



HAL
open science

Exploring the Chemistry of Ruthenium Complexes with a Bidentate Barbiturate-Imidazo[1,5-a]pyridinylidene Ligand

Pawel Krzesiński, Katarzyna Gajda, Laure Vendier, Anna Kajetanowicz, Karol Grela, Stéphanie Bastin, Vincent César

► **To cite this version:**

Pawel Krzesiński, Katarzyna Gajda, Laure Vendier, Anna Kajetanowicz, Karol Grela, et al.. Exploring the Chemistry of Ruthenium Complexes with a Bidentate Barbiturate-Imidazo[1,5-a]pyridinylidene Ligand. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2024, pp.e202400199. 10.1002/zaac.202400199 . hal-04785126

HAL Id: hal-04785126

<https://hal.science/hal-04785126v1>

Submitted on 15 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Exploring the Chemistry of Ruthenium Complexes with a Bidentate Barbiturate-Imidazo[1,5-*a*]pyridinylidene Ligand

Paweł Krzesiński,^[a,b] Katarzyna Gajda,^[a,b] Laure Vendier,^[a] Anna Kajetanowicz,^{*,[b]} Karol Grela,^{*,[b]} Stéphanie Bastin,^{*,[a]} Vincent César^{*,[a]}

[a] Dr. P. Krzesiński, K. Gajda, Dr. L. Vendier, Dr. S. Bastin, Dr. V. César
LCC-CNRS
Université de Toulouse, CNRS, UPS
205 route de Narbonne, 31077 Toulouse cedex 4, France
E-mail: stephanie.bastin@lcc-toulouse.fr
vincent.cesar@lcc-toulouse.fr

[b] Dr. P. Krzesiński, K. Gajda, Dr. A. Kajetanowicz, Prof. K. Grela
Biological and Chemical Research Centre, Faculty of Chemistry
University of Warsaw
Żwirki i Wigury 101
02-089 Warsaw, Poland
E-mail: a.kajetanowicz@uw.edu.pl
klgre@uw.edu.pl

Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate.))

Abstract:

A novel reactivity of 5-barbiturate imidazo[1,5-*a*]pyridinium 1·H with [Ru(2-methylallyl)₂(COD)] was explored which led to the formation of an uncommon, zwitterionic complex [Ru(1')(1·H)], composed of the NHC ligand 1', cyclometallated at one *ortho*-methyl position of the N-mesityl substituent, and the zwitterionic precursor 1·H. Barbiturate moieties coordinate either through a η³ mode or through coordination of the anionic oxygen atom to ensure the coordination saturation and stability to the complex. The addition of pivalic acid results in the protonolysis of the Ru-C_{alkyl} bond and demetallation of the N-mesityl, while triphenylphosphine and pyridine are able to displace the rather labile 1·H ligand. Attempts to incorporate an alkylidene fragment from these complexes led to the isolation of a rare complex **7** bearing an alkylidene tethered to a η⁵-cyclopentadienyl ligand formed by phenylacetylene tetramerization.

Introduction

N-Heterocyclic Carbenes (NHCs) have been established as powerful and versatile carbon-donor ligands in modern chemical sciences^[1] with numerous applications in molecular chemistry^[2] and catalysis^[3] as well as in material science.^[4] Owing to the synthetic flexibility towards their azolium precursors,^[5] NHCs have become key unit components in the design of tailor-made ligand systems.

Over the last two decades, ruthenium-based olefin metathesis has especially benefited from the advent of NHC ligands, as their

introduction in the second generation of olefin metathesis pre-catalysts impart better stability, activity and a broader reaction generality compared to the phosphine-based first generation of pre-catalysts.^[6] As a consequence, the scope of olefin metathesis has been considerably extended, establishing it as a leading synthetic methodology in organic synthesis.^[7] In 2011, Grubbs and co-workers disclosed the first efficient *Z*-selective Ru-based olefin metathesis catalyst **A**, in which the *Z*-selectivity was imparted by the combination of a chelating (*C,C*)-cyclometalated *N*-(1-adamantyl)-NHC and of a pivalate both acting as bidentate LX-type ligands (Figure 1).^[8] The same group further investigated the effect of the *N*-chelating group on the stability and efficiency of the catalysts and concluded that 1-adamantyl substituent was the optimal choice.^{[9],[10]}

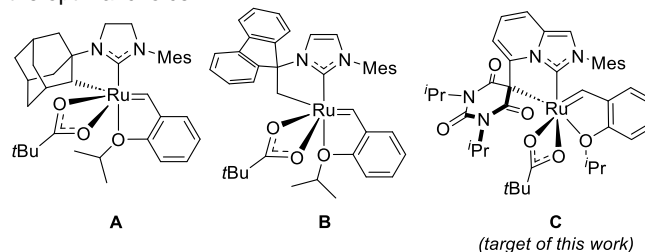


Figure 1. Ruthenium alkylidene complexes bearing a chelating LX-type C(sp³)-NHC ligand. Mes = 2,4,6-trimethylphenyl.

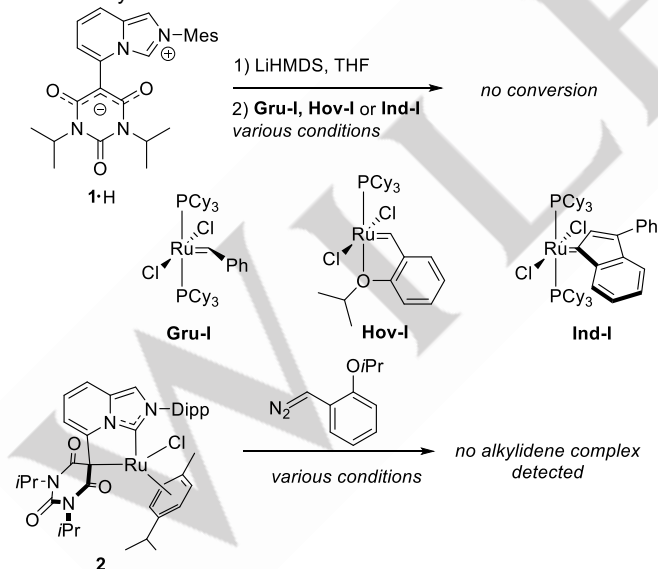
We also recently reported the *Z*-selective olefin metathesis catalyst **B**, based on a cyclometalated *N*-(9-methylfluorenyl)NHC, which led to good *Z/E* stereoselectivity but appeared quite fragile (Figure 1).^[11] The *Z*-selective (*C,C*)-cyclometalated NHC catalysts described so far in the literature suffer from great sensitivity and

RESEARCH ARTICLE

fragility, most probably arising from the presence of a non-stabilized alkyl ligand. We thus reasoned that replacing the non-stabilized alkyl moiety with a more stabilized C(sp³) ligand in the chelating NHC ligand would afford better stability and hence generality to the catalyst. We thus devised to access the alkylidene complex of type **C**, bearing a chelating 5-barbiturate-imidazo[1,5-a]pyridinylidene (Barb-ImPy) ligand, which was shown to stabilize several d⁶ and d⁸ transition metal centers.^[12] We report herein our progress towards the synthesis of an alkylidene ruthenium complex supported by the anionic Barb-ImPy ligand.

Results and Discussion

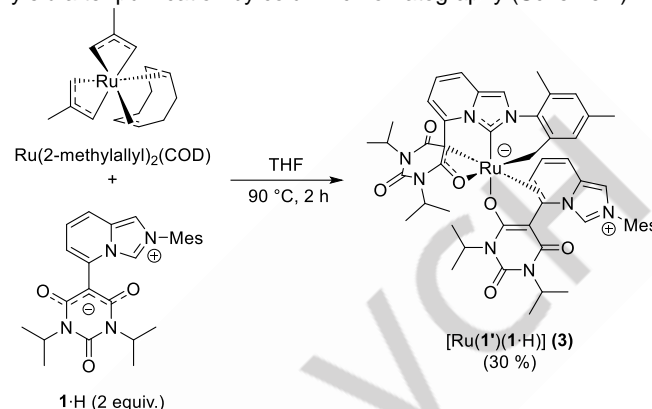
We first investigated the possibility of displacing the PCy₃ ligand in Grubbs first generation **Gru-I**, Grubbs-Hoveyda **Hov-I** and indenylidene **Ind-I** complexes by the *in situ* generated anionic NHC [1]Li (Scheme 1). This strategy is the most classical method to introduce an NHC ligand on Ru-based metathesis catalysts. Disappointingly, we did not observe any conversion, even by varying the reaction conditions. Therefore, we first envisaged to coordinate the NHC ligand 1⁻ onto ruthenium and to install the alkylidene group in a subsequent reaction. Fogg and co-workers reported that the second-generation Hoveyda catalyst **Hov-II** could be obtained by a reaction between the *p*-cymene complex [RuCl₂(SIMes)(*p*-Cym)] and the diazo compound ArCHN₂ (Ar = *o*-C₆H₄-O*i*Pr).^[13] Hence, complex **2**, previously synthesized by our groups,^[12] was reacted with the same diazo compound but no conversion of **2** nor formation of a benzylidene complex could be detected by ¹H NMR.



Scheme 1. First attempts to synthesize an alkylidene ImPy-ruthenium complex.

From the increased stability of **2** when compared with RuCl₂(SIMes)(*p*-Cym), we hypothesized that the lack of reactivity might stem from a reduced lability of the *p*-cymene ligand and devised to coordinate ligand 1⁻ on a ruthenium complex with more labile ligands. Towards this task, we chose the commercially

available complex [Ru(2-methylallyl)₂(COD)] as the precursor, which was previously shown by Glorius and coworkers to react readily with imidazolium precursors to generate highly efficient hydrogenation catalysts.^[14] Gratifyingly, the reaction of 2 equivalents of **1-H** with [Ru(2-methylallyl)₂(COD)] in THF at 90 °C for 2 hours led to the isolation of the zwitterionic complex **3** in 30% yield after purification by column chromatography (Scheme 2).^[15]



Scheme 2. Synthesis of the zwitterionic complex **3**.

Complex **3** was fully characterized by spectroscopic and analytical techniques and its molecular structure was firmly established by an X-Ray diffraction experiment (Figure 2).

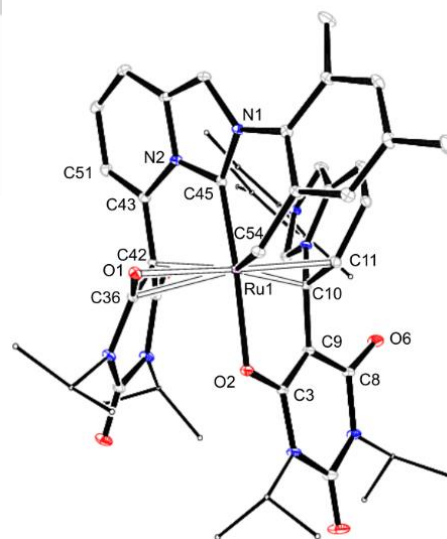


Figure 2. Molecular structure of complex **3** (ellipsoids drawn at 30% probability level). Solvent and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1-C45 1.928(2), Ru1-C54 2.088(2), Ru1-O1 2.2349(17), Ru1-C36 2.380(2), Ru1-C42 2.488, Ru1-O2 2.1833(17), Ru1-C10 2.103(2), Ru1-C11 2.157, C10-C11 1.436(3), C43-C51 1.355(4), C45-Ru1-C54 83.93(10), C45-Ru1-O1 83.48(8), C54-Ru1-O1 86.43(8), C54-Ru1-O2 94.39(8).

Complex **3** exhibits a distorted octahedral coordination geometry, in which the ruthenium center is surrounded by two molecules derived from the zwitterionic precursor **1-H**. The first one is the cyclometalated NHC ligand 1', in which the imidazolium position and one of the *ortho*-methyl groups of the *N*-mesityl substituent were deprotonated by the 2-methylallyl ligands of [Ru(2-

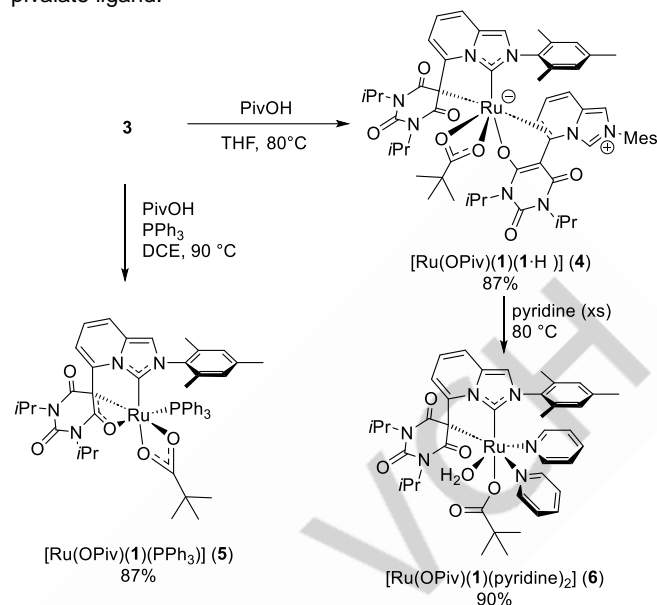
RESEARCH ARTICLE

methylallyl)₂(COD)], which served as internal bases. The Ru1-C45 [1.928(2) Å] and Ru1-C54 [2.088(2) Å] bond lengths are within the typical range for Ru-C_{NHC} and Ru-C_{alkyl} bond lengths respectively, the Ru1-C45 bond being relatively short due to the constrained geometry of ligand **1'**. Interestingly, while in our previous work the barbiturate moiety in (Barb-ImPy) ligands was reported to coordinate metal centers only in a η^1 fashion through the central malonate carbon atom,^[12] the barbiturate moiety of the cyclometalated ligand **1** was found to coordinate the ruthenium center in a distorted η^3 coordination mode [Ru1-O1 2.2349(17) Å, Ru1-C36 2.380(2) Å, Ru1-C42 2.488 Å]. In addition, the pyramidalization of the central malonate carbon ($\Sigma_{\alpha}C42 = 353.38^\circ$) is significantly lower than in the previously reported complex **2**, in which the bidentate ligand **1** exhibits a η^1 coordination of the barbituric malonate ($\Sigma_{\alpha}C_{\text{malo}} = 336.1^\circ$). Ligand **1'** could thus be viewed as a tetradentate ligand with the NHC moiety as the central unit. This could explain the relatively low yaw angle $\theta^{[16]}$ [$\theta = 7.67^\circ$] relative to the values measured previously for bidentate ligand **1** [$\theta = 11\text{--}14^\circ$].^[12] Rather than retaining the cyclooctadiene (COD) ligand, the ruthenium center was stabilized by the coordination of a molecule of zwitterionic precursor **1·H**, which acts as a second bidentate ligand, by coordination of an oxygen atom of the barbiturate moiety [Ru1-O2 2.1833(17) Å] and, more surprisingly, by π -coordination of the C10-C11 double bond [Ru1-C10 2.103(2) Å, Ru1-C11 2.157 Å], which was previously involved in the aromatic system of the imidazopyridinium core. This coordination induced a significant pyramidalization of carbon C10 ($\Sigma_{\alpha}C10 = 336.1^\circ$) and a strong elongation of the C=C bond [C10-C11 1.436(3) Å] relative to the aromatic imidazopyridinium precursor **1·H** [1.361(2) Å]^[17] or NHC **1** [for example C43-C51 1.355(4) Å].

The NMR spectra were consistent with the formulation and *C*₁-symmetry of complex **3**. The chemical shift of the coordinated carbene atom was observed in the typical range of Ru-NHC complexes at δ_{C} 182.2 ppm. The cyclometallation was confirmed by the presence of an AB system at δ_{H} 4.93 and 4.12 ppm ($^1J_{\text{HH}} = 5.9$ Hz) corresponding to the diastereotopic *CH*₂ protons of the cyclometalated mesityl ligand and by the resonance at δ_{C} 24.1 ppm in the ¹³C{¹H} NMR spectrum. Likewise, the coordination of the C₅-C₆ double bond of **1·H** (C10-C11 in the crystal structure) was testified by a strongly-shielded doublet at δ_{H} 2.99 ppm corresponding to the C₆-H proton and by upfield-shifted signals at δ_{C} 77.5 and 51.8 ppm corresponding to the quaternary C₅ and C₆-H carbon atoms respectively. Eventually, the two doublets at δ_{H} 8.38 and 6.35 ppm ($^4J_{\text{HH}} = 1.6$ Hz) were characteristic of the imidazolium ring in ligand **1·H**.

While complex **3** constituted an interesting entry for further derivatization, the cyclometallation of the mesityl group in ligand **1'** could be a problem and we thus turned our attention to a protonolysis protocol of this Ru-C_{alkyl} bond. A clean reaction occurred when reacting complex **3** with 2 equivalents of pivalic acid in THF to give **4** as a red complex in 87 % yield (Scheme 3). The formation of **4** was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy, where the release of a free *N*-mesityl group was indicated by the disappearance of the characteristic signals of the Ru-CH₂ group of **3** and the simultaneous emergence of a singlet

signal at δ_{H} 0.88 ppm corresponding to the *tert*-butyl group of the pivalate ligand.



Scheme 3. Synthesis of ruthenium complexes 4-6.

The molecular structure of **4** was firmly established by a single-crystal X-Ray diffraction experiment (Figure 3 and Table 1). Complex **4** exhibits a distorted octahedral geometry and is best described as a zwitterionic complex, with three bidentate ligands surrounding the ruthenium center, namely the pivalate, the precursor **1·H** and NHC **1**. While the coordination parameters of the precursor **1·H** were similar to the ones observed previously in complex **3**, the coordination mode of the barbiturate moiety of ligand **1** changed from η^3 in **3** to a more classical η^1 mode, which was characterized by a shorter Ru-C_{malo} bond distance [Ru1-C32 2.2392(15) Å in **4**, Ru1-C42 2.488 Å in **3**], a higher sp³-hybridization of C_{malo} reflected by a high degree of pyramidalization [$\Sigma_{\alpha}C32 = 338.68^\circ$], and by a bite angle [C39-Ru1-C32 79.79(6) $^\circ$] closely fitting with those of the previously reported series.^[12] As a consequence of the freeing of the *N*-mesityl arm, the Ru-C_{NHC} was elongated [Ru1-C39 2.0243(15) Å] and the yaw angle was significantly increased to 15.15 $^\circ$, which is the highest value of the series.

The imidazopyridinium ligand **1·H** could also be displaced when PPh₃ was added to pivalic acid during the protonolysis reaction. This clean reaction led to complex **5** as a yellow-orange solid in 87% yield (Scheme 3), which was fully characterized by spectroscopic and analytical techniques. In particular, the coordination of PPh₃ was inferred from the ³¹P{¹H} NMR spectrum, where a singlet signal was observed at δ_{P} 67.2 ppm. The crystal structure of **5** indicated a distorted octahedral coordination geometry (Figure 3, Table 1), in which the PPh₃ ligand is in *cis* position relative to the NHC ligand, most probably due to steric repulsion between the phosphine ligand and the lateral barbituric heterocycle of **1**. Not affected by the strong *trans* influence of NHC ligands, the Ru1-P1 bond length of 2.2485(7) Å is significantly shorter than in other NHC/PPh₃ ruthenium complexes (range: 2.28-2.48 Å).^[19] Noteworthy, the barbiturate heterocycle remained η^3 -coordinated in order to stabilize the coordination sphere and to get a saturated 18e⁻ complex.

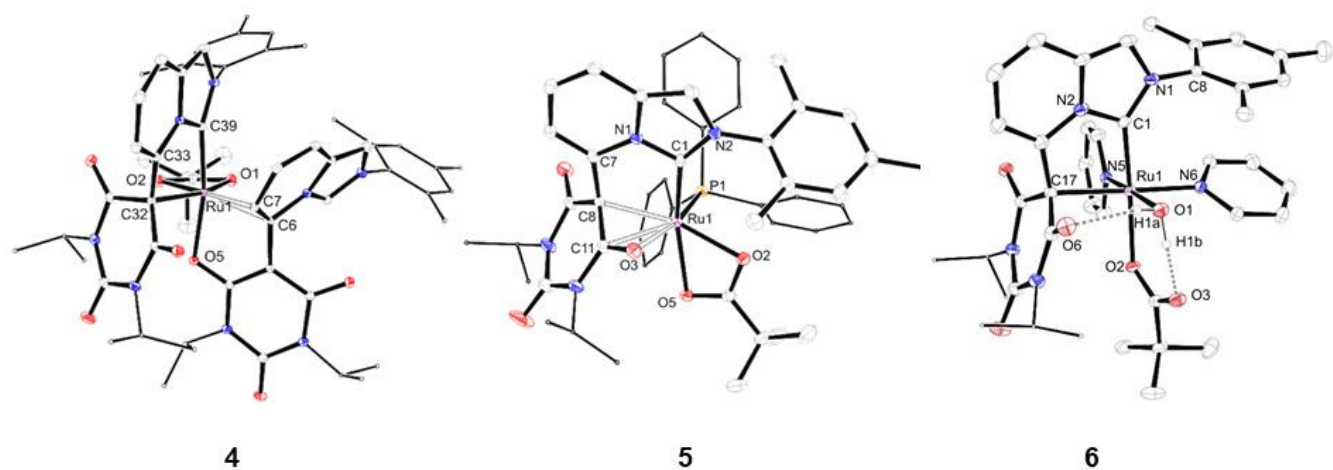


Figure 3. Molecular structures of complexes **4** (left), **5** (center), **6** (right). Ellipsoids drawn at 30% probability level. Hydrogen atoms (except the two of the water molecule ligand in **6**) have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg) for complexes **4-6**.

	4	5^l	6
Ru1-C39	2.0243(15)	Ru1-C1	1.987(3)
Ru1-C32	2.2392(15)	Ru1-C8	2.222(3)
Ru1-C6	2.1200(15)	Ru1-C11	2.262(3)
Ru1-C7	2.2280(15)	Ru1-O3	2.2443(19)
Ru1-O1	2.1430(11)	Ru1-O2	2.1279(19)
Ru1-O2	2.1561(11)	Ru1-O5	2.2315(19)
Ru1-O5	2.1402(11)	Ru1-P1	2.2485(7)
C6-C7	1.414(2)		
C39-Ru1-C32	79.79(6)	C1-Ru1-C8	79.51(10)
O1-Ru1-O2	60.90(4)	O2-Ru1-O5	60.00(7)
Yaw angle θ^a	15.15	Yaw angle θ^a	11.46
$\Sigma_{\alpha}C32$	338.68	$\Sigma_{\alpha}C8$	346.19
		$\Sigma_{\alpha}C17$	341.25

^a $\theta = [(N_{Im}-C_{NHC}-Ru)-(N_{Py}-C_{NHC}-Ru)]/2$

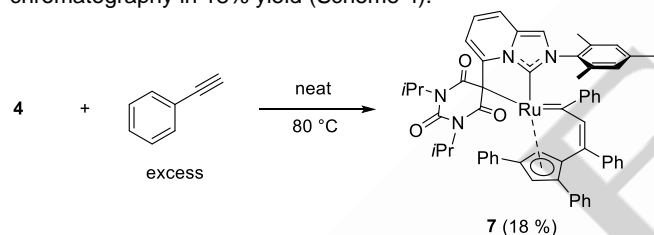
We then attempted the installation of pyridine ligands in the hope of having labile ligands suitable for the introduction of an alkylidene ligand. Hence, complex **4** was reacted with neat pyridine at 80 °C and cleanly gave the pyridine complex **6** in 90% as a brown solid after purification by column chromatography. Although complex **6** was stable when stored in a protective atmosphere, the column chromatography had to be performed with dried and degassed solvents to avoid a rapid decomposition of **6** on silica gel. From the integration of signals in the aromatic region of the 1H NMR spectrum and the number of aromatic signals in $^{13}C\{^1H\}$ NMR, it was deduced that complex **6** contained two molecules of pyridine, which replaced the imidazopyridinium ligand **1-H**. Interestingly, the crystal structure of complex **6**

revealed a monodentate pivalate ligand and the presence of an additional water molecule as the sixth ligand (Figure 3, Table 1), which both stabilized the structure due to *i*) the formation of a nearly perfect octahedral geometry around ruthenium center and *ii*) the generation of two hydrogen bonds between the water protons and oxygen atoms of pivalate (H1b-O3) and barbiturate (H1a-O6). The water molecule was most probably trapped by complex **6** during the work-up and purification through silica gel chromatography, even though dry solvents were used. The barbiturate moiety of **1** showed a η^1 coordination mode with characteristics similar to complex **4** and the other complexes of the series previously reported.^[12] Noteworthy, the *N*-mesityl group is bent out of the ImPy core plane with a torsion angle Ru1-C1-

RESEARCH ARTICLE

N1-C8 of 17.45°, which may be the consequence of the π - π stacking interaction between the *N*-mesityl group and the pyridine ligand below that forces both rings to be parallelly displaced to match their partial charges for attractive electrostatic interaction. The π - π interaction could be evidenced by a nearly planar alignment of the two rings (intersection angle of the two planes of 8.65°) and a small centroids distance of 3.570 Å.^[20]

Having in hand the three ruthenium complexes **4-6** supported by the targeted bidentate ligand **1**, we then studied the introduction of an alkylidene ligand, by first using the diazo compound ArCHN₂ (Ar = *o*-C₆H₄-O*i*Pr), which is the historical method.^[21] Despite the various reaction conditions tested, no reaction was observed and the starting complexes remained unchanged. Even the very promising pyridine complex **6** exhibited no reactivity at all. Another efficient protocol to install an indenylidene ligand is the reaction with 1,1-diphenylpropargyl alcohol through the intermediacy of an allenylidene complex.^[22] In this case, the reaction between complexes **4-6** and 1,1-diphenylpropargyl alcohol at 80 °C led to some reactivity but only intractable mixtures were obtained and no defined product could be isolated. Finally, we turned our attention to phenylacetylene as an alkylidene precursor, since it would give access to Ru-vinylidene complexes.^[23] Similarly to the reaction with propargyl alcohol, complex mixtures were obtained but in the reaction of complex **4** with an excess of phenylacetylene, we were able to isolate complex **7** as the major product by column chromatography in 18% yield (Scheme 4).^[24]



Scheme 4. Reaction between **4** and phenylacetylene

The installation of an alkylidene ligand was inferred from the ¹³C{¹H} NMR spectrum by the presence of a highly deshielded signal at δ_c 282.7 ppm. We could also deduce from the NMR spectra that one bidentate ligand **1** is present in complex **7**, as well as four units of phenylacetylene by integration of the aromatic signals in the ¹H NMR spectrum. This was confirmed by mass spectrometry (ESI-mode) with the observation of a single peak at $m/z = 954.3$ u.a. corresponding to the molecular mass. The complete structure of complex **7** was unambiguously established through an X-ray diffraction experiment on single crystals of **7** (Figure 4). Actually, a tetramerization of phenylacetylene occurred producing a η^5 -coordinated cyclopentadienyl ligand tethered to the alkylidene moiety through an alkenyl bridge. The 18e⁻ saturated complex **7** thus featured a piano-stool coordination geometry. Ligand **1** is bidentate with a classical η^1 barbiturate moiety and exhibits characteristics similar to the ones in corresponding complexes.^[12] The Ru1-C14 bond length of 1.964(7) Å appeared longer as standard Ru-C_{alkylidene} bonds in metathesis pre-catalysts [range = 1.81-1.86 Å],^[6a] most probably due to the conjugation within the tether C14-C4AA-C12 and some steric hindrance.

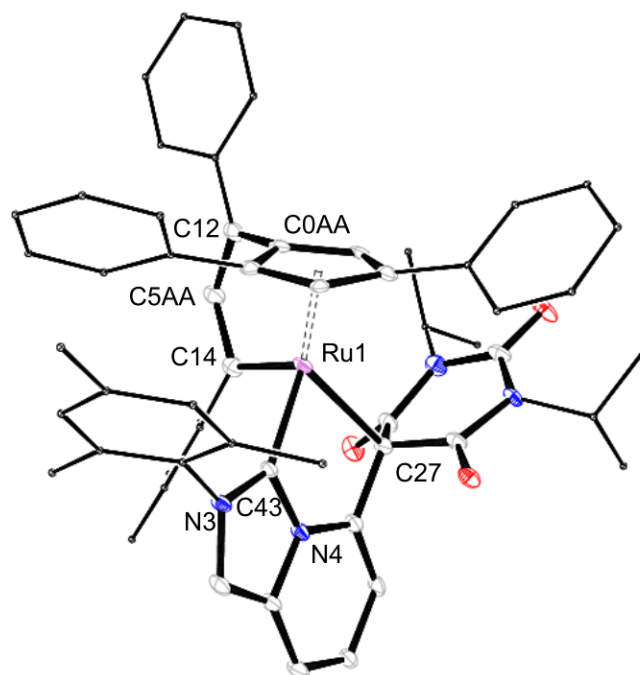
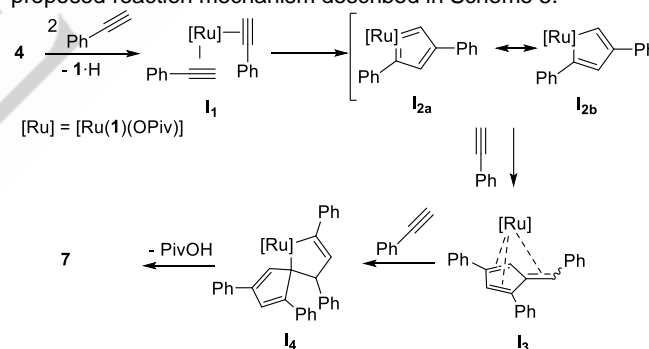


Figure 4. Molecular structure of complex **7** (ellipsoids drawn at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1-C14 1.964(7), Ru1-C43 2.049(7), Ru1-C27 2.260(6), C14-C5AA 1.443(10), C5AA-C12 1.358(10), C12-C0AA 1.483(11), C43-Ru1-C27 77.8(2), Σ_i C27 334.68.

The formation of complex **7** could be rationalized through the proposed reaction mechanism described in Scheme 5.



Scheme 5. Proposed mechanism for the formation of complex **7**.

The first step is thought to proceed by substitution of the relative labile imidazopyridinium precursor **1-H** by two molecules of phenylacetylene to give the bis-acetylene intermediate **I₁**. A subsequent oxidative coupling of the two acetylene ligands would generate the intermediate **I₂**, which could be represented as a metallacyclopentatriene **I_{2a}** or a metallacyclopentadiene **I_{2b}**. As the real structure depends on the nature of the metal and of the ligand framework, it was not possible here to discriminate between the two limiting forms for **I₂**. Intermediates of type **I₂** are well-known in literature and constitute key intermediates for C-C coupling reactions of alkynes.^{[25],[26]} A third molecule of phenylacetylene would then enter into the coordination sphere to lead to the fulvene complex **I₃** through a rare but documented

[2+2+1]-cyclootrimerization reaction.^[27] A second oxidative cyclization between a fourth molecule of phenylacetylene and the exocyclic alkene function of the fulvene ligand would give access to complex **4**. Upon release of pivalic acid and change of hapticity of the Cp-type ligand, complex **4** would interconvert into the final, thermodynamically favored final complex **7**.

Despite the presence of an alkylidene moiety in **7**, no conversion at all was observed when **7** was engaged as a pre-catalyst in the ring-closing metathesis reaction of diethyl diallylmalonate substrate. This could be easily explained by the strong bonding of the tethered Cp-alkylidene ligand in **7**, which precludes any vacant coordination site from coordinating an incoming alkene. As a final alternative, based on the work of Mauduit and co-workers reporting that it is possible to generate *in situ* a Ru-alkylidene complex for the metathesis reaction,^[28] we tested this possibility with phenylacetylene as activator, but met with no further success.

Conclusion

With the ultimate goal to synthesize a Ru-alkylidene complex supported by the LX-type, bidentate barbiturate-imidazopyridinylidene ligand **1**, we have reported a series of complexes whose starting point is the reaction of the zwitterionic precursor **1**·H with [Ru(2-methylallyl)₂(COD)]. Although the quest for a ruthenium complex bearing ligand **1** active in olefin metathesis remains unchallenged, some interesting reactivities and features have been unveiled such as: *i*) the cyclometalation of one *ortho*-methyl position of the *N*-mesityl substituent, *ii*) the clean protonolysis of the corresponding Ru-C_{alkyl} bond with pivalic acid, *iii*) the unexpected coordination of the zwitterionic precursor **1**·H to ruthenium, and *iv*) the high flexibility of the coordination of the malonate moiety of the lateral barbiturate group (κ -C, κ -O, or η^3 modes), which allows the ligand to adapt to the needs of the coordination sphere.

Experimental Section

General Comments

All manipulations were carried out in dry glassware under a nitrogen atmosphere using standard vacuum line and Schlenk techniques or in an MBraun glovebox under an argon atmosphere. Phenyl acetylene was purified by column chromatography using pentane as eluant, degassed by three freeze/pump/thaw cycles and stored under N₂ over activated 4 Å molecular sieves at -20 °C. 5-bromo-2-mesitylimidazo[1,5-*a*]pyridinium bromide,^[29] *N,N*-diisopropyl barbituric acid,^[17] complex **2**,^[12] N₂CH(*o*-(*O*Pr)Ph),^[30] and diethyl diallylmalonate^[31] were prepared according to literature procedures. All other reagents were commercially available and used without further purification unless otherwise stated. Dry and oxygen-free organic solvents (THF, Et₂O, CH₂Cl₂, toluene) were obtained using a LabSolv (Innovative Technology) purification system. Dry DCE and pyridine were freeze/pump/thaw degassed and stored under Ar over activated 4 Å molecular sieves for at least 12 h prior to use. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Agilent Mercury 400 MHz, Bruker Avance 400 MHz, Avance III HD 400 MHz, or Avance 300 MHz spectrometers. Chemical shifts (δ) are given in ppm and referred to residual solvent signals.^[32] Coupling constants (*J*) are reported in hertz (Hz). Mass spectra (ESI mode) were obtained using a Xevo G2 QTof (Waters) spectrometer and were performed by the mass spectrometry service of the "Institut de chimie de Toulouse". High-resolution

electrospray mass spectra (ESI-HRMS) were recorded on a Quattro LC triple quadrupole mass spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. The obtained data were processed with the software Omnic32. Wavenumbers are given in cm⁻¹. Elemental analysis was performed by Elementary Analysis Laboratory of Organic Chemistry Institute of Polish Academy of Sciences (Warsaw) using UNICube, Elementar analyzer.

Synthesis of zwitterionic precursor **1**·H

NaH (245 mg, 60% in mineral oil, 6.12 mmol, 2.2 equiv.) was slowly added to a solution of *N,N*-diisopropylbarbituric acid (1.3 g, 6.12 mmol, 2.2 equiv.) in DMF (7 mL) at room temperature, and the reaction mixture was stirred for 20 min. 5-bromo-2-mesitylimidazo[1,5-*a*]pyridinium bromide (1.0 g, 2.78 mmol) was added as a solid and the reaction mixture was stirred at 70 °C overnight. All volatiles were evaporated under vacuum and the crude mixture was dissolved in CH₂Cl₂ (50 mL) and washed with water (3 x 50 mL) and brine (50 mL), dried over Mg₂SO₄, filtered and concentrated *in vacuo*. The solid residue was washed with Et₂O to remove almost all unreacted materials and was purified through column chromatography (SiO₂, hexane/EtOAc: 4/1 then DCM/MeOH: 95/5) to give a yellow solid (1.035 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ = 8.32 (dd, *J* = 1.9, 0.7 Hz, 1H, N₂CH), 7.47-7.32 (m, 4H, CHAr), 7.07 (s, 2H, CHMes), 5.24 (hept, *J* = 6.8 Hz, 2H, CH(CH₃)₂), 2.39 (s, 3H, CH₃ Mes para), 2.10 (s, 6H, CH₃ Mes ortho), 1.48 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂) ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 162.6, 152.5, 141.4, 135.9, 134.6, 131.9, 131.8 (C_{Ar}), 129.8 (CHMes), 127.4 (CH Py), 126.6 (N₂CH), 119.9 (CH Py), 111.9 (CH Py), 110.6 (CH Im), 83.3 (C(CO)₂), 44.5 (CH(CH₃)₂), 21.2 (CH₃ Mes para), 20.3 (CH(CH₃)₂), 17.4 (CH₃ Mes ortho). IR (ATR): ν = 3170, 2975, 1674, 1651, 1584, 1536, 1500, 1428, 1408, 1377, 1361, 1302, 1219, 1182, 1153, 1085, 1075, 1056, 866, 828, 797, 782, 772, 741, 680, 655 cm⁻¹. MS (ESI): *m/z* (%): 447 (100) [M + H]⁺ Elemental analysis: calcd (%) for C₂₆H₃₀N₄O₃ + 0.2 CH₂Cl₂ (MW = 463.53): C, 67.89; H, 6.61; N, 12.09 found: C, 67.69; H, 6.87; N, 12.06.

Complex [Ru(1')(1-H)] (**3**)

Inside a glovebox, ligand precursor **1**·H (510 mg, 1.14 mmol, 2 equiv.) was mixed with [Ru(2-methylallyl)₂(COD)] (182.4 mg, 0.571 mmol, 1 equiv.) in a 200 mL Fisher-Porter vessel. THF (44 mL) was added to the tube, which was closed. The latter was heated at 90 °C for 2 h. The solvent was removed *in vacuo* and the crude product was washed with dry pentane (50 mL). The crude reaction mixture was solubilized in DCM and the obtained solution was put on a short silica gel pad, which was then washed with DCM. The solvent was removed *in vacuo* and the product was taken up with minimal amount of DCM. The product was precipitated with pentane (50 mL) and the supernatant was filtered off. The obtained precipitate was dried under the reduced pressure of an oil pump for several minutes to give 288 mg of red crystals obtained as a mixture of complex **2** and recovered **1**·H in a 1 to 1.5 molar ratio (as determined by ¹H NMR). This corresponds to 172 mg (0.173 mmol) of pure **3** and 30% yield. Such a mixture of **3** and **1**·H was used for the following synthetic steps. Analytically pure **3** was procured as deep red crystals by column chromatography using hexane/EtOAc mixtures as eluant (95/5 to 85/15). Crystals of **3** suitable for XRD experiments were grown by layering a DCM complex solution with pentane. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.38 (d, *J* = 1.1 Hz, 1H), 7.63 – 7.46 (m, 2H), 7.04 (s, 1H), 7.00 (s, 1H), 6.97 – 6.89 (m, 3H), 6.66 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.38 (d, *J* = 6.6 Hz, 1H), 6.35 (d, *J* = 1.5 Hz, 1H), 5.49 (d, *J* = 9.7 Hz, 1H), 5.21 (dd, *J* = 9.7, 6.0 Hz, 1H), 5.13 – 4.85 (m, 5H), 4.11 (d, *J* = 10.3 Hz, 1H), 2.98 (d, *J* = 5.9 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 2.14 (s, 3H), 1.65 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.44 – 1.37 (m, 9H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.25 (dd, *J* = 6.8, 2.9 Hz, 9H). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ = 182.3, 167.7, 167.4, 161.0, 157.5, 151.7, 151.2, 147.1, 141.4, 140.9, 137.7, 137.2, 136.4, 136.2, 135.9, 134.2, 132.2, 130.3, 129.8, 129.6, 129.6, 129.4, 128.2, 127.9, 124.7, 114.5, 113.8, 112.5, 109.2, 102.6, 87.8, 77.5, 73.2, 51.8, 47.7, 46.0, 44.4, 44.1, 24.1, 22.4, 21.3, 21.1, 20.5, 20.2, 20.1, 20.0, 19.9, 19.9, 17.6, 17.4. IR (ATR) ν = 2964, 2925, 2872, 1693, 1679, 1630, 1607, 1547, 1502, 1440, 1373, 1341, 1261 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₅₂H₅₉N₈O₈Ru [M+H]⁺

993.3615, found 993.3628. Elemental analysis calcd. for $C_{52}H_{58}N_8O_6Ru$: C, 62.95; H, 5.89; N, 11.29. Found C, 62.49; H, 6.01; N, 10.87.

Complex [Ru(OPiv)(1)(1-H)] (4)

The mixture of complex **3** and 1-H (1 to 1.5 molar ratio, 92.1 mg), which corresponds to 55.0 mg (55.4 μ mol, 1 equiv.) of pure **3**, was dissolved in anhydrous THF (4 mL) in a Schlenk flask. Pivalic acid (12.2 mg, 0.122 mmol, 2.2 equiv.) was added and the flask was heated at 80 °C (bath temperature) overnight. Volatiles were removed *in vacuo* and the product was isolated through a silica gel chromatography (hexane/EtOAc: 70/30 to 50/50). After solvent evaporation, the complex **4** was dried under the reduced pressure of an oil pump for several minutes. The product was isolated as a light-red precipitate (53 mg, 48.4 μ mol, 87%). Crystals of **4** suitable for an X-Ray diffraction experiment were grown by layering a hexafluorobenzene solution of complex **4** with heptane. 1H NMR (400 MHz, CD_2Cl_2): δ = 8.28 (s, 1H), 7.14 (d, J = 9.2 Hz, 1H), 7.04 (dd, J = 15.1, 6.1 Hz, 3H), 6.96 (s, 1H), 6.74 (d, J = 6.6 Hz, 2H), 6.57 (d, J = 11.0 Hz, 2H), 6.36 (dd, J = 9.6, 5.8 Hz, 1H), 6.14 (d, J = 9.7 Hz, 1H), 5.02 (hept, J = 6.7 Hz, 1H), 4.83 (ddp, J = 33.6, 13.4, 6.7 Hz, 3H), 4.31 (d, J = 5.7 Hz, 1H), 2.35 (s, 3H), 2.20 (s, 3H), 2.10 (s, 3H), 1.83 (d, J = 7.6 Hz, 6H), 1.69 (s, 3H), 1.63 (d, J = 7.0 Hz, 3H), 1.38 (d, J = 6.7 Hz, 3H), 1.32 (dd, J = 6.8, 3.5 Hz, 6H), 1.25 – 1.18 (m, 9H), 0.96 (d, J = 7.0 Hz, 3H), 0.88 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 194.8, 175.2, 173.8, 169.6, 166.6, 161.5, 151.9, 151.4, 145.4, 143.2, 141.5, 138.5, 138.2, 136.7, 136.3, 135.1, 134.9, 132.4, 132.2, 131.8, 130.6, 130.0, 129.9, 129.4, 128.5, 125.7, 114.4, 114.3, 112.6, 112.6, 106.4, 95.3, 90.6, 58.8, 46.4, 45.7, 44.2, 43.9, 40.2, 26.9, 21.2, 21.1, 20.9, 20.6, 20.3, 20.2, 20.1, 19.9, 19.9, 19.5, 18.6, 17.9, 17.8, 17.2. IR (ATR) ν = 3060, 2976, 2928, 1706, 1684, 1646, 1627, 1608, 1579, 1538, 1471, 1437, 1378, 1361, 1335, 1260, 1168, 764 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{57}H_{68}N_8O_6Ru$ [M+H]⁺ 1095.4298, found 1095.4312. Elemental analysis calcd. for $C_{57}H_{68}N_8O_6Ru$: C, 62.56; H, 6.26; N, 10.24. Found C, 62.31; H, 6.32; N, 10.25.

Complex [Ru(OPiv)(1)(PPh₃)] (5)

The mixture of complex **3** and 1-H (1 to 1.5 molar ratio, 268.0 mg), which corresponds to 160.0 mg (0.161 mmol, 1 equiv.) of pure **3**, was dissolved in anhydrous DCE (5 mL) in a Schlenk flask. PPh₃ (50.8 mg, 0.194 mmol, 1.2 equiv.) and pivalic acid (19.8 mg, 0.194 mmol, 1.2 equiv.) were added and the flask was heated at 80 °C for 6 h. After solvent removal *in vacuo*, the product was isolated through silica gel chromatography (hexane/EtOAc: 85/15). After solvent evaporation, the product was dried under the reduced pressure of an oil pump for several minutes. The product was isolated as an orange solid (127 mg, 0.140 mmol, 87%). Crystals of **5** suitable for an X-Ray diffraction experiment were grown by layering a DCM complex solution with pentane. 1H NMR (300 MHz, CD_2Cl_2): δ = 7.32 – 7.06 (m, 9H), 6.92 (ddt, J = 13.4, 9.1, 6.3 Hz, 9H), 6.41 (dd, J = 6.6, 0.7 Hz, 1H), 6.17 (ddd, J = 10.6, 8.3, 1.2 Hz, 2H), 4.90 (h, J = 6.8 Hz, 1H), 4.22 (hept, J = 6.7 Hz, 1H), 2.46 (s, 3H), 2.15 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H), 1.42 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.95 (s, 3H), 0.57 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 194.3, 174.4, 174.2, 151.5, 147.4, 140.7, 139.3, 138.7, 136.8, 135.6, 135.4, 135.1, 135.0, 134.4, 133.6, 132.4, 131.1, 129.8, 129.7, 129.7, 129.2, 128.5, 128.1, 128.1, 127.4, 125.4, 114.2, 112.8, 112.6, 46.4, 46.0, 39.5, 26.3, 21.3, 20.9, 20.4, 20.0, 20.0, 18.6, 16.5. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 67.23. IR (ATR) ν = 3057, 2957, 2923, 2861, 1698, 1650, 1526, 1502, 1483, 1431, 1404, 1373, 1361, 1342, 1320, 1274, 1210, 1093, 1053, 989, 903, 787, 765, 750 cm^{-1} . HRMS (MALDI): m/z calcd. for $C_{49}H_{53}N_4O_5PRu$ [M]⁺ 910.2811, found 910.2847. Elemental analysis calcd. for $C_{49}H_{53}N_4O_5PRu$: C, 64.67; H, 5.87; N, 6.16. Found C, 64.68; H, 5.85; N, 6.14.

Complex [Ru(OPiv)(1)(Py)₂(H₂O)] (6)

Complex **4** (40.0 mg, 36.6 μ mol, 1 equiv.) was dissolved in anhydrous pyridine (2 mL, excess) in a Schlenk flask. The flask was heated at 80 °C for 2 h. Next, the pyridine was evaporated *in vacuo*. The product was

isolated by filtration through silica gel chromatography (SiO₂ dried in an oven at 120 °C, prior to use) (dry hexane/EtOAc: 50/50). It was imperative to use dry solvents for the chromatography as otherwise the complex readily decomposed. The solvents were evaporated *in vacuo* and a minimal amount of anhydrous DCM was added to solubilize the substance. The product was precipitated using anhydrous pentane (10 mL) and the supernatant was removed. The obtained precipitate was washed with dry pentane (3 x 5 mL) and dried under the reduced pressure of an oil pump for several minutes. The complex **6** was obtained as a brown powder (27.0 mg, 32.8 μ mol, 90% yield). Crystals of **6** suitable for XRD experiments were grown by layering an Et₂O/DCM solution of complex **6** with pentane. 1H NMR (400 MHz, CD_2Cl_2): δ = 9.02 (d, J = 5.2 Hz, 1H), 7.70 (d, J = 6.1 Hz, 1H), 7.38 (tt, J = 7.4, 1.5 Hz, 2H), 7.21 (tt, J = 7.5, 1.6 Hz, 2H), 7.15 (dd, J = 9.3, 1.0 Hz, 1H), 7.11 – 6.61 (m, 6H), 6.57 (s, 1H), 6.26 – 6.14 (m, 2H), 5.05 (hept, J = 6.8 Hz, 1H), 4.20 – 3.57 (brs, 1H), 2.06 (s, 3H), 1.88 (s, 3H), 1.73 (s, 3H), 1.41 (dd, J = 6.9, 2.0 Hz, 6H), 1.19 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.92 (s, 9H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 191.3, 182.1, 178.3, 174.0, 160.6, 156.1, 154.9, 151.9, 144.9, 138.6, 137.5, 137.2, 134.4, 133.4, 133.3, 133.0, 129.3, 128.6, 125.9, 123.1, 123.1, 123.0, 123.0, 114.6, 112.6, 112.2, 46.1, 45.4, 40.4, 28.3, 21.2, 20.8 (d, J = 3.4 Hz), 20.3, 19.4, 18.3, 17.6. IR (ATR) ν = 2962, 2924, 2871, 1689, 1633, 1608, 1583, 1479, 1428, 1411, 1346, 1323, 792, 764, 751 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{41}H_{50}N_6O_6Ru$ [M]⁺ 824.2847, found 824.2803; for $C_{41}H_{48}N_6O_5Ru$ [M-H₂O]⁺ 806.2730, found 806.2740; for $C_{36}H_{46}N_5O_6Ru$ [M-C₅H₅N+H]⁺ 746.2486, found 746.2408; for $C_{36}H_{43}N_5O_5Ru$ [M-C₅H₅N-H₂O]⁺ 727.2308, found 727.2317. Elemental analysis calcd. for $C_{41}H_{50}N_6O_6Ru$: C, 59.77; H, 6.12; N, 10.20. Found C, 60.28; H, 6.32; N, 9.83.

Complex {Ru(1)(=C(Ph)-CH=CPh-[2,4-(Ph₂)Cp]} (7)

In a Schlenk flask starting complex **4** (100 mg, 91.4 μ mol, 1 equiv.) was dissolved in phenylacetylene (2 mL, excess). The flask was heated at 80 °C for 10 h (after that time TLC showed full conversion of **4**). The excess of phenylacetylene was evaporated *in vacuo* and the product was isolated through column chromatography (SiO₂, hexane/EtOAc: 100/0 to 85/15). After solvent removal, the product was dried under the reduced pressure of an oil pump for several minutes. The complex **7** was obtained as a deep red powder (16.0 mg, 16.8 μ mol, 18%). Crystals of **7** suitable for an X-Ray diffraction experiment were obtained by vapor diffusion of pentane into a solution of **7** in THF. 1H NMR (400 MHz, CD_2Cl_2): δ = 7.87 (s, 1H), 7.67 – 7.62 (m, 2H), 7.41 – 7.33 (m, 5H), 7.26 – 7.22 (m, 1H), 7.19 – 7.13 (m, 3H), 7.01 – 6.91 (m, 6H), 6.91 – 6.87 (m, 1H), 6.84 (t, J = 7.7 Hz, 2H), 6.80 (s, 1H), 6.71 – 6.64 (m, 3H), 6.19 – 6.09 (m, 2H), 5.95 (dd, J = 6.6, 0.7 Hz, 1H), 5.67 (d, J = 2.0 Hz, 1H), 4.64 (hept, J = 6.9 Hz, 1H), 3.92 (hept, J = 6.8 Hz, 1H), 2.19 (s, 3H), 1.82 (s, 3H), 1.57 (s, 3H), 1.34 (d, J = 6.9 Hz, 3H), 1.29 (d, J = 6.9 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H), 0.50 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 282.7, 176.2, 176.0, 174.8, 162.1, 159.5, 151.8, 147.5, 146.3, 138.7, 138.4, 136.3, 136.1, 134.6, 134.2, 133.9, 132.3, 130.0, 129.7, 129.2, 128.6, 128.6, 127.8, 127.8, 127.7, 127.4, 127.3, 127.2, 127.1, 126.6, 126.0, 124.2, 121.0, 119.0, 108.2, 99.0, 94.3, 47.5, 47.2, 21.7, 21.2, 21.2, 20.1, 18.9, 18.4. IR (ATR) ν = 3153, 3055, 2965, 2924, 2870, 1707, 1638, 1596, 1492, 1419, 1393, 1328, 1313, 1195, 1172, 1160, 1068, 985 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{58}H_{52}N_4O_3Ru$ [M]⁺ 954.3077, found 954.3088.

Crystallographic Experimental Details

Data were collected at low temperature either on a Gemini Agilent diffractometer using a graphite-monochromated Cu-K α Enhance radiation (λ = 1.54184 Å) and equipped with an Oxford Instrument Cooler Device or on a Bruker Kappa Apex II diffractometer using a Mo-K α radiation (λ = 0.71073 Å) micro-source, both equipped with an Oxford Cryosystems Cooler Device. The structures have been solved using the new dual-space algorithm program SHELXT,^[33] and refined by means of least-squares procedures using either SHELXL-2018^[33] program included in the software package WinGX version 1.639.^[34] The Atomic Scattering Factors were taken from International Tables for X-Ray crystallography.^[35] Hydrogen

atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms were anisotropically refined. Ellipsoid plots in the figures of the crystallography section were generated using the software ORTEP-35.^[36] The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 2361553 (3), 2361552 (4), 2361554 (5), 2361555 (6), and 2380108 (7).

Supporting Information

The authors have cited additional references within the Supporting Information.

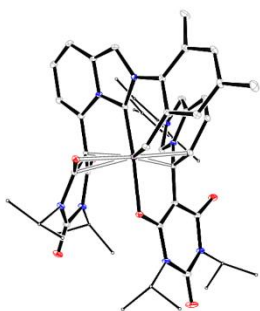
Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique (CNRS) and the University of Warsaw. The French

- [1] (a) P. Bellotti, M. Koy, M. N. Hopkinson, F. Glorius, *Nature Reviews Chemistry* **2021**, *5*, 711-725; (b) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485-496.
- [2] (a) T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, *45*, 6327-6344; (b) A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994-7112; (c) C. Romain, S. Bellemin-Lapponnaz, S. Dagorne, *Coord. Chem. Rev.* **2020**, *422*, 213411; (d) R. Jazzar, M. Soleilhavoup, G. Bertrand, *Chem. Rev.* **2020**, *120*, 4141-4168; (e) S. Ibáñez, M. Poyatos, E. Peris, *Acc. Chem. Res.* **2020**, *53*, 1401-1413; (f) M. Mora, M. C. Gimeno, R. Visbal, *Chem. Soc. Rev.* **2019**, *48*, 447-462.
- [3] (a) V. César, C. Fiedel, A. Labande, in *Chiral Ligands: Evolution of Ligand Libraries for Asymmetric Catalysis* (Ed.: M. Dieguez), Taylor & Francis, **2021**, pp. 195-232; (b) Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.* **2020**, *120*, 1981-2048; (c) J. Thongpaen, R. Manguin, O. Baslé, *Angew. Chem. Int. Ed.* **2020**, *59*, 10242-10251; (d) C. Fiedel, A. Labande, E. Manoury, R. Poli, *Coord. Chem. Rev.* **2019**, *394*, 65-103; (e) E. Peris, *Chem. Rev.* **2018**, *118*, 9988-10031.
- [4] (a) C. A. Smith, M. R. Narouz, P. A. Lummis, I. Singh, A. Nazemi, C.-H. Li, C. M. Crudden, *Chem. Rev.* **2019**, *119*, 4986-5056; (b) H. Amouri, *Chem. Rev.* **2023**, *123*, 230-270; (c) Y. Wang, J.-P. Chang, R. Xu, S. Bai, D. Wang, G.-P. Yang, L.-Y. Sun, P. Li, Y.-F. Han, *Chem. Soc. Rev.* **2021**, *50*, 13559-13586; (d) M. Koy, P. Bellotti, M. Das, F. Glorius, *Nature Catalysis* **2021**, *4*, 352-363.
- [5] L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lapponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705-2733.
- [6] (a) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708-3742; (b) O. M. Ogbay, N. C. Warner, D. J. O'Leary, R. H. Grubbs, *Chem. Soc. Rev.* **2018**, *47*, 4510-4544; (c) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2009**, *110*, 1746-1787.
- [7] (a) K. Grela, in *Olefin Metathesis: Theory and Practice* (Ed.: K. Grela), John Wiley & Sons, Inc., Hoboken, **2014**; (b) R. H. Grubbs, Wenzel, Anna G., O'Leary, Daniel J., Khosravi, Ezat in *Handbook of Metathesis* (Ed.: R. H. Grubbs, Wenzel, Anna G., O'Leary, Daniel J., Khosravi, Ezat), Wiley-VCH, Weinheim, **2015**.
- [8] K. Endo, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 8525-8527.
- [9] (a) B. K. Keitz, K. Endo, P. R. Patel, M. B. Herbert, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *134*, 693-699; (b) L. E. Rosebrugh, M. B. Herbert, V. M. Marx, B. K. Keitz, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 1276-1279; (c) M. B. Herbert, B. A. Suslick, P. Liu, L. Zou, P. K. Dorman, K. N. Houk, R. H. Grubbs, *Organometallics* **2015**, *34*, 2858-2869.
- [10] (a) A. Dumas, R. Tarriau, T. Vives, T. Roisnel, V. Dorcet, O. Baslé, M. Mauduit, *ACS Catal.* **2018**, *8*, 3257-3262; (b) Y. Xu, J. J. Wong, A. E. Samkian, J. H. Ko, S. Chen, K. N. Houk, R. H. Grubbs, *J. Am. Chem. Soc.* **2020**, *142*, 20987-20993.
- [11] K. Gajda, A. Sytniczuk, L. Vendier, B. Trzaskowski, N. Lugan, A. Kajetanowicz, S. Bastin, K. Grela, V. César, *Eur. J. Inorg. Chem.* **2023**, *26*, e202300169.
- [12] I. Benaissa, K. Gajda, L. Vendier, N. Lugan, A. Kajetanowicz, K. Grela, V. Michelet, V. César, S. Bastin, *Organometallics* **2021**, *40*, 3223-3234.
- [13] C. S. Day, D. E. Fogg, *Organometallics* **2018**, *37*, 4551-4555.
- [14] (a) N. Ortega, S. Urban, B. Beiring, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 1710-1713; (b) S. Urban, B. Beiring, N. Ortega, D. Paul, F. Glorius, *J. Am. Chem. Soc.* **2012**, *134*, 15241-15244; (c) J. Wysocki, N. Ortega, F. Glorius, *Angew. Chem. Int. Ed.* **2014**, *53*, 8751-8755; (d) D. Paul, B. Beiring, M. Plois, N. Ortega, S. Kock, D. Schlüns, J. Neugebauer, R. Wolf, F. Glorius, *Organometallics* **2016**, *35*, 3641-3646; (e) C. Schleppehorst, M. P. Wiesenfeldt, F. Glorius, *Chem. Eur. J.* **2018**, *24*, 356-359.
- [15] A 2/1 stoichiometry was shown to be optimal, as a 1/1 stoichiometry of the reaction led to the same complex 3, albeit to lower yields. Using 3 equivalents of 1H did not further improve the yield.
- Gouvernement is acknowledged for part of a PhD grant to K. G. This work has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 860322 (Coordination Chemistry Inspires Molecular Catalysis, CCIMC). A CC-BY public copyright license has been applied by the authors to the present document and will be applied to all subsequent versions up to the Author Accepted Manuscript arising from this submission, in accordance with the grant's open access conditions.

Keywords: Ruthenium • N-heterocyclic Carbene • Cyclometallation • Carbene Complexes • Heterocycles

Entry for the Table of Contents



The coordination and further reactivity of a ImPy-type N-Heterocyclic Carbene ligand, flanked with a lateral barbiturate moiety, with the precursor $[\text{Ru}(\text{2-methylallyl})_2(\text{COD})]$ are reported.

@LCC_CNRS, @GrelaGroup, @vinc_cesar, @Bastin31