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Group 10 Metal Complexes with Chelating Macrocyclic Dicarbene Ligands Bearing a 2,6-Lutidinyl Bridge: Synthesis, Reactivity, and Catalytic Activity

Andrea Biffis,*[,†] Matteo Cipani,[†] Edoardo Bressan,[†] Cristina Tubaro,[†] Claudia Graiff,[‡] and Alfonso Venzo[§]

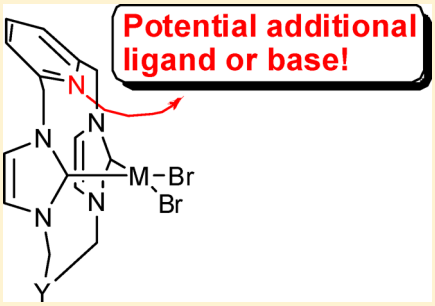
[†]Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy

[‡]Dipartimento di Chimica, Università di Parma, Viale delle Scienze 17/A, 43100 Parma, Italy

[§]IENI-CNR, c/o Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy

Supporting Information

ABSTRACT: Palladium(II) and platinum(II) complexes of the title ligands have been prepared; the two carbene moieties of the ligand coordinate to the metal in *cis* fashion, while the bridging pyridyl group remains outside the metal coordination sphere but close to the metal center. In this peculiar situation, the pyridyl group can assist the oxidation of the metal center to the +IV oxidation state upon coordination to the metal in the product. Furthermore, the pyridyl group is found to promote the catalytic role of the palladium(II) complexes in copper- and amine-free Sonogashira reactions.

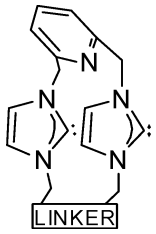


INTRODUCTION

Transition metal complexes in which the ligands are able not only to influence the physicochemical properties, the reactivity, and/or the stability of the metal center but also to exert a function in their own right have nowadays come to the forefront of organometallic and coordination chemistry research. Such "non-innocent" ligands can for example act as an electron relay toward the metal center (redox-active ligands),[1] take up an active role in a catalytic event promoted by the metal complex (cooperative catalysis),[2] or more simply provide a handle for the construction of more complicated structures such as higher nuclearity metal complexes and clusters, supramolecular systems, or metal organic frameworks (MOFs).

The development of ligands of this kind has however seldom involved up to now the use of N-heterocyclic carbene (NHC) moieties.[3] In this context, we have become recently interested in metal complexes with ligands bearing the structure outlined in Scheme 1. A short linker between the two imidazolylidene moieties should allow the preparation of mononuclear complexes with d^8 metal centers in which the carbene moieties occupy two mutually *cis* coordination sites in a square planar geometry, thus preventing the pyridyl group from coordinating to the metal, while at the same time maintaining it close to the metal; in such a situation, the pyridyl group should remain available for working cooperatively with the metal in catalysis, for example by acting as a base toward an incoming substrate or as a stabilizing ligand toward the metal following its oxidation (with a consequent change in coordination geometry to square pyramidal or octahedral) in the course of the catalytic cycle. We are intrigued by these possibilities, as it has been demonstrated in recent years that complexes with monocarbene ligands bearing pendant pyridyl groups can display remarkable catalytic properties due to such a cooperative effect.[4] Although one example of a Pd(II) complex with a macrocyclic ligand of this kind has been previously published,[5] the presence of a pendant pyridyl group in such kind of complexes has not been put to advantage to any significant extent up to now.

Scheme 1. Nature of the Ligands Investigated in This Work



Thus, in the frame of our continuing studies on the chemistry of poly-NHC complexes of late transition metals,[6] we present in this contribution results concerning the preparation and reactivity of complexes of macrocyclic dicarbene ligands of the type highlighted above with group 10 metals in the +II oxidation state. We show that the pyridyl group remains uncoordinated in these complexes, but it can become

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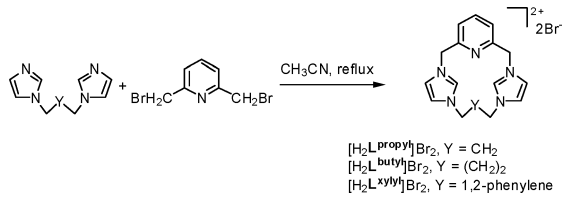
coordinated upon oxidation of the metal center to the +IV oxidation state. Finally, we investigate on the application of Pd complexes of this kind as catalysts for the copper- and amine-free Sonogashira reaction, in which pendant basic groups close to the metal center are expected to promote proton abstraction from a π-coordinated alkyne and consequently to facilitate catalysis.

RESULTS AND DISCUSSION

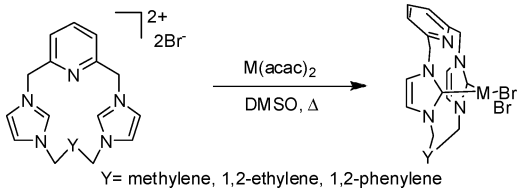
Synthesis of the Macrocyclic Ligand Precursors. The macrocyclic precursors of dicarbene ligands employed in this work are featured by a 2,6-lutidinyl bridge between the NHC groups as well as by a linker 3 or 4 carbon atoms long (1,3-propylene, *o*-xylylene, 1,4-butylene). The choice of such short linkers was made to prevent the possibility of the ligands forming complexes with the two NHC groups coordinated to the metal in *trans*-fashion, which would also imply coordination of the pyridyl nitrogen to yield CNC pincer complexes; formation of complexes of this kind is indeed very common with d^8 metal centers and open-chain dicarbene ligands connected by a 2,6-lutidinyl bridge,[7] and the same holds in the case of macrocyclic ligands containing long linkers.[8] The ligand precursors were prepared by a slight modification of literature procedures, using dilution to ensure efficient cyclization between the reagents 2,6-bis(bromomethyl)pyridine and the various employed bis(imidazoles) (Scheme 2).[9]

Scheme 2. Synthetic Strategy for the Preparation of the Diimidazolium Ligand Precursors



Synthesis of the Metal Complexes. The metal complexes were synthesized directly from the diimidazolium salts upon reaction with the corresponding metal acetylacetonate (Scheme 3). Use of $Pt(acac)_2$ as reagent in the synthesis of Pt-NHC complexes was pioneered by the group of Strassner,[10] and in our hands it was very useful for preparing the Pt(II) complexes of all three macrocyclic ligands. Furthermore, the method was extended also to the preparation of Pd(II) complexes, as the use of $Pd(acac)_2$ gave better results in terms of yield and product purity compared with the previously published route employing $Pd(OAc)_2$.[5]

Scheme 3. Synthetic Strategy for the Preparation of Pd(II) and Pt(II) Complexes with Macrocyclic Dicarbene Ligands



We planned to extend the application of this synthetic strategy to the preparation of Ni(II) complexes as well, but unfortunately we never obtained any evidence of the formation of Ni(II)−carbene complexes of any kind, despite extensive changes in the reaction conditions and also in the nature of the employed nickel source; use of preformed silver(I) complexes of the ligands[9] as reagents for ligand transmetalation toward nickel(II) centers also proved unsuccessful (see the Supporting Information for details). These failed attempts are in contrast to the easy and well-known preparation of CNC pincer complexes of Ni(II) with open-chain ligands of this kind[11] and lead us to conclude that the geometric constraints imposed by the employed short linker to the macrocyclic ligand structure do not allow the preparation of stable Ni(II) complexes. Consequently, we left aside Ni(II) as a metal center for this chemistry and concentrated rather on Pd(II) and Pt(II).

We also attempted the preparation of tetracarbene complexes of Pt(II) complexes bearing two macrocyclic ligand units per metal; unfortunately, these synthetic attempts also failed, both when the synthesis was performed upon reaction of $Pt(acac)_2$ in the presence of 2 equiv of ligand precursor and NaOAc as external base and when it was performed upon ligand transmetalation from preformed silver(I) complexes toward metal complexes bearing one macrocyclic ligand unit per metal (see the Supporting Information for details). In the former case only the 1:1 metal/macrocyclic ligand complex was obtained, highlighting the instability of the corresponding 1:2 adducts.

Characterization of the Metal Complexes. The elemental analyses of the Pd(II) and Pt(II) dicarbene complexes are consistent with their proposed description as mononuclear complexes with one ligand unit chelating the metal center through the carbene moieties (Scheme 3). The deprotonation of the diimidazolium salt is also confirmed by the absence, in the ^{1}H NMR spectra of the reaction products, of the signal of the proton in position 2 of the imidazole rings. Furthermore, upon coordination to the metal centers, the dicarbene ligand is forced to adopt a rigid structure, with consequent loss of magnetic equivalence for the benzyl protons of the 2,6-lutidinyl group and the protons of the other bridge.

A closer inspection of the NMR spectra of these complexes highlights however several untrivial features. Concerning the Pt(II) complexes, it turns out that most of the ^{1}H and ^{13}C signals of the complexes appear doubled in the spectra. This feature is particularly evident for the benzylic protons of the 2,6-lutidinyl group (doubling of the signal noticeable already at 300 MHz), but it becomes apparent for many other signals using higher frequency (400 or 600 MHz) NMR instruments. For example, in the case of complex $PtBr_2(L^{propyl})$ doubling of all the ^{1}H signals but those due to the proton in position 4 of the pyridyl group and the protons of the central methylene group of the linker is evident at 600 MHz. Nevertheless, the observation that at least some of the signals remain non-doubled, together with the unicity of the ^{195}Pt resonance (recorded at −2245 ppm in complex $PtBr_2(L^{propyl})$), suggests an explanation in terms of an overall molecular asymmetry of the complexes, rather than in terms of the copresence of two geometrical or conformational isomers in slow chemical exchange.

An even more complicated situation is apparent with the Pd(II) complexes. In these cases, despite extensive purification and satisfactory elemental analyses, the NMR spectra of all the complexes invariably point out the presence of other minor sets of signals besides the main one. Consequently, we started to envisage the presence of some sort of equilibrium in solution, in which the original complexes form other species to some extent. In this connection, ESI-MS analysis of solutions of the

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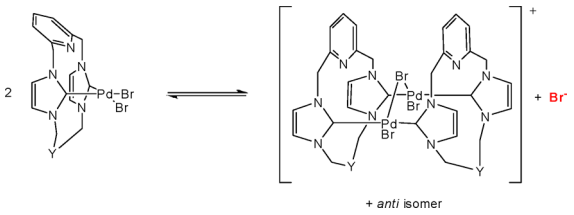
complexes pointed out that, besides the expected mononuclear complex $PdBr(L)^+$, significant amounts of dinuclear complexes of general formula $Pd_2Br_3(L)_2^+$ were also present. This observation suggested the presence of an equilibrium of the type highlighted in Scheme 4, described some years ago by Albrecht for dicarbene palladium(II) complexes.[12]

Scheme 4. Mononuclear−Dinuclear Equilibrium Taking Place with the Pd(II) Complexes



Further support for this interpretation is brought by the study of the effect of the deliberate addition of bromide anions to the solution (Supporting Information, Figure 1). As expected, addition of LiBr switches the equilibrium to the left, and consequently the mononuclear complex is the only species present in solution. This is confirmed by the ESI-MS spectra, which after LiBr addition show only the signal of the mononuclear complexes.

Crystal Structure of Complex $PtBr_2(L^{propyl})$. The structure of complex $PtBr_2(L^{propyl})$ has been further confirmed by single-crystal X-ray analysis of a sample grown in DMF solution. The complex crystallizes as a dimethylformamide monosolvate. A view of the crystal structure of $PtBr_2(L^{propyl})$ is shown in Figure 1, together with the atomic labeling scheme. A

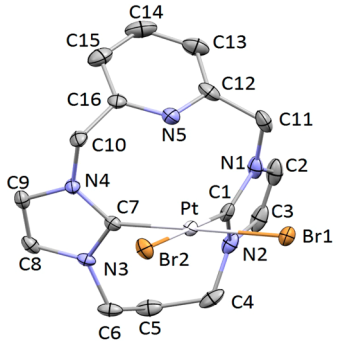


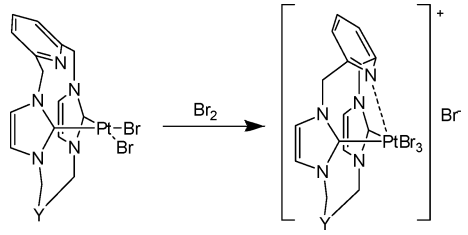
Figure 1. ORTEP drawing of complex $PtBr_2(L^{propyl})$. Ellipsoids are drawn at their 30% probability level. Hydrogen atoms and solvent molecule of dimethylformamide have been omitted for clarity. Selected bond distances (Å) and angles (deg): C1−Pt 1.977(4), C7−Pt 1.983(3), Br1−Pt 2.5003(4), Br2−Pt 2.4913(4), C1−N2 1.355(5), C1−N1 1.378(5), C7−N4 1.359(4), C7−N3 1.366(4); C1−Pt−C7 93.42(14), C1−Pt−Br2 179.85(10), C7−Pt−Br2 86.71(10), C1−Pt−Br1 88.74(10), C7−Pt−Br1 177.80(10), Br2−Pt−Br1 91.128(14), N2−C1−N1 104.7(3), N2−C1−Pt 127.2(3), N1−C1−Pt 128.1(3), N4−C7−N3 104.3(3), N4−C7−Pt 129.2(2), N3−C7−Pt 126.4(3).

list of the most important bond distances and angles is also reported in the figure caption. The Pt atom is disposed in a quasi-square planar environment, comprising the two donors of the carbene ligand mutually *cis* and the two halide donors occupying the other pair of mutually *cis* sites. The metal atom is coordinated outside the cavity of the macrocyclic ligand in an analogous manner to that observed in the parent palladium compound described in ref 5. The $C_{carbene}-Pt-C_{carbene}$ angle is 93.42(14)° and the Br−Pt−Br one is 91.128(14)°. The dihedral angles between the $PtBr_2C_2$ coordination mean plane and those of the carbene moieties are 71.58(2)° and 73.32(2)°, while the dihedral angle between the mean planes of the carbene moieties is 78.32(2)°. Although the ligand is potentially tridentate, the pyridine-nitrogen atom N5 is at a distance of 2.949(3) Å from platinum, thus preventing any bond interaction. The Pt−Br and $Pt-C_{carbene}$ bond distances fall in the range for related complexes of the type *cis*-$[PtBr_2(NHC)_2]$.[13]

Reactivity of the Complexes with Bromine. There is a steadily growing interest in the chemistry of organometallic complexes of late transition metals in high oxidation state, both from the fundamental and applied point of view; such interest is driven in particular by the recognized formation of these complexes as intermediates in several catalytic processes leading to C−H activation and (oxidative) functionalization.[14] The macrocyclic ligands described herein appear particularly suited for the preparation of Pt or Pd complexes in high oxidation state: upon oxidation of the metal center to the +IV state, the pyridyl group is expected to enter the coordination sphere of the complex, with the ligand becoming altogether *fac*-tricoordinated in an octahedral geometry. Such a coordination set closely mimics that of analogous Pd complexes, which have recently proven useful for C−H oxidative functionalization processes.[15] Furthermore, it has been suggested that *fac*-tricoordinated complexes are particularly suited for carrying out such processes.[16]

On the basis of the above, we have carried out a preliminary evaluation of the possibility to prepare Pd or Pt complexes in high oxidation state with our macrocyclic ligand systems. Oxidation with elemental bromine was chosen as preparation method, following a route already proven useful for related complexes.[17] It turned out that all Pt(II) complexes yielded well-defined products in good yields after treatment with excess bromine in DMSO (Scheme 5).

Scheme 5. Synthetic Strategy for the Preparation of Pt(IV) Complexes with Macrocyclic Dicarbene Ligands



The elemental analyses and ESI-MS characterization of the Pt(IV) dicarbene complexes are consistent with their proposed description as mononuclear complexes of general formula $PtBr_4(L)$. For the complexes, we proposed a structure in which the ligand is tricoordinated to the metal through the carbene moieties and the pyridyl nitrogen; three bromide anions complete the octahedral coordination set, and an additional bromide serves as counteranion. The formation of such complexes is also confirmed by the NMR spectra, which show the expected changes upon oxidation of the metal center and coordination of the pyridyl nitrogen. In particular, all signals in the ^1H NMR spectra of the complexes are shifted to lower fields compared to the corresponding Pt(II) complexes,

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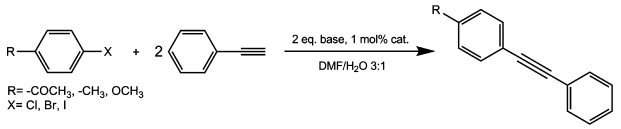
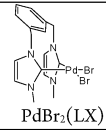
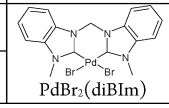
Table 1. Sonogashira Reaction Catalyzed by Pd(II) Complexes with Macrocyclic Dicarbene Ligands



Entry	Aryl halide	Catalyst	Base	T(°C)	Time (h)	Yield (%)[a]
1	4-bromoacetophenone	$PdBr_2(L^{propyl})$	K_2CO_3	100	1	67
					2	70
2	4-bromoacetophenone	$PdBr_2(L^{xylyl})$	K_2CO_3	100	1	65
					2	74
					4	87
3	4-bromoacetophenone	$PdBr_2(L^{butyl})$	K_2CO_3	100	1	83
					2	85
					17	90
4	4-bromoacetophenone	$PdBr_2(L^{butyl})$	K_2CO_3	80	2	22
					70	>99
5	4-bromoacetophenone	$PdBr_2(L^{propyl})$	K_2CO_3	80	2	25
					22	71
6	4-bromoacetophenone	$PdBr_2(L^{propyl})$	K_2CO_3	50	2	0
					22	7
7	4-bromoacetophenone	$PdBr_2(L^{propyl})$	K_2CO_3	100	17	90
8	4-bromoacetophenone	$PdBr_2(L^{propyl})$	Cs_2CO_3	100	2	83
					4	92
					6	93
					17	93
9	4-bromotoluene	$PdBr_2(L^{propyl})$	K_2CO_3	100	2	47[b]
					17	80[b]
10	4-bromoanisole	$PdBr_2(L^{propyl})$	K_2CO_3	100	2	15
					17	71
11	4-bromoanisole	$PdBr_2(L^{propyl})$	Cs_2CO_3	100	2	35
					17	58
12	4-iodoacetophenone	$PdBr_2(L^{propyl})$	K_2CO_3	100	2	84
					17	85
13	4-iodotoluene	$PdBr_2(L^{propyl})$	K_2CO_3	100	2	57[b]
14	4-chloroacetophenone	$PdBr_2(L^{propyl})$	K_2CO_3	100	17	14
15	4-bromoacetophenone	 $PdBr_2(LX)$	K_2CO_3	100	2	8
					17	22
16	4-bromoacetophenone	 $PdBr_2(diBIm)$	K_2CO_3	100	2	41
					17	63

[a]Yield determined by ^1H NMR analysis of the reaction mixture ($CDCl_3$). [b]Mixture of products.

suggesting ligand coordination to a more electron-withdrawing metal center. Furthermore, formation of a more rigid complex in the case of Pt(IV) is apparent from the much larger difference in chemical shift recorded between the diastereotopic protons of the methylene groups directly bound to the imidazole nitrogens. In the ^{13}C NMR spectra, the same shift of the signals to lower field is evident, apart from the carbene carbons, which are instead found at higher field compared to the corresponding Pt(II) complexes; nevertheless, this apparently anomalous shift was also expected, since in this case the deshielding at the carbene carbon originated by the increasingly electron-withdrawing metal center is overcompensated by delocalization on the carbene carbon of electron density from the imidazolylidene rings.[17] Finally, also the extensive downfield shift observed upon reaction in the ^{195}Pt NMR spectrum of the complexes (e.g., −253 ppm vs −2245 ppm in complex $PtBr_2(L^{propyl})$) points toward oxidation of the metal. Remarkably, no doubling of any NMR signal is observed in the Pt(IV) complexes, in contrast to the corresponding Pt(II) complexes, which is indicative of a less distorted structure of the ligands in the Pt(IV) case.

Several attempts were made to crystallize the Pt(IV) complexes from DMF or DMSO solutions, in order to obtain the structure and consequently a conclusive proof of the coordination of the pyridyl nitrogen to the metal center. Unfortunately, all attempts performed up to now were unsuccessful. Nevertheless, strong support toward coordination of the pyridyl nitrogen in these complexes is provided by ^{15}N NMR spectroscopy. Whereas the signal of the pyridyl nitrogen is recorded at almost the same chemical shift (312 ppm) in the imidazolium precursor $[H_2L^{propyl}]Br_2$ and in the Pt(II) complex $PtBr_2(L^{propyl})$, indicating no coordination of the pyridyl nitrogen to the metal, a considerable shift is observed on going to the Pt(IV) complex, where the signal falls at 183 ppm. Thus, it can be safely stated that the pyridyl nitrogen is indeed coordinated to the Pt(IV) metal center. Additional support for the proposed structure is provided by the invariance of the ^1H NMR spectra of the Pt(IV) complexes upon reaction with 1 equiv of $AgNTf_2$ in DMSO despite the evident precipitation of

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AgBr: this proves that one of the bromides is not coordinated to the metal and can be easily exchanged without affecting the structure of the complex in solution.

Reaction of excess bromine with the Pd(II) complexes does not produce instead any Pd(IV) complex, and the starting Pd(II) complexes are recovered unchanged after reaction. Efforts are under way to prepare these complexes with stronger oxidants, as it has been recently reported in the literature that Pd(II) complexes with similar coordination sets can be oxidized to Pd(IV) with, for example, chlorine instead of bromine.[15]

Catalytic Efficiency of the Pd(II) Complexes in Copper-Free Sonogashira Coupling Reactions. The Sonogashira reaction, i.e., the coupling of aryl halides with terminal alkynes to yield arylalkynes, is one of the most widely known cross-coupling reactions.[18] Pd-based catalysts with Cu(I) salts as cocatalysts are generally employed to promote the reaction. Remarkably, whereas Pd-phosphine complexes represent undoubtedly the most efficient catalysts known to date, much less success has been reported with Pd-NHC complexes, in spite of the extremely high levels of catalytic efficiency achieved with these complexes in related cross-coupling reactions, such as Heck or Suzuki couplings.[19] This is particularly true for the so-called copper-free Sonogashira reaction, which is run without the Cu(I) cocatalyst. Efficient catalysts for this variant of the Sonogashira reaction are much sought after, since the Cu(I) cocatalyst speeds up the process but on the other hand renders the reaction air-sensitive and promotes other unwanted reactions such as the Glaser–Hay coupling of the alkyne.[20] An often employed trick to promote the reactivity of the catalyst under copper-free conditions is to use a large excess of an organic amine both as base and as reaction promoter.[18] In this connection, it is interesting to remark that the most efficient Pd-NHC catalysts known to date for the copper-free Sonogashira reaction contain NHC ligands with pendant Lewis basic groups,[21] which could possibly promote the reaction by facilitating the deprotonation of an alkyne π-bound to the metal and its consequent transformation into a σ-bound alkynyl, without the intermediacy of a Cu(I) cocatalyst and the need for the presence of excess base; the σ-bound alkynyl is then reductively coupled with a metal-bound aryl group to yield the product. Therefore, we chose to perform a screening of our Pd(II) complexes as catalysts for the copper- and amine-free Sonogashira reaction, under conditions previously reported for other functionalized Pd-NHC complexes. The results are reported in Table 1.

Initial tests were conducted with all three catalysts $PdBr_2(L^{propyl})$, $PdBr_2(L^{xylyl})$, and $PdBr_2(L^{butyl})$ using 4-bromoacetophenone as substrate. Gratifyingly, all complexes gave good yields after 1 h of reaction at 100 °C with 1 mol % catalyst loading (67%, 65%, and 83%, respectively, entries 1–3), higher than those obtained with other Pd-NHC complexes with pendant Lewis basic groups reported in the literature (max. 43% at 3 mol % catalyst loading)[21c] and comparable to those recently reported with a CNC pincer-type di(1,2,4-triazolin-5-ylidene)Pd(II) complex.[22]

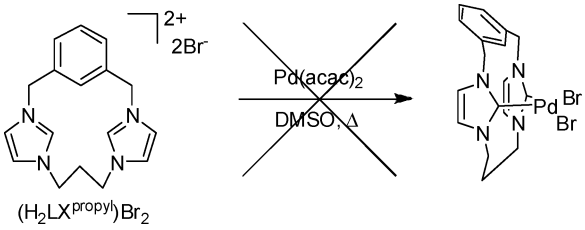
Looking at the evolution of the reaction yield with time, it is apparent that all catalysts are mostly active in the first hour of reaction, with the activity subsequently decreasing significantly with time (see in particular entries 3 and 8). This is an indication of catalyst deactivation, possibly due to catalyst decomposition under the reaction conditions. Indeed, running the reaction at 80 °C decreases the initial catalytic activity but allows reaching complete conversions at longer reaction times (entries 4 and 5), whereas at 50 °C the activity becomes too low to be practical (entry 6).

The effect of the nature of the employed inorganic base (K_2CO_3 or Cs_2CO_3) was also briefly considered: Cs_2CO_3 ensured a slightly higher initial catalytic activity (compare for example entries 7 and 8), but also a more rapid catalyst deactivation (compare entries 10 and 11). In view of the much lower cost of K_2CO_3 compared to Cs_2CO_3, the former was considered as the preferred alternative.

A screening of different aryl halide reactants was then performed using catalyst $PdBr_2(L^{propyl})$. Aryl bromides with more electron-donating substituents such as 4-bromoanisole reacted as expected more sluggishly compared to 4-bromoacetophenone (entries 10 and 11), but good yields were still reached at longer reaction time. In the case of 4-bromotoluene (entry 9), the reaction was however not clean, and besides the main Sonogashira product other minor products were recorded, which await further characterization. The effect of the nature of the halide was also considered: as expected, aryl iodides were reactive substrates for the reaction (entries 12 and 13), and it was even possible to achieve some turnovers also with a less reactive aryl chloride such as 4-chloroacetophenone (entry 16).

Finally, in order to establish if the presence of the bridging pyridyl group indeed promotes catalytic activity, we compared the behavior under the same reaction conditions of related catalysts not containing the pyridyl group. Ideally, we intended to employ as benchmark a complex bearing an *m*-xylylene bridge instead of the 2,6-lutidinyl bridge. The synthesis of such a complex was attempted starting from the macrocyclic ligand precursor $[H_2LX^{propyl}]Br_2$ (Scheme 6), previously synthesized

Scheme 6. Attempted Synthesis of a Benchmark Pd(II) Complex with a Macrocyclic Dicarbene Ligand without the Pyridyl Group



by our group,[9] but the reaction yielded a complex product mixture, from which it proved impossible to isolate the desired complex in pure form (see the Supporting Information for details).

Therefore, we resolved to employ a related complex with an open-chain dicarbene ligand and a bridging *m*-xylylene group, such as complex $PdBr_2(LX)$ (Table 1, entry 15), which was prepared following a procedure previously reported by Cavell et al.[23] Indeed, the catalytic activity of this complex proved much poorer (entry 15) than that of the complexes bearing the bridging pyridyl group. We additionally employed another benchmark Pd-dicarbene catalyst such as $PdBr_2(diBIm)$ (Table 1, entry 16): the catalytic activity was improved with respect to the previous benchmark, but it turned out to be again lower than that of the complexes bearing the bridging pyridyl group. Therefore, we conclude that indeed the presence of the bridging pyridyl group seems to exert a positive effect on the catalytic activity of this class of complexes.

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CONCLUSIONS

In conclusion, we have demonstrated that it is possible to tailor macrocyclic di-NHC ligands containing 2,6-lutidinyl bridges in a way that allows coordination to d^8 metal centers of the carbene moieties but not of the pyridyl group, which remains close to the metal but outside its coordination sphere. We have also shown that the pyridyl group may enter the coordination sphere of the metal center upon metal oxidation, as well as that the presence of the pyridyl group exerts a positive effect on the catalytic efficiency of the complexes in standard Sonogashira reactions. Efforts are under way in order to assess the role of the pyridyl group in the catalytic cycle, as well as in order to apply such complexes as catalysts in other reactions that specifically involve the metal(II)/metal(IV) catalytic manifold.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon or dinitrogen. The reagents were purchased by Aldrich as high-purity products and generally used as received. All solvents were technical grade and used as received. The preparation of diimidazolium salts $[H_2L^{propyl}]Br_2$, $[H_2L^{xylyl}]Br_2$, $[H_2L^{butyl}]Br_2$, and $[H_2LX^{propyl}]Br_2$ was accomplished according to previously published procedures.[9] The complexes $PdBr_2(LX)$[23] and $PdBr_2(diBIm)$[24] were prepared following literature procedures. NMR spectra were recorded on an Avance 300 MHz (300.1 MHz for ^1H and 75.5 for ^{13}C), on an Avance 400 MHz (400.13 MHz for ^1H and 100.61 for ^{13}C), and on an Avance 600 MHz (600.01 MHz for ^1H and 150.07 for ^{13}C); chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals for both ^1H and ^{13}C, to aqueous $^{15}NH_4NO_3$ for ^{15}N, and to aqueous K_2PtCl_4 (adjusted to $\delta = -1628$ ppm from Na_2PtCl_6) for ^{195}Pt. ESI-MS spectra were recorded on a Thermo LCQ-Duo ESI-MS.

Synthesis of the Pd(II) and Pt(II) Complexes. The syntheses were performed following a literature procedure for related dicarbene complexes.[10]

General Procedure. A 0.160 mmol amount of $Pd(acac)_2$ or $Pt(acac)_2$ and 0.160 mmol (1 equiv) of the diimidazolium dibromide ligand precursor were placed in a Schlenk tube under an inert atmosphere. The reagents were dissolved in 6 mL of DMSO, and the resulting solution was heated under stirring to 60 °C for 2 h, 80 °C for another 2 h, and finally 110 °C for 2 h. Heating was subsequently turned off, and stirring was continued overnight. The solvent was removed under reduced pressure, and the remaining solid was washed three times with 2 mL aliquots of acetonitrile and finally dried under reduced pressure.

$PdBr_2(L^{propyl})$. Yield: 65%. Anal. Calcd for $C_{16}H_{17}Br_2N_5Pd\cdot 0.5CH_3CN$: C, 36.05; H, 3.29; N, 13.61. Found: C, 36.21; H, 3.65; N, 13.66. ^1H NMR (DMSO-d_6) main species: δ 7.85 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-H_{para}), 7.44 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-H_{meta}), 7.36 (s, 2H, NCH), 7.26 (s, 2H, NCH), 5.70 (d, $^2J_{HH}$ = 14.1 Hz, 2H, NCHH′C_{Ar}), 5.26 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCHH′C_{Ar}), 4.99–4.90 (m, 2H, NCHH′CH_2), 4.43–4.37 (m, 2H, NCHH′CH_2), 2.45–2.35 (m, 1H, NCH_2CHH'), 1.88–1.78 (m, 1H, NCH_2CHH'). ^{13}C NMR (DMSO-d_6) main species: δ 162.4 (NCN), 154.0 (Ar-C_{ortho}), 138.3 (Ar-C_{para}), 123.6 (NCH), 121.7 (Ar-C_{meta}), 120.1 (NCH), 53.7 (NCH_2C_{Ar}), 52.6 (NCH_2CH_2), 31.0 (NCH_2CH_2). ESI-MS (positive ions, CH_3CN): m/z 1010.7 $[Pd_2L_2Br_3]^+$, 506.6 $[PdLBr(CH_3CN)]^+$, 466.0 $[PdLBr]^+$.

$PdBr_2(L^{xylyl})$. Yield: 68%. Anal. Calcd for $C_{21}H_{19}Br_2N_5Pd$: C, 41.51; H, 3.15; N, 11.53. Found: C, 40.72; H, 3.24; N, 11.14. ^1H NMR (DMSO-d_6) main species: δ 7.93–7.92 (m, 2H, Ar_{xyl}-H_{ortho}) 7.86–7.81 (m, 1H, Ar_{pyr}-H_{para}), 7.73 (s, 2H, NCH), 7.48–7.42 (m, 6H, NCH, Ar_{pyr}-H_{meta}, Ar_{xyl}-H_{meta}), 6.71 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCHH′C_{xyl}), 5.75 (d, $^2J_{HH}$ = 13.5 Hz, 2H, NCHH′C_{pyr}), 5.26 (d, $^2J_{HH}$ = 13.5 Hz, 2H, NCHH′C_{pyr}), 5.19 (d, $^2J_{HH}$ = 14.4 Hz, 2H, NCHH′C_{xyl}). ^{13}C NMR (DMSO-d_6) main species: δ 161.1 (NCN), 154.5 (Ar_{pyr}-C_{ortho}), 138.7 (Ar_{pyr}-C_{para}), 135.2 (Ar_{xyl}-C_{ipso}), 131.1 (Ar_{xyl}-C_{ortho}), 129.2 (Ar_{xyl}-C_{meta}), 125.1 (NCH), 120.9 (Ar_{pyr}-C_{meta}), 120.5 (NCH), 54.4 (NCH_2C_{pyr}), 50.8 (NCH_2C_{xyl}). ESI-MS (positive ions, CH_3CN): m/z 1134.8 (42%) $[Pd_2L_2Br_3]^+$, 605.8 (14%) $[PdLBr_2 - 2H]^+$, 568.7 (30%) $[PdLBr(CH_3CN)]^+$, 528.1 (100%) $[PdLBr]^+$.

$PdBr_2(L^{butyl})$. Yield: 60%. Anal. Calcd for $C_{17}H_{19}Br_2N_5Pd$: C, 36.47; H, 3.42; N, 12.52. Found: C, 36.71; H, 3.45; N, 12.63. The NMR characterization data of the main species in solution matched those previously reported for the same complex.[2] ESI-MS (positive ions, CH_3CN): m/z 1038.8 (90) $[Pd_2L_2Br_3]^+$, 557.7 (19%) $[PdLBr_2 - 2H]^+$, 479.9 (65%) $[PdLBr]^+$, 398.1 (100%) $[PdL]^+$.

$PtBr_2(L^{propyl})$. Yield: 76%. Anal. Calcd for $C_{16}H_{17}Br_2N_5Pt$: C, 30.30; H, 2.70; N, 11.04. Found: C, 30.61; H, 2.61; N, 10.44. ^1H NMR (DMSO-d_6): δ 7.91 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H_{para}), 7.52–7.47 (m, 4H, NCH), 7.41 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-H_{meta}), 5.52–5.35 (m, 4H, NCH_2C_{Ar}), 4.91–4.79 (m, 2H, NCHH′CH_2), 4.48–4.38 (m, 2H, NCHH′CH_2), 2.44–2.37 (m, 1H, NCH_2CHH'), 1.94–1.88 (m, 1H, NCH_2CHH'). ^{13}C NMR (DMSO-d_6): δ 153.6, 153.4 (Ar-C_{ortho}), 149.7 (NCN), 138.8 (Ar-C_{para}), 124.0, 123.8 (NCH), 122.5, 122.2 (Ar-C_{meta}), 121.1, 121.0 (NCH), 53.8, 53.5 (NCH_2C_{Ar}), 52.8, 52.4 (NCH_2CH_2), 31.3 (NCH_2CH_2). ^{15}N NMR (DMSO-d_6): δ 312. ^{195}Pt NMR (DMSO-d_6): δ −2245. Crystals of the compound suitable for X-ray diffraction were grown upon slow diffusion of diethyl ether into a solution of the complex in *N,N*-dimethylformamide.

$PtBr_2(L^{xylyl})$. Yield: 40%. Anal. Calcd for $C_{21}H_{19}Br_2N_5Pt$: C, 36.20; H, 2.75; N, 10.06. Found: C, 36.07; H, 2.80; N, 9.34. ^1H NMR (DMSO-d_6): δ 7.99–7.89 (m, 3H, Ar_{xyl}-H_{ortho}, Ar_{pyr}-H_{para}), 7.87 (s, 2H, NCH), 7.63 (s, 2H, NCH), 7.55–7.46 (m, 4H, Ar_{pyr}-H_{meta}, Ar_{xyl}-H_{meta}), 6.67 (m, 2H, NCHH′C_{xyl}), 5.57 (d, $^2J_{HH}$ = 13.8 Hz, 1H, NCHH′C_{pyr}), 5.40–5.30 (m, 5H, NCHH′C_{pyr}, NCHH′C_{xyl}). ^{13}C NMR (DMSO-d_6): δ 154.1, 153.8 (Ar_{pyr}-C_{ortho}), 148.5 (NCN), 139.2 (Ar_{pyr}-C_{para}), 134.8, 134.7 (Ar_{xyl}-C_{ipso}), 131.4 (Ar_{xyl}-C_{ortho}), 129.6 (Ar_{xyl}-C_{meta}), 125.5, 125.4 (NCH), 121.5 (Ar_{pyr}-C_{meta}), 120.9 (NCH), 54.6, 54.2 (NCH_2C_{pyr}), 50.8, 50.6 (NCH_2C_{xyl}). ^{195}Pt NMR (DMSO-d_6): δ −2188.

$PtBr_2(L^{butyl})$. Yield: 58%. Anal. Calcd for $C_{17}H_{19}Br_2N_5Pt$: C, 31.50; H, 2.95; N, 10.80. Found: C, 31.91; H, 3.18, N, 10.81. ^1H NMR (DMSO-d_6): δ 7.93 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H_{para}), 7.56–7.45 (m, 6H, NCHand Ar-H_{meta}), 5.54–5.32 (m, 4H, NCH_2C_{Ar}), 5.20–5.06 (m, 2H, NCH_2CH_2), 4.22–4.18 (m, 2H, NCH_2CH_2), 1.97 (bs, 2H, NCH_2CH_2), 1.29–1.11 (m, 2H, NCH_2CH_2). ^{13}C NMR (DMSO-d_6): δ 155.5 (Ar-C_{ortho}), 149.7 (NCN), 139.0 (Ar-C_{para}), 125.5 (Ar-C_{meta}), 122.0 (NCHCHN), 54.5 (NCH_2C_{Ar}), 47.0 (NCH_2CH_2), 25.0 (NCH_2CH_2).

Oxidation of the Pd(II) and Pt(II) Complexes with Bromine. *General Procedure.* In a 50 mL round-bottomed flask were placed the complex reagent (50–100 mg) and the minimum quantity of DMSO necessary to dissolve it. Around 9 equiv of bromine was then added, and the reaction mixture was stirred at room temperature overnight. The addition of CH_2Cl_2 (10–20 mL) caused the precipitation of a yellow solid, which was filtered, washed with 3 mL of CH_2Cl_2, and dried at reduced pressure.

$PtBr_4(L^{propyl})$. Yield: 25%. Anal. Calcd for $C_{16}H_{17}Br_4N_5Pt\cdot 0.8C_2H_6OS\cdot 0.6Br_2$: C, 22.17; H, 2.31; N, 7.35. Found: C, 21.68; H, 2.35; N, 7.38. ^1H NMR (DMSO-d_6): δ 8.36 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H_{para}), 7.89 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-H_{meta}), 7.75 (d, $^3J_{HH}$ = 1.5 Hz, 2H, NCHCHN), 7.65 (d, $^3J_{HH}$ = 1.8 Hz, 2H, NCHCHN), 6.99 and 5.90 (AB system, 4H, NCH_2C_{Ar}), 5.92–5.80 (m, 2H, NCH_2CH_2), 4.57–4.50 (m, 2H, NCH_2CH_2), 2.72–2.54 (m, 1H, NCH_2CH_2), 2.18–1.96 (m, 1H, NCH_2CH_2). ^{13}C NMR (DMSO-d_6): δ 156.9 (Ar-C_{ortho}), 143.2 (Ar-C_{para}), 127.3 (NCHCHN), 126.6 (Ar-C_{meta}), 123.4 (NCHCHN), 117.5 (NCN), 56.6 (NCH_2C_{Ar}), 49.8 (NCH_2CH_2), 30.3 (NCH_2CH_2). ^{15}N NMR (DMSO-d_6): δ 183. ^{195}Pt NMR (DMSO-d_6): δ −253. ESI-MS (positive ions, CH_3CN): m/z 713.7 (100%) $[PtLBr_3]^+$, 634.8 (37%) $[PtLBr_2]^+$, 594.8 (44%) $[PtLBr(CH_3CN)]^+$, 571.6 (35%) $[PtLBr(H_2O)]^+$, 554.0 (24%) $[PtLBr]^+$.

$PtBr_4(L^{xylyl})$. Yield: 30%. Anal. Calcd for $C_{21}H_{19}Br_4N_5Pt\cdot 1.3C_2H_6OS\cdot 1.1Br_2$: C, 25.09; H, 2.39; N, 6.20. Found: C, 25.10; H, 2.38; N, 6.22. ^1H NMR (DMSO-d_6): δ 8.35–8.29 (m, 3H, Ar_{pyr}-H_{para} and NCH), 8.00–7.96 (m, 2H, Ar_{xyl}-H), 7.85–7.77 (m, 4H, Ar_{pyr}-H_{meta} and NCH), 7.43–7.40 (m, 2H, Ar_{xyl}-H), 7.30 (d, $^3J_{HH}$ = 15.3 Hz, 2H, NCH_2C_{xyl}), 6.91 (d, $^3J_{HH}$ = 18.3 Hz, 2H, NCH_2C_{pyr}), 5.87 (d, $^3J_{HH}$ =

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18.6 Hz, 2H, NCH_2C_{pyr}), 5.46 (d, $^3J_{HH}$ = 15.0 Hz, 2H, NCH_2C_{xyl}). ^{13}C NMR (DMSO-d_6): δ 156.3 (Ar_{pyr}-C_{ortho}), 144.3 (Ar_{pyr}-C_{para}), 136.5 (Ar_{xyl}-C_{ipso}), 132.4 (Ar_{xyl}-C), 130.7 (Ar_{xyl}-C), 127.0 (NCH), 126.8 (NCH), 124.9 (Ar_{pyr}-C_{meta}), 116.2 (NCN), 55.4 (NCH_2C_{pyr}), 49.3 (NCH_2C_{xyl}). ^{195}Pt NMR (DMSO-d_6): δ −186. ESI-MS (positive ions, CH_3CN): m/z 775.8 (6%) $[PtLBr_3]^+$, 693.9 (12%) $[PtLBr_2]^+$, 616.1 (34%) $[PtLBr]^+$.

$PtBr_4(L^{butyl})$. Yield: 65%. Anal. Calcd for $C_{17}H_{19}Br_4N_5Pt{\cdot}0.4Br_2$: C, 23.52; H, 2.20; N, 8.08. Found: C, 23.86; H, 2.22; N, 7.92. ^1H NMR (DMSO-d_6): δ 8.36 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar-H_{para}), 7.90−7.55 (d, Ar-H_{meta} and NCH), 6.92 and 5.92 (AB system, 4H, NCH_2C_{Ar}), 5.80 (m, 2H, NCH_2CH_2), 4.38 (m, 2H, NCH_2CH_2), 2.00 (m, 1H, NCH_2CH_2), 1.41 (m, 1H, NCH_2CH_2). ^{13}C NMR (DMSO-d_6): δ 156.4 (Ar-C_{ortho}), 144.1 (Ar-C_{para}), 127.0 (Ar-C_{meta}), 126.5 (NCH), 126.0 (NCH), 116.5 (NCN), 56.4 (NCH_2C_{Ar}), 46.3 (NCH_2CH_2), 45.9 (NCH_2CH_2), 24.8 (NCH_2CH_2), 24.6 (NCH_2CH_2). ^{195}Pt NMR (DMSO-d_6): δ −141. ESI-MS (positive ions, CH_3CN): m/z 727.7 (100%) $[PtLBr_3]^+$, 646.9 (27%) $[PtLBr_2]^+$, 568.0 (67%) $[PtLBr]^+$.

Catalytic Tests in the Sonogashira Reaction. The reaction protocol was derived with some modification from a publication by Samantaray et al.[6] General procedure: In a Schlenck tube were introduced under an inert atmosphere 1 equiv of aryl halide (around 0.600 mmol), 2 equiv of base (K_2CO_3 or Cs_2CO_3), and 1 mol % catalyst. A 10 mL amount of a mixture DMF/H_2O (3:1) was then added, and the reaction mixture was left to stir for a few minutes. Finally, 2 equiv of phenylacetylene was added, and the tube was then placed in an oil bath thermostated at the reaction temperature (usually 100 °C). Samples of the reaction mixture (1 mL) were taken at intervals and analyzed by ^1H NMR ($CDCl_3$) after solvent removal.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental procedures and X-ray crystallographic details in cif format for complex $PtBr_2(L^{propyl})$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +39-049-8275216. Fax: +39-049-8275223. E-mail: andrea.biffis@unipd.it.

Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

In the version of this paper published on April 22, 2014, there was an error in the reaction scheme given in Table 1. The version of the paper that appears as of May 12, 2014, has the correct reaction scheme.