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Note

New PC(sp^3)P pincer complexes of platinum and palladium☆

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ABSTRACT

We describe the synthesis, characterization and properties of the new electrophilic palladium and platinum complexes bearing electron-rich PC(sp^3)P pincer ligands. We found that Lewis acidity of the compounds is low due to the strong σ-donation of the sp^3-carbometalated ligand backbone.

1. Introduction

Carbometalated pincer-type complexes were discovered over the past 35 years (Fig. 1) [1,2]. Since then, these compounds have been studied extensively and became very popular in many areas of chemistry. For instance, they are widely used as homogeneous catalysts and stoichiometric promoters in a variety of chemical transformations [3], as building blocks for the construction of advanced functional materials [4] and as components in supramolecular systems [4,5]. Furthermore, carbometalated pincer complexes were found relevant to biological applications [6].

Carbometalated pincer complexes are organometallic compounds bearing tridentate monocarbanionic ligands that coordinate metal in a η^3-*mer* fashion. This coordination mode gives rise to the formation of the thermodynamically favored C–M bond-sharing bicyclic structures [7] that are usually translated into robust materials featuring exceptional thermal stability [8]. On the other hand, the ligand scaffold and the coordinating groups can be tailored to control reactivity of the carbon-metal bond by controlling steric and electronic environment of the metal center [3,9]. The combination of these factors makes pincer complexes very popular in many areas of chemistry.

By far the most popular scaffold used to design DCD pincer ligands relies on aromatic moieties (Fig. 1, left). This is not surprising because availability of the synthetic methods for their facile modification highlight the C(sp^2)-metalated pincer complexes as ideal candidates for systematic studies.

In opposite, reports on the chemistry and practical applications of aliphatic C(sp^3)-metalated pincer complexes (Fig. 1, right) are far more occasional [10], arguably, because the stronger σ-donating nature of the sp^3–hybridized ligand significantly increases electron density at the metal center turning them into less thermally stable [1] and more difficult-to-manipulate compounds [11].

Recently, we demonstrated the utilization of the barrelene-type scaffold, as a platform for the construction of the first representative of a new class of sp^3-carbometalated complexes [12–14]. The desired compounds can be synthesized via either the C–H activation or cycloaddition strategies (Scheme 1). The traditional C–H activation of *bis*-phosphinated barrelenes is somewhat limited to large electrophilic metals (*e.g.* iridium, platinum and ruthenium) due to a relatively low acidity of the methine hydrogen [15], however the cycloaddition route perfectly complements it, giving raise to diverse libraries of the target compounds.

In contrast to the most of known all-aliphatic C(sp^3)-metalated compounds, the novel ones exhibited excellent thermal and conformational stability even under very harsh and non-inert conditions, likely, due to the lack of labile α- or β-hydrogens. Moreover, they proved themself as highly active catalysts for the transfer hydrogenation of ketones [12], as well as transfer [16] and acceptorless dehydrogenation of alcohols [17].

In this article, we wish to report on the synthesis and characterization of new derivatives of PC(sp^3)Ps addressing a possible effect of σ-donating nature of the sp^3–hybridized ligands on the properties of the complexes with more electrophilic metal centers.

☆ The paper is dedicated to Dr. Shmuel Cohen on the occasion of his retirement.

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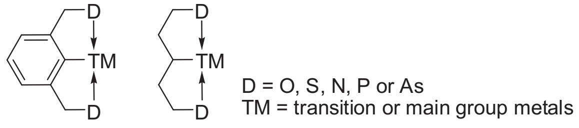
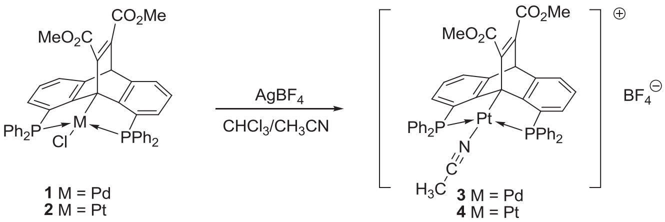


Fig. 1. Carbometalated pincer complexes.



Scheme 2.

2. Results and discussion

Cationic complexes were prepared by reacting the previously reported precursors **1**–**2** with silver tetrafluoroborate (Schemes 2 and 3) [14]. The target complex **3** was obtained as pale yellow powder in 75% yield, while **4** formed as white solid in 69% yield. Both were found completely stable toward air and moisture in both solid state and solution.

All new complexes have been characterized by NMR spectroscopy using samples prepared in $CDCl_3$. Observation of one signal in the $^{31}P\{^1H\}$ NMR spectra in these complexes confirmed the equivalence of the two phosphorus nuclei, while the magnitude of the coupling constant measured for the platinum complex ($J = 1518$ Hz) supported their mutually *trans* disposition [18]. The presence of a coordinated acetonitrile molecule in **3** and **4** was indicated by a singlet resonance in their ^1H NMR spectra ($CDCl_3$).

Despite quite an unambiguous characterization of the complexes by NMR, x-ray crystallographic analysis of the species was undertaken (Fig. 2). As one would expect for the complexes bearing strongly bent dibenzobarrelene-based ligands, the palladium center in **3** is distorted from the square planar geometry toward a butterfly-like environment. For example, the observed interplanar angle between the C(1)–Pd(1)–P(1) and C(1)–Pd(1)–P(2) planes is 157.2°, while the C(1)–Pt(1)–N(1) angle is 173.34(2)°.

Another series of complexes bearing labile carboxylate ligands has been prepared via interaction of **2** and **5** with silver trifluoroacetate and silver 2-ethylheptanoate according to Scheme 2. The reactions were virtually quantitative according to the ^{31}P NMR monitoring and the products **6**–**9** were isolated in 75–90% yield as white solids.

Single crystals grown from the acetonitrile/chloroform solution of **8** were analyzed using x-ray crystallography. We found that platinum center is strongly distorted from the square planar geometry toward a butterfly-like environment (the ORTEP illustrations are shown on Fig. 3). For example, the observed P(1)–Pt–P(2), C(1)–Pt–O(1) angles for **8** are 156.99(4)° and 177.44(4)°, respectively. Other bonds angles and distances fall into the usual range. The trifluoroacetate ligand is clearly bound in a η^1 fashion.

Due to the lability of the carboxylate ligands, their complexes are often seen as neutral analogs of the cationic ones. However, a greater electrophilicity of the metal centers in both the naked (**3**–**4**) and "masked" (**6**–**9**) cationic complexes bearing the electron-rich PC(sp^3)P ligands was not pronounced at all, as reflected in their very slight downfield ^{31}P chemical shifts compared to those of the corresponding parent compounds (**1**, **2** and **5**), as well as in the M···NCMe M···O_2CR bond lengths that fall within the average range [19]. For example, the palladium-based **3** demonstrated a shift of only ca. 6 ppm (δ 47.8 vs 41.9 for **1**), while in the case of **4** and **6**–**9** the difference between them was summed up less than 1 ppm.

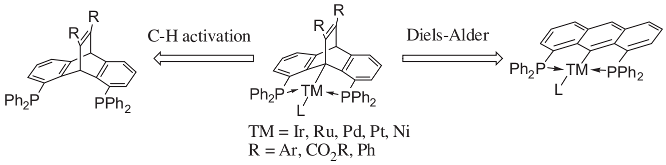
To get further clue into the level of Lewis acidity of the metal centers, the complexes **3**–**4** were dissolved and stirred in 1:1 CH_3CN/pyridine mixture. NMR analysis of the product mixture taken after evaporation of the solvent showed almost equal distribution of the acetonitrile and pyridine adducts (based on the integration of the signal assigned to the methyl carboxylate groups). Similarly, full conversion of **6** into to the parent **2** by treatment with excess of LiCl proceeds slowly and requires long reaction time of 48 h. This behavior, apparently, suggests that positive charge on the metal centers is almost fully compensated by the σ-donation from the sp^3-hybridized backbone [20].

Furthermore, attempted employment of the new complexes in electrophilic metal-catalyzed reactions met a limited success. So aldol addition of methyl α-isocyanoacetate to benzaldehyde that is known to be promoted by cationic pincer complexes failed completely using **3** and **4** supporting a very low Lewis acidity of the cationic complexes bearing the new ligands [21].

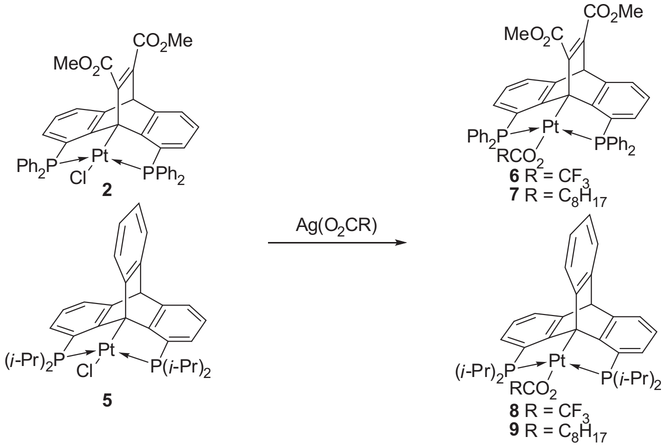
Complexes **6**–**9** were found moderately active in Pt-catalyzed H/D exchange at aromatic rings, a benchmark reaction often used to evaluate the reactivity of the carbometalated compounds. A brief experimentation showed that H/D exchange of benzene does take place in the presence of 2 mol% of **6**–**8** in CD_3CO_2D, CF_3CO_2D, CD_3OD or D_2O although complete deuterium incorporation was achieved only in TFA-*d* using **6** and **8** (Table 1).

In a typical run, a mixture of benzene, 2 mol% catalyst, and deuterium source were sealed in a 20 ml pressure tube and heated at 100 °C for 24 h. The obtained mixture was extracted with hexane after cooling to room temperature. The extracts were concentrated and purified using short silica-gel column chromatography. The product was analyzed by GC–MS and ^1H NMR.

Compared to the known catalytic systems [22], the activity is modest; it was shown that **6** and **8** promote complete deuteration



Scheme 1.



Scheme 3.

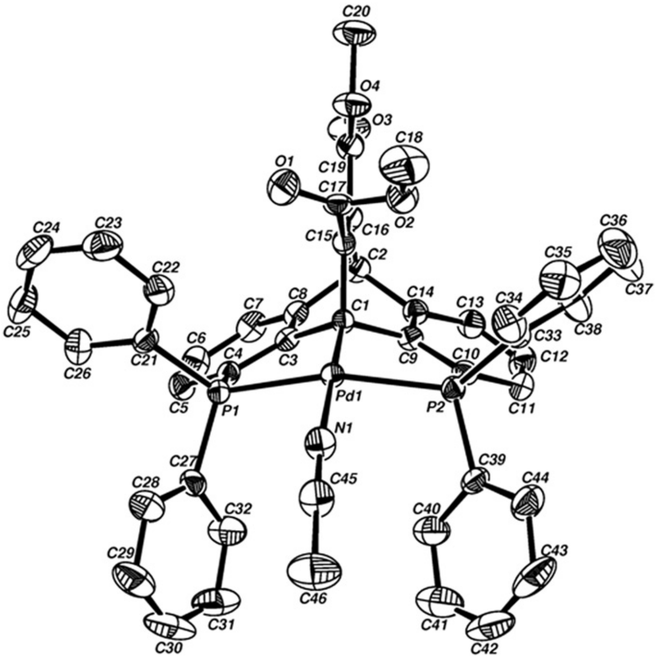


Fig. 2. ORTEP drawing (50% probability ellipsoids) of the structures **3**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg.) for 3: Pd1–N1 (2.082(2)), Pd1–C1 (2.056(2)), Pd1–P1 (2.3032(7)), Pd1–P2 (2.2958(7)). C15–C1–Pd1 (120.81(17)), C1–Pd1–N1 (173.46(10)), P1–Pt1–P2 (155.50(2)). Selected bond lengths (Å) and angles (deg.) for 4: Pt1–N1 (2.009(12)), Pt1–C1 (1.924(11)), Pt1–P1 (2.304(3)), Pt1–P2 (2.305(3)). C15–C1–Pt1 (128.0(8)), C1–Pt1–N1 (176.7(5)), P1–Pt1–P2 (156.46(12)).

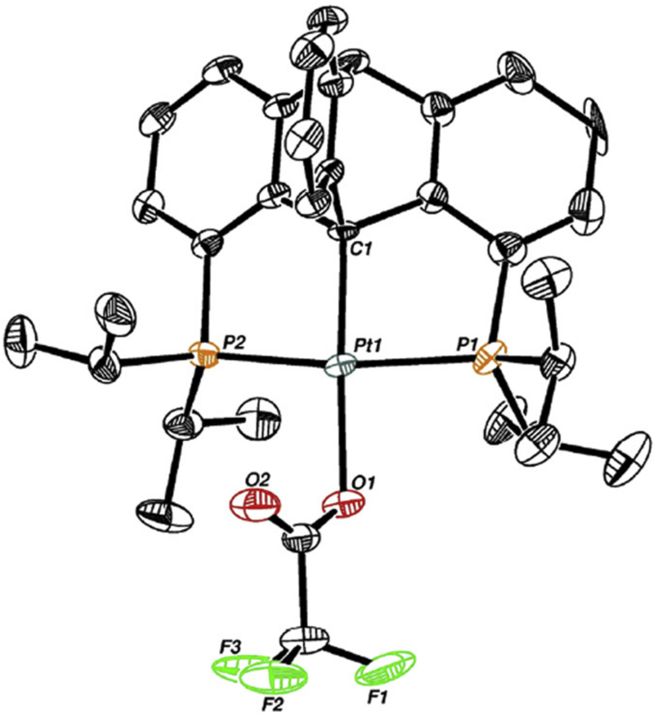
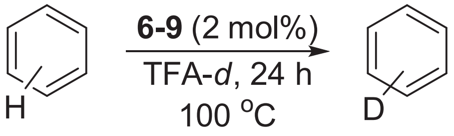


Fig. 3. ORTEP drawing (50% probability ellipsoids) of the structures **8**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg.) for **3**: Pt1–O1 (2.139(3)), Pt1–C1 (2.045(4)), Pt1–P1 (2.2797(12)), Pt1–P2 (2.2980(11)), C33–O1 (1.249(7)), C33–O2 (1.206(7)). C15–C1–Pd1 (120.2(3)), C1–Pt1–O1 (177.44(18)), P1–Pt1–P2 (156.99(4)).

Table 1
Representative results of Pt-catalyzed H/D exchange at arenes.



Run	Catalyst	Substrate	%D incorporation
1	**6**	Benzene	99
2	**7**	Benzene	79
3	**8**	Benzene	99
4	**9**	Benzene	81
5	**6**	Toluene	32
6	**8**	Toluene	26
7	**6**	Tetralin	50

of benzene (Table 1, runs 1 and 3), although deuterium incorporation into toluene and tetralin under the same conditions is only 32 and 50%, respectively.

To conclude, in this work we synthesized, characterized and examined properties of the some new cationic complexes of palladium and platinum bearing PC(sp^3)P pincer ligands. It was found that positive charge on the metal centers is compensated by electron-rich backbone. These observations suggest that catalytic applications requiring high Lewis acidity of the metal centers, apparently, cannot be targeted using this, otherwise powerful, family of compounds.

Acknowledgment

This research was supported by the Israel Science Foundation. We especially thank Dr. Shmuel Cohen for solving X-Ray structures.

Appendix A. Supplementary material

CCDC 843593; **3**, 843594; **4**, 843595; **8** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.11.007.

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