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Synthesis of electron-rich platinum centers: Platinum^0(carbene)(alkene)$_2$ complexes

Marcel A. Duin [a], Martin Lutz [b], Anthony L. Spek [b], Cornelis J. Elsevier [a,*]

[a] *Van 't Hoff Institute of Molecular Sciences, Molecular Inorganic Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

[b] *Bijvoet Center for Biomolecular Research, Vakgroep Kristal- en Struktuurchemie, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands*

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Abstract

The synthesis and molecular structure of the zero-valent platinum-mono-carbene-bis-alkene complexes [Pt^0(NHC)(dimethyl fumarate)$_2$] (NHC = 1,3-dimesityl-imidazol-2-ylidene (**1a**); 1,3-dimesityl-dihydroimidazol-2-ylidene (**2a**); diphenyl-dihydroimidazol-2-ylidene (**2b**) are described. Two routes have been evaluated for the synthesis of **1a** and **2a**, involving reaction of a zero-valent platinum compound either with an isolated carbene ligand, or with an in situ generated carbene ligand. The in situ method proved to be easier and gave similar yields of about 50% after crystallization. Attempts have been made to synthesize similar compounds with *N*-phenyl and *N*-alkyl groups, of which the latter met with little success. However, (1,3-diphenyl-dihydroimidazol-2-ylidene)-bis(η^2-dimethyl fumarate) platinum(0) (**2b**) could be obtained in 49% yield, after crystallization, from the appropriate *Wanzlick* dimer.

Compound **1a** reacts with H_2 and D_2 in sequences of oxidative addition, migration–insertion involving dimethyl fumarate, and reductive elimination to form neutral hydrido platinum (II) carbene complexes, probably containing a metallacyclic (R)–C=O ... Pt unit.

Keywords: N-Heterocyclic carbene; Alkene; Low-valent; Insertion; Addition; C–H activation

1. Introduction

N-Heterocyclic carbenes (NHCs) are being applied more and more frequently as ligands in metal-mediated synthesis and homogeneous catalysis [1,2]. For almost all d^{10}-metals, complexes with NHC ligands have been reported, which are able to catalyze reactions, such as Heck and Suzuki coupling (Pd, Ni) [3–7], aryl amination (Pd, Ni) [8,9], hydrosilylation (Pt) [10,11], Grignard cross-coupling (Ni) [12] and Stille coupling (Pd) [13]. These transition-metal-NHC-catalysts have several advantages and potential for catalysis [4]. Promising features are, apart from generally good to high turnover numbers and high rates, the excellent catalyst stability, due to high thermal and hydrolytic durability resulting from exceptionally stable M–C bonds, i.e., long shelf-life and stability to oxidation. Fortunately, many NHC and their metal complexes are readily accessible, requiring only stoichiometric amounts of the free ligand; there is generally no need to employ an excess of the NHC.

Despite the increasing interest in this class of NHC d^{10}-metal complexes, relatively few examples of isolated and well-characterized nickel(0)-, palladium(0)- or platinum(0)-carbene complexes are known [10–19]. One of these compounds (Fig. 1, left) is a highly efficient catalyst for for telomerization of 1,3-dienes with alcohols

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* Corresponding author. Tel.: +31 0 205255653; fax: +31 0 205256456.
E-mail address: elsevier@science.uva.nl (C.J. Elsevier).

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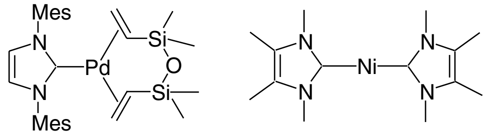

Fig. 1. Pd(0)- and Ni(0)-NHC complexes reported by Beller [14] and Cavell [15].

(TON = 2.67 × 10^5) [14]. Concerning platinum (0) complexes with NHCs, apart from the seminal report by Arduengo et al. describing the synthesis of a platinum (0) biscarbene compound [19], only recently several isolated complexes (Fig. 2) have been reported by Marko and by our group, that are active in hydrosilylation [10,11]. Although the Arduengo complex is formally a 14-electron species, it is thermally rather stable, which is probably due to the large mesityl-substituents on the N-atoms of the imidazolium-based carbene. In this way the platinum center is shielded by these large ligands and thereby very difficult to approach by other ligands or reagents. Since the $Pt^0(IMes)_2$ complex lacks reactivity, we reasoned that one of its carbene ligands should be replaced by one or two more labile ligands, thereby facilitating dissociative routes into active platinum complexes for, for instance, oxidative addition and catalysis.

As an approach to compounds having an electron-rich platinum center, we endeavored to synthesize a new class of platinum (0) complexes containing one carbene ligand and two alkenes. The carbene ligand is deemed to endow a rather high electron density on the metal center, which may have an accelerating effect on oxidative addition of C–X, C–H and H–H bonds to such compounds. The alkene should dissipate some of the electron density and provide reasonable thermal stability, yet be an easily (relative to the NHC) dissociating ligand.

Previously, the efficient synthesis of a number of zero-valent [$Pt^0(L)_2$(fumarate)] and [Pt^0(L)(fumarate)$_2$] complexes has been detailed [20]. We reasoned that, although the fumarate will – due to π-backdonation from the metal center – be relatively strongly bonded in many [$Pt^0(L)_2$(fumarate)] and [Pt^0(L)(fumarate)$_2$] compounds, it will probably be less strongly bonded than an NHC type carbene ligand in [Pt^0(NHC)(fumarate)$_2$]. So, although such compounds would be thermally stable, they could yet be prone to fumarate dissociation, opening pathways to activity in catalysis.

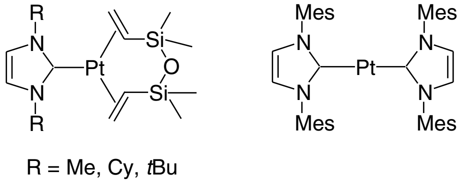

Fig. 2. Pt(0) NHC-complexes reported by Markó [10] and Arduengo [19].

The pre-eminent method for the synthesis of these platinum complexes in our hands started from $Pt(nbe)_3$ (nbe = norbornene) or $Pt(cod)_2$ (cod = 1,5-cyclooctadiene). In this paper, we describe the synthesis of novel compounds [Pt^0(NHC)(dmfu)$_2$], which were prepared by this approach [21]. Furthermore, the reactivity of these novel compounds towards dihydrogen will be reported.

2. Results and discussion

2.1. Synthesis of [Pt(IMes)(dmfu)$_2$] and [Pt(SIMes)(dmfu)$_2$]

These zero-valent platinum(NHC)bis(dimethyl fumarate) compounds were prepared via two methods. The first method (A, see Scheme 1) consists of two steps: First, the free carbene, 1,3-dimesityl-imidazol-2-ylidene (IMes) or 1,3-dimesityl-dihydroimidazol-2-ylidene (SIMes) has been prepared [22]. Second, one equivalent of [$Pt(cod)_2$] (cod = 1,5-dicyclo-octadiene) and two equivalents of the alkene, dimethyl fumarate (dmfu), were added to the free carbene in THF at room temperature. Immediate reaction resulted in the formation of thermally stable, white products in good yields (55–73%).

The second method (B, see Scheme 1) concerns the reaction of $Pt(cod)_2$ with two equivalents of dmfu, one equivalent of a imidazolium salt (IMesHCl) or imidazolinium salt (SIMesHCl) and sodium hydride. The latter is used as a base for deprotonation of (S)IMesHCl, providing the free carbene in situ. This method is somewhat more time consuming than the first one, but obviates the additional step of isolating the free carbene; overall this method benefits from easier workup. $Pt(nbe)_3$ can be used as the starting material instead of [$Pt(cod)_2$]. However, according to ^1H NMR spectroscopy, overnight stirring yields a mixture of [Pt(carbene)(dmfu)(nbe)] and Pt(carbene)(dmfu)$_2$. So, the substitution of the last nbe from Pt(carbene)(dmfu)(nbe) to Pt(carbene)(dmfu)$_2$ is not complete at room temperature. It appeared to be necessary to add more dmfu, as well as to stir the reaction mixture at elevated temperature (40–50 °C). In situ preparation of $Pt(cod)_2$ by addition of cod to $Pt(nbe)_3$ [23] before adding the other reagents, can overcome this problem. However, employing $Pt(cod)_2$ is to be preferred, and leads to overall exhaustive displacement of cod by using two equivalents of dimethyl fumarate.

The [Pt(carbene)(η^2-alkene)$_2$] complexes [Pt(IMes)(dmfu)$_2$], (**1a**, IMes = 1,3-dimesityl-imidazol-2-ylidene) and [Pt(SIMes)(dmfu)$_2$], (**2a**, SIMes = 1,3-dimesityl-dihydroimidazol-2-ylidene) can be handled in air without significant decomposition and are stable for