitrogen atom and the carbon atom of the N-CH amido group are stereocenters, and this justifies the nonequivalence of the CH$_2$ protons of the CH$_2$SiMe$_3$ chain. Finally, the most upfield signals in the ^{1}H NMR spectrum of **3** are a doublet at δ = 0.20 ppm attributed to the CH$_2$ group of a yttrium-coordinated CH$_2$SiMe$_3$ ligand, with $^{2}J_{YH}$ = 2.7 Hz, and a strong singlet centered at δ = 0.08 ppm attributed to the SiMe$_3$ groups of the isolated product. All the silicon-bonded carbon atoms of **3** correspond to a single, slightly broad ^{13}C signal at δ = –1.8 ppm, which was partially resolved by means of sine-bell apodization. From its NMR spectroscopic data, compound **3** can be formulated as the neutral quinoline–amide–phenoxide alkyl complex [Y(CH$_2$SiMe$_3$){NN(CH$_2$SiMe$_3$)O}(thf)] {NN(CH$_2$SiMe$_3$)O = 2-*tert*-butyl-6-[1-(quinolin-8-ylamido)-2-trimethylsilanylethyl]phenoxide} sketched in Scheme 3. The heaviest fragment observed in the mass spectrum (*m*/*z* = 536) corresponds to the molecular ion after the loss of thf and two methyl fragments.



Scheme 3. Proposed mechanism for the formation of [Y(CH$_2$SiMe$_3$){NN(CH$_2$SiMe$_3$)O}(thf)] (**3**).

A possible reaction mechanism leading to the formation of complex **3** is outlined in Scheme 3. The first reaction step is probably constituted by a fast acid–base reaction between one of the CH$_2$SiMe$_3$ groups of the Y(CH$_2$SiMe$_3$)$_3$·2thf organometallic precursor and the phenol group of the free neutral ligand NNO^{H}, with the elimination of tetramethylsilane and the formation of an intermediate quinoline–imine–phenoxide yttrium dialkyl complex. Intermolecular migration of a CH$_2$SiMe$_3$ ligand from the metal center to the coordinated imine carbon atom can be supposed as the second step of the reaction pathway leading the formation of final product **3**.

Intermolecular nucleophilic attack on the imine carbon atom by the alkyl ligand was simulated by using the semiempirical PM6 Hamiltonian. Computed data are reported in Table 2. Once optimized, the geometries of both the two ground states and the transition state of the "CH$_2$SiMe$_3$ migration" pathway represented in Scheme 3, the computed enthalpy difference between the supposed intermediate and the product is about –13 kcal/mol, which, from a thermodynamic point of view, justifies why we did not isolate the expected quinoline–imine–phenoxide yttrium dialkyl complex depicted in Scheme 3 (intermediate) after the hydrogenolysis reaction between NNO^{H}-H and Y(CH$_2$SiMe$_3$)$_3$·2thf. Moreover, the computed energy barrier between the transition state and the intermediate for the proposed

Table 2. Computational results for the proposed intermolecular alkyl migration leading to the formation of **3**.

Compound	Heat of formation [kcal/mol]	Imaginary frequency [cm^{-1}]
Intermediate	–236.5	–
Transition state	–197.3	I835
Final product	–249.4	–

mechanism is about 39 kcal/mol, sufficiently low to kinetically allow the intermolecular alkyl migration from the metal center to the imine group. A picture of the optimized transition-state geometry is reported in Figure 3. It is to be noted that a similar reaction was already observed in a previous work by following the reaction between the organometallic precursor $Zr(CH_2Ph)_4$ and the ligand NNO^H-H by NMR spectroscopy.[6]

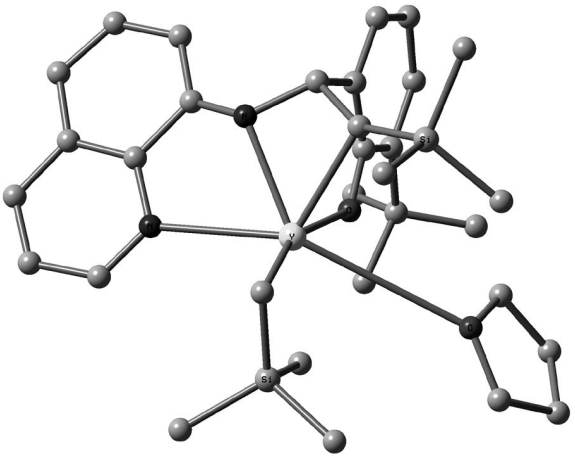


Figure 3. PM6 optimized geometry of the transition state leading to the formation of **3**. Hydrogen atoms are omitted for the sake of clarity.

Conclusions

The described work was focused on the reactivity of the imine group of a yttrium-coordinated quinoline–imine–phenoxide ancillary ligand towards carbanion intra- and intermolecular nucleophilic attack. The nature of the isolated products strongly highlighted the ease of inter- and intramolecular reactions between the coordinated –CH=N– fragment and alkyl nucleophile sources, with the formation of new complexes such as tetranuclear magnesium dimer **2**. Also, the computed results for the proposed reaction mechanism leading to quinoline–amide–phenoxide yttrium alkyl complex **3** underline from both thermodynamic and kinetic points of view that the obtainment of stable group 3 and lanthanide alkyl complexes with imine-based ancillary ligands can be a demanding objective.

Experimental Section

Materials and Methods: All inorganic manipulations were carried out under oxygen- and moisture-free atmosphere in a Braun MB 200 G-II glove box. All reaction solvents were thoroughly deoxygenated and dehydrated under argon by refluxing over suitable drying agents, whereas NMR solvents were kept in the dark over molecular sieves. The salt YCl_3 (Strem) was used as received, like 8-aminoquinoline, 3-*tert*-butyl-2-hydroxybenzaldehyde (Aldrich) and 2-methyl-8-nitroquinoline (Lancaster). Also, potassium *tert*-butoxide, thallium ethoxide, anhydrous magnesium sulfate and tin(II) chloride dihydrate were purchased from Aldrich. The neutral ligand NNO^H-H, 2-*tert*-butyl-6-(quinolin-8-yliminomethyl)phenol, was prepared by following a reported procedure.[6] The same method was followed for the synthesis of the analogous ligand NNO^{Me}-H, 2-*tert*-butyl-6-[(2-methyl-quinolin-8-ylimino)methyl]-phenol, that is, by treating 2-methyl-8-aminoquinoline and 3-*tert*-butyl-2-hydroxybenzaldehyde in refluxing methanol in the presence of anhydrous magnesium sulfate and molecular sieves (yield > 60%). 2-Methyl-8-aminoquinoline was obtained on the basis of a reported procedure by reducing 2-methyl-8-nitroquinoline with tin(II) chloride in acidic media.[8] Tl(NNO^H) and Tl(NNO^{Me}), that is, the thallium(I) salts of the NNO^H-H and NNO^{Me}-H ligands, were prepared by treating a stoichiometric amount of thallium ethoxide with the free ligands in thf. The organometallic precursor $Y(CH_2SiMe_3)_3$·2thf was synthesized by following a literature method by treating YCl_3 with trimethylsilylmethyllithium.[10]

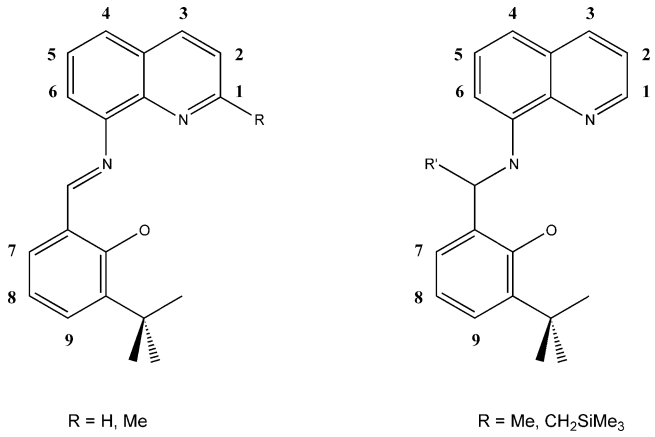
Microanalyses were performed at the Istituto di Chimica Inorganica e delle Superfici, CNR, Padova. ^{1}H NMR, ^{13}C{^{1}H} NMR, COSY, NOESY and ^{13}C APT were recorded at 298 K with a Bruker Avance 300 spectrometer operating at 300 MHz (^{1}H) and 75 MHz (^{13}C). NMR chemical shifts are internally referred to the solvent resonance and are quoted relative to tetramethylsilane (δ = 0 ppm). The SwaN-MR and MestRe-C software packages were used for NMR spectroscopic data treatment and spin systems simulation.[11] NMR deuterated solvents ($CDCl_3$, C_6D_6, CD_2Cl_2, [D_8]-thf) were purchased from Euriso-Top. Mass spectra (EI, 70 eV) were recorded with a Finnigan Trace GC–MS equipped with a probe controller for the sample direct inlet. Sample temperature was varied between 80 and 280 °C. The assignments were done by comparison between theoretical and experimental isotopic clusters and the most intense signals of each characterized cluster are reported.

Crystal data of compound **2** were collected with a Nonius Kappa CCD diffractometer by using graphite monochromated Mo-K_α radiation (λ = 0.7107 Å) at low temperature (120 K). Data sets were integrated with the Denzo-SMN package[12] and corrected for Lorentz-polarization and absorption[13] effects. The structure was solved by direct methods (SIR97)[14] and refined by full-matrix least square methods with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. The methyl groups $C20H_3$ and $C21H_3$ were found disordered and refined over two positions with occupancy 0.5 each. The correct absolute configuration, (*R*), of the C10 carbon atom bonded to N2 was obtained by the value of the Flack parameter[15] of 0.09(2), calculated after the last cycle of refinement. All calculations were performed by using SHELXL-97[16] and PARST[17] implemented in WINGX system of programs.[18]

Semiempirical computational geometry optimizations were carried out with the MOPAC2007 software package.[19] In all the calculations the PM6 Hamiltonian[20] was used. The singlet multiplicity was always considered; thus, the "restricted" formalism was applied. Calculations were carried out without symmetry constrains and all the resultant stationary points were characterized as true minima (i.e. no imaginary frequencies) or transition state geometries (i.e., one imaginary frequency).

NNO^{Me}-H: Refer to Scheme 4 for numbering. ^{1}H NMR ($CDCl_3$, 298 K): δ = 14.58 (s, 1 H, OH), 9.03 (s, 1 H, C*H*=N), 8.07 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, H3), 7.67 (t, $^3J_{HH}$ = 4.8 Hz, 1 H, H5), 7.51, 7.50 (2 d, $^3J_{HH}$ = 4.8 Hz, 2 H, H4-H6), 7.44 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1 H, H9), 7.35 (d, $^3J_{HH}$ = 8.3 H, 1 H, H2), 7.32 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1 H, H7), 6.90 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, H8), 2.79 (s, 3 H, Me), 1.55 (s, 9 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): 165.9 (*C*H=N); 136.4 (C3); 131.1 (C7); 130.6 (C9); 126.2 (C5); 126.0, 119.8 (C4–C6); 122.8 (C2); 118.3 (C8); 161.8,

159.6, 145.0, 142.2, 138.2, 127.8, 120.0 (quaternary aromatic carbon atoms), 35.5 (*t*Bu); 29.8 (*t*Bu); 26.2 (Me) ppm. $C_{21}H_{22}N_2O$ (318.41): calcd. C 79.2, H 6.96, N 8.80; found C 79.1, H 7.10, N 8.65.



Scheme 4. Numbering scheme for the aromatic atoms of the ligands.

Tl(NNO^{H}): Refer to Scheme 4 for numbering. ^{1}H NMR (C_6D_6, 298 K): δ = 8.31 (s, 1 H, C*H*=N); 8.12 (dd, $^3J_{HH}$ = 4.2 Hz, $^3J_{HH}$ = 1.6 Hz, 1 H), 7.70 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.9 Hz, 1 H), 7.48 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1 H), 7.22–7.13 (m, 3 H), 8.82 (t, $^3J_{HH}$ = 4.4 Hz, 1 H), 6.74 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 4.2 Hz, 1 H), 6.65 (t, $^3J_{HH}$ = 7.5 Hz, 1 H) aromatic protons; 1.89 (s, 9 H, *t*Bu) ppm. $C_{20}H_{19}N_2OTl$ (507.76): calcd. C 47.3, H 3.77, N 5.52; found C 47.0, H 3.65, N 5.70.

Tl(NNO^{Me}): Refer to Scheme 4 for numbering. ^{1}H NMR (C_6D_6, 298 K): δ = 8.33 (s, 1 H, C*H*=N); 7.69 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.9 Hz, 1 H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 1 H), 7.25–6.80 (m, 3 H), 6.82 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 2.2 Hz, 1 H), 6.70–6.58 (m, 2 H) aromatic protons; 2.12 (s, 3 H, Me); 1.89 (s, 9 H, *t*Bu) ppm. $C_{21}H_{21}N_2OTl$ (521.79): calcd. C 48.3, H 4.06, N 5.37; C 48.5, H 4.15, N 5.25.

Synthesis of [YCl$_2$(NNO^{H})] (1^{H}) and [YCl$_2$(NNO^{Me})] (1^{Me})

Method a: To a solution of the ligand NNO^{H}-H or NNO^{Me}-H (1.1 mmol) in thf (20 mL) was slowly added a stoichiometric amount of potassium *tert*-butoxide (0.123 g, 1.1 mmol) at room temperature. After 15 min under magnetic stirring, solid YCl_3 (0.215 g, 1.1 mmol) was added, and the resulting mixture was allowed to react at room temperature for 12 h. The solvent was removed by evaporation under reduced pressure, and the solid residue was extracted with CH_2Cl_2 (5 × 20 mL). The resulting bright-yellow solution was concentrated under reduced pressure to 5 mL. By slow addition of ethyl ether (20 mL) a yellow microcrystalline product precipitated, which was filtered, washed with ethyl ether and dried under vacuum. Yield > 75%.

Method b: A suspension of YCl_3 (0.198 g, 1.01 mmol) in thf (50 mL) was heated under reflux for 1 h. After cooling to –50 °C, a solution of Tl(NNO^{H}) or Tl(NNO^{Me}) (1.01 mmol) was added drop by drop. The resulting reaction mixture was allowed to slowly warm to room temperature and left overnight whilst stirring. The solvent was removed by evaporation at reduced pressure, and the product was extracted from the resulting solid by extraction with CH_2Cl_2 by using a Soxhlet. The resulting yellow solution was concentrated at reduced pressure and, by addition of *n*-hexane, a yellow product precipitated, which was filtered, washed with *n*-hexane and dried under vacuum. Yield > 85%.

1^{H}: Refer to Scheme 4 for numbering of aromatic H atoms. ^{1}H NMR (CD_2Cl_2 + 10% [D$_8$]thf, 298 K): δ = 8.97 (dd, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, H1), 8.88 (d, $^3J_{YH}$ = 1.2 Hz, 2 H, C*H*=N), 8.36 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H3), 7.91 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, H6), 7.82 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, H4), 7.75 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H5), 7.53 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.5 Hz, 1 H, H2), 7.44 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H7), 7.39 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H9), 6.69 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, H8), 1.19 (s, 9 H, *t*Bu) ppm. MS (EI, 70 eV): *m*/*z* = 462 [M]$^{+\cdot}$, 447 [M – CH$_3$]$^+$, 427 [M – Cl]$^+$, 411 [M – Cl – Me]$^{+\cdot}$. $C_{20}H_{19}Cl_2N_2OY$ (463.19): calcd C 51.86, H 4.13, N 6.05, Cl 15.3; found C 51.6, H 4.55, N 6.05, Cl 15.1.

1^{Me}: Refer to Scheme 4 for numbering of aromatic H atoms. ^{1}H NMR (CD_2Cl_2 + 10% [D$_8$]thf, 298 K): δ = 8.18 (d, $^3J_{YH}$ = 1.2 Hz, 1 H, C*H*=N), 8.05 (d, $^3J_{YH}$ = 8.4 Hz, 1 H, H3), 7.56 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H6), 7.42 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H5), 7.31 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H4), 7.25 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H2), 7.20 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H9), 7.02 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H7), 6.38 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H8), 2.77 (s, 3 H, Me), 1.31 (s, 9 H, *t*Bu) ppm. MS (EI, 70 eV): *m*/*z* = 477 [M]$^{+\cdot}$, 442 [M – Cl]$^+$, 425 [M – Cl – Me]$^{+\cdot}$. $C_{21}H_{21}Cl_2N_2OY$ (477.22): calcd. C 52.85, H 4.44, N 5.87, Cl 14.9; found C 53.0, H 4.65, N 5.65, Cl 15.2.

[Mg$_2$BrCl(NN(Me)O^{H})(thf)]$_2$ (2): To a solution of **1^{H}** (0.667 g, 1.44 mmol) in thf (50 mL), cooled to –40 °C was dropwise added a solution of MeMgBr (3 M in Et_2O, 0.96 mL, 2.88 mmol) diluted to 15 mL with thf. The color immediately turned from yellow to dark red. The reaction mixture was allowed to stir at –40 °C for 2 h and then allowed to slowly reach room temperature and left overnight whilst stirring. The solvent was removed by evaporation at reduced pressure and toluene (20 mL) was added. The solution was centrifuged to remove residual solids and concentrated to 5 mL. Addition of *n*-hexane allowed the product to separate as red microcrystals, which were filtered, washed with *n*-hexane and dried under vacuum. Yield > 60%. Crystals suitable for X-ray structure diffraction were obtained by slow cooling of toluene/*n*-hexane solutions. Refer to Scheme 4 for numbering scheme. ^{1}H NMR (CD_2Cl_2, 298 K): δ = 7.90 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H3), 7.83 (dd, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H1), 7.26 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.7 Hz, 1 H, H9), 7.16 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, H5), 7.01 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.5 Hz, 1 H, H2), 6.87 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.7 Hz, 1 H, H7), 6.64 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, H8), 6.26 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, H4–H6), 4.54 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, C*H*), 3.48 (m, 4 H, thf), 1.76 (s, 9 H, *t*Bu), 1.49 (m, 4 H, thf), 0.65 (d, $^3J_{HH}$ = 6.6 Hz, Me) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ = 142.5 (C1); 137.9 (C3); 130.7 (C5); 129.2 (C7); 125.8 (C9); 120.2 (C2); 117.5 (C8); 102.2, 102.1 (C4–C6); 154.2, 138.6, 135.3, 131.6, 122.3, 102.2 (non H-bonded aromatic carbon atoms); 69.6 (thf); 59.7 (CH); 34.0 (quaternary *t*Bu); 32.5 (*t*Bu); 22.3 (thf); 20.2 (Me) ppm. $C_{50}H_{60}Br_2Cl_2Mg_4N_4O_4$ (1108.97): calcd. C 54.1, H 5.45, N 5.05; found 53.9, H 5.50, N 4.90. Crystal data: formula $C_{50}H_{60}Br_2Cl_2Mg_4N_4O_4$; *M* = 1108.98; System = Orthorhombic; Space group = *Fdd2*; Space group number = 43; *a* = 26.4038(7) Å; *b* = 38.9380(13) Å; *c* = 10.1479(2) Å; *U* = 10433.2(5) Å^3; *Z* = 8; D_c = 1.412 g cm^{-3}; μ = 17.51 cm^{-1}; *T* = 120 K; θ(min–max) = 3.26–27.50°; Measured reflns = 18770; Unique reflns = 3136; R_{int} = 0.061; Obs. reflns [$I > 2\sigma(I)$] = 2723; *R* (Obs. reflns) = 0.0672; R_W (all reflns) = 0.2054; *GOF* = 1.109; No. variables = 317; Flack parameter = 0.09(2); $\Delta\rho_{max}$ = 0.655 e Å^{-3}; $\Delta\rho_{min}$ = –1.019 e Å^{-3}.

[Y(CH$_2$SiMe$_3$)(NN(CH$_2$SiMe$_3$)O)(thf)] (3): To a stirred solution of Y(CH$_2$SiMe$_3$)$_3$·2thf (1.147 g, 2.32 mmol) in toluene (70 mL) at room temperature was very slowly added a solution of NNO^{H}-H

(0.706 g, 2.32 mmol) in toluene (30 mL). The time required for the addition of the ligand solution was about 30 min. The resulting dark-red reaction mixture was allowed to react at room temperature for 2 h, then the solvent was reduced to about 15 mL by evaporation at reduced pressure. Slow addition of *n*-hexane (about 100 mL) allowed a red solid to separate, which was filtered. The crude product was purified by cooling a toluene/*n*-hexane saturated solution at –25 °C. Yield after purification > 40%. Refer to Scheme 4 for numbering scheme. ^{1}H NMR (C_6D_6, 298 K): δ = 7.66 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H1), 7.50 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H3), 7.49 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H9), 7.04 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, H2), 6.94 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H5), 6.64 (dd, $^3J_{HH}$ = 4.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, H7), 6.63 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.4 Hz, 1 H, H8), 6.40 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, H6), 6.30 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, H4), 4.54 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 10.0 Hz, 1 H, N-C*H*-CH_2SiMe_3), 3.74 (br. m, 4 H, thf), 1.80 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 10.0 Hz, 1 H, N-CH-CH_2SiMe$_3$), 1.60 (s, 9 H, *t*Bu), 1.42 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, N-CH-CH_2SiMe$_3$), 1.40 (br. m, 4 H, thf), 0.20 (d, $^2J_{YH}$ = 2.7 Hz, 2 H, Y-CH_2), 0.08 (s, 18 H, SiMe_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 143.3 (C7); 136.0 (C9); 130.5 (C1); 129.3 (C5); 124.8 (C3); 119.2 (C8); 115.0 (C2); 105.2 (C4); 104.4 (C6); 163.2, 156.7, 142.3, 137.7, 136.9, 128.8 (non H-bonded aromatic carbon atoms); 68.2 (thf); 61.4 (N-CH-CH_2SiMe_3); 34.1 (quaternary *t*Bu); 31.2 (N-CH-CH_2SiMe_3); 30.4 (*t*Bu); 24.5 (thf); –1.8 (slightly br.; Y-CH_2 + $SiMe_3$) ppm. MS (EI, 70 eV): *m*/*z* = 536 $[M - 2Me]^{+}$. $C_{32}H_{49}N_2O_2Si_2Y$ (638.82): calcd. C 60.2, H 7.73, N 4.39; found C 60.3, H 7.65, N 4.50.

CCDC-687376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected 1D and 2D ^{1}H NMR spectra.

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[1] For some references, see: a) F. T. Edelmann in *Comprehensive Organometallic Chemistry III* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2007**, vol. 4, pp. 1–190; b) M. E. Thompson, J. E. Berkaw, *Pure Appl. Chem.* **1984**, *56*, 1–11; c) W. E. Piers, D. J. H. Emsile, *Coord. Chem. Rev.* **2002**, *233*, 131–155; d) P. Mountford, B. D. Ward, *Chem. Commun.* **2003**, 1797–1803 (review); e) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404–2433; f) S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953–1976; g) P. M. Zeimentz, J. Okuda, *Organometallics* **2007**, *26*, 6388–6396.

[2] For some references, see: a) S. Arndt, K. Beckerle, P. M. Zeimentz, T. P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* **2005**, *44*, 7473–7477; b) B. D. Ward, S. Bellemain-Laponnaz, L. H. Gade, *Angew. Chem. Int. Ed.* **2005**, *44*, 1668–1671; c) C. S. Tredget, F. Bonnet, A. R. Cowley, P. Mountford, *Chem. Commun.* **2005**, 3301–3303; d) S. Arndt, T. P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* **2003**, *42*, 5075–5079; e) D. P. Long, P. A. Baconi, *J. Am. Chem. Soc.* **1996**, *118*, 12453–12454; f) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* **1999**, *38*, 227–230; g) S. Arndt, J. Okuda, *Adv. Synth. Catal.* **2005**, *347*, 339–354; h) Z. Hou, Y. Luo, X. Li, *J. Organomet. Chem.* **2006**, *691*, 3114–3121.

[3] a) D. J. H. Emslie, W. E. Piers, R. MacDonald, *J. Chem. Soc., Dalton Trans.* **2002**, 293–294; b) D. J. H. Emsile, W. E. Piers, M. Parvez, R. MacDonald, *Organometallics* **2002**, *21*, 4226–4240; c) D. J. H. Emslie, W. E. Piers, M. Parvez, *Dalton Trans.* **2003**, 2615–2620; d) A. Lara-Sanchez, A. Rodriguez, D. L. Hughes, M. Schormann, M. Bochmann, *J. Organomet. Chem.* **2002**, *663*, 63–69; e) P. Blech, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc., Dalton Trans.* **1990**, 3557–3561.

[4] a) M. Calligario, L. Randaccio in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, vol. 2, ch. 20.1, pp. 715–738; b) X. Zhou, M. Zhu, *J. Organomet. Chem.* **2002**, *647*, 28–49; reviewc) Y. Obora, T. Ohta, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 3745–3755; d) C. Qian, T. Huang, *J. Organomet. Chem.* **1997**, *548*, 143–147; e) C. Floriani, *Polyhedron* **1989**, *8*, 1717–1722; f) B. Li, Y. Wang, Y. Zhang, Q. Shen, *Inorg. Chem. Commun.* **2008**, *11*, 349–352.

[5] G. Paolucci, A. Zanella, M. Bortoluzzi, S. Sostero, P. Longo, M. Napoli, *J. Mol. Catal. A* **2007**, *272*, 258–264.

[6] G. Paolucci, A. Zanella, L. Sperni, V. Bertolasi, M. Mazzeo, C. Pellecchia, *J. Mol. Catal. A* **2006**, *258*, 275–283.

[7] G. Paolucci, M. Bortoluzzi, P. Longo, M. Napoli, *J. Mol. Cat. A: Chemical* **2008**, *287*, 121–127.

[8] a) R. C. Elderfield, W. J. Gensler, T. H. Bembry, T. A. Williamson, H. Weisl, *J. Am. Chem. Soc.* **1946**, *68*, 1589–1591; b) R. C. Elderfield, W. J. Gensler, T. A. Williamson, J. M. Griffing, S. M. Kupchan, J. T. Maynard, F. J. Kreysa, J. B. Wright, *J. Am. Chem. Soc.* **1946**, *68*, 1584–1587.

[9] M. N. Burnett, C. K. Johnson, *ORTEP-III: Oak Ridge Thermal Ellipsoids Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, TN, **1996**.

[10] K. C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228–243.

[11] a) G. Balacco, *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235; b) J. C. Cobas Gómez, F. J. Sardina López, *MesRe-C*, Universidad de Santiago de Compostela, Spain, **2006**.

[12] Z. Otwinowski, Z. Minor in *Methods in Enzymology* (Eds.: C. W. Carter, R. M. Sweet), Academic, London, **1977**, vol. 276, part A, pp. 307–326.

[13] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

[14] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[15] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

[16] G. M. Sheldrick, *SHELXL97: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

[17] M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659.

[18] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[19] J. J. P. Stewart, *MOPAC2007* (version 7.295W), Stewart Computational Chemistry; http://openmopac.net.

[20] J. J. P. Stewart, *J. Mol. Mod.* **2007**, *13*, 1173–1213.

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