



Decoding catalytic activity of platinum carbene hydrosilylation catalysts



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ABSTRACT

A series of complexes of the formula [Pt(dvtms)(ImPy-R)] (dvtms = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane, ImPy-R = 2-R-imidazo[1,5-a]pyridine-3-ylidene; R = 4-cyanophenyl (**4a**), 4-trifluoromethylphenyl (**4b**), phenyl (**4c**), 4-methoxyphenyl (**4d**), mesityl (**4e**), pentafluorophenyl (**4f**), *tert*-butyl (**4g**)) are presented. These compounds are synthesized from Karstedt's catalyst [Pt₂(dvtms)₃] and the respective imidazo[1,5-a]pyridinium salts using ^tBuOK as base. **4a–g** were characterized (¹H, ¹³C, ¹⁹F, ¹⁹⁵Pt NMR, EA, IR, UV–Vis) and investigated by cyclic voltammetry. The compounds are efficient and selective catalysts in the model hydrosilylation reaction of oct-1-ene with HSi₃O₂Me₇. The combination of spectroscopic and theoretical studies on the B3LYP/6-31G** level of theory reveals a distinct correlation of HOMO energy levels *E*_{HOMO}, oxidation potential *E*_{ox} and catalytic activity (TOF). The impact of the substitution pattern introduced at the ImPy-R ligand can be interpreted based on electronics (Hammett correlation) and sterics of the residues R.

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1. Introduction

Hydrosilylation is one of the most important industrial applications of homogeneous catalysis, providing access to a variety of useful products such as moldings, adhesives, release coatings, surfactants and fluids [1–9]. The reaction comprises the addition of a hydrosilane HSiR₃ to a carbon–carbon double or triple bond and is characterized by its atom-efficiency and broad substrate scope (Scheme 1). Owing to their unparalleled catalytic activity, industry still relies on platinum catalysts for this key transformation [1–17].

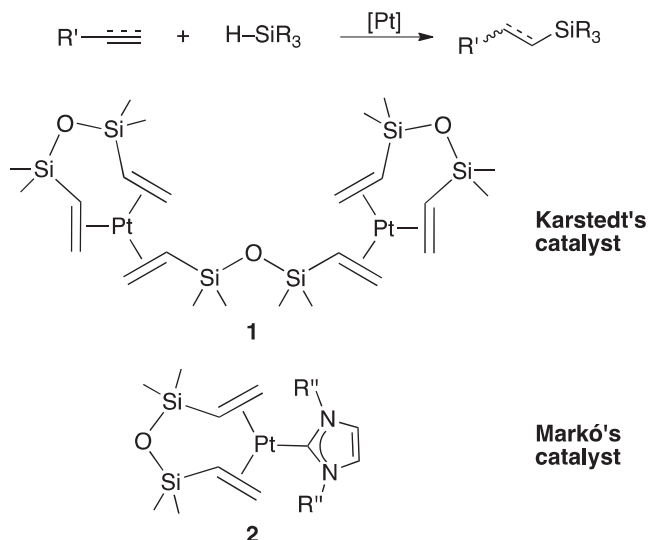
The use of *N*-heterocyclic carbene (NHC) ligands presented by Markó et al. has extended the scope of Pt(0) complexes in hydrosilylation [14–18]. The introduction of NHCs as spectator ligands often increases complex stability due to their strong σ -donating and poor π -accepting character [16,19]. Indeed, complexes of the type [Pt(dvtms)(NHC)] (Markó's catalyst, **2**; dvtms = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane) are stable toward air and moisture

and show remarkable selectivity and efficiency in hydrosilylation of alkenes and alkynes [14–17,20]. A number of structurally derived Pt(0) NHC complexes have been reported in recent years, designed to exploit the strong Pt–C_{carbene} bond while maintaining a high reactivity in hydrosilylation catalysis [18,20–23]. It has been established that steric encumbrance caused by bulky aryl substituents is instrumental for achieving high selectivity and catalytic activity [16].

Imidazo[1,5-a]pyridine-3-ylidenes (ImPy-R) rank among the strongest heteroatomic σ -donors and tally with 1,3-disubstituted imidazolylidenes in terms of steric demand [24–27]. Their bicyclic structure facilitates a unique stereoelectronic environment and has thus sparked interest in the catalytic application of derived transition metal complexes [24–30]. These characteristics render ligands of this type highly interesting candidates for a further development of Markó's catalyst, considering that, to the best of our knowledge, no reports of platinum complexes bearing ImPy-R ligands or their application in hydrosilylation are known to date. Thus, this report describes the synthesis and characterization of seven novel complexes of the type [Pt(dvtms)(ImPy-R)] (**4a–g**), a detailed study of their respective electronic features and their application in olefin hydrosilylation.

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Scheme 1. Hydrosilylation using Pt complexes. Karstedt's catalyst **1** [10,11] and Markó's catalyst **2** [14–17] are commonly used for hydrosilylation [1–9]. In this work, R' = mesityl.

2. Materials and methods

2.1. General remarks

Commercially available solvents and reagents were used without further purification. All reactions were carried out under ambient conditions. Elemental analyses were performed at the Microanalytical Laboratory of Technische Universität München. Spectroscopic data were recorded on the following instruments: IR spectra: Jasco FT/IR 460 PLUS; UV–Vis spectra: Varian Cary 50 spectrophotometer in a UV quartz cuvette (10 mm); NMR spectra: Bruker DPX-400, Bruker Avance III 400 and Bruker Avance III 500C. NMR peaks were referenced to the residual solvent signals [31]. **3b**, **3c–e** and **3g** were synthesized according to the reaction protocol published by Hutt et al. [25]. **3c** and **3f** were synthesized analogously to **3a** according to the same literature procedure [25].

2.2. Crystallographic details

For detailed information see [Supporting Information](#). Crystallographic Data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1440875 (**4e**) and CCDC 1440876 (**4g**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Computational details

All calculations were performed with GAUSSIAN-09 [32] using the density functional/Hartree–Fock hybrid method Becke3LYP [33–35] and the double- ζ 6-31G** basis set [36,37]. The Stuttgart-97 ECP was used to treat Pt [38,39]. No symmetry or internal coordinate constraints were applied during optimizations. All reported geometries were verified as being true minima by the absence of negative eigenvalues in vibrational frequency analysis. Reported Gibbs energies were computed at $T = 198.15$ K, $p = 1$ atm.

2.4. Cyclic voltammetry

Cyclic voltammograms were measured using a Gamry potentiostat employing a gastight three-electrode cell under an argon

atmosphere. A platinum disk electrode ($\varnothing = 1$ mm) was used as working electrode, and a Ti/Pt electrode employed as counter electrode. The potential was measured against Ag/AgCl (3.4 M KCl) and referenced to ferrocene (Fc/Fc⁺) as internal standard. A scan rate of 100 mV/s was employed. [NBu₄][PF₆] (0.1 M in dichloromethane) was used as base electrolyte and the concentration of the respective complex solution was [4] = 1 mM.

2.5. Hydrosilylation experiments

In a typical experiment, a pressure NMR tube was equipped with oct-1-ene (80.2 μ L, 0.51 mmol, 1.0 equiv), HSi₃O₂Me₇ (138.8 μ L, 0.51 mmol, 1.0 equiv), naphthalene (40 mg, 0.31 mmol) and 281 μ L of xylene-*d*₁₀. After a zero point ¹H NMR and preheating of the NMR, catalysis was started by injection of the catalyst ([Pt] = 300 ppm with respect to olefin and silane) in 200 μ L of xylene-*d*₁₀. The reaction was monitored by in situ ¹H NMR.

3b. Yield: 74% (193.3 mg, 0.47 mmol) – C₁₄H₁₀N₂F₉P calcd. C 41.19 H 2.47 N 6.86; found C 41.25 H 2.42 N 6.82. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 10.40 (d, 1H, ³J_{H,H} = 1.2 Hz, NHN), 8.87–8.78 (m, 1H, H_{ar}), 8.82 (s, 1H, H_{ar}), 8.65–8.56 (m, 1H, H_{ar}), 8.16 (m, 4H, H_{ar}), 7.95 (d, ³J_{H,H} = 9.3 Hz, 1H, H_{ar}), 7.37 (dd, 1H, ³J_{H,H} = 6.4, 9.6 Hz), 7.29 (t, 1H, ³J_{H,H} = 7.3 Hz). ¹³C NMR (126 MHz, DMSO-*d*₆, δ): 138.2 (NCN), 130.7 (C_{ar}), 130.4 (C_{ar}), 129.8 (C_{ar}), 127.6 (q, CF₃, ¹J_{C,F} = 3.8 Hz), 126.4 (C_{ar}), 125.5 (C_{ar}), 125.0 (C_{ar}), 124.3 (C_{ar}), 124.0 (C_{ar}), 122.3 (C_{ar}), 118.6 (C_{ar}), 118.4 (C_{ar}), 112.4 (C_{ar}). ¹⁹F NMR (376 MHz, DMSO-*d*₆, δ): –61.18 (s, 3F), –70.14 (t, ¹J_{P,F} = –711.2 Hz, 2F). ³¹P NMR (162 MHz, DMSO-*d*₆, δ): –144.21 (h, ¹J_{P,F} = –711.2 Hz, 1P).

3f. Yield: 68% (187.2 mg, 0.44 mmol) – C₁₃H₆F₁₁N₂P calcd. C 36.30 H 1.41 N 6.51; found C 36.44 H 1.27 N 6.39. ¹H NMR (500 MHz, DMSO-*d*₆, δ): 10.21 (s, 1H, NHN), 8.72 (d, ³J_{H,H} = 7.9 Hz, 1H, H_{ar}), 8.62 (s, 1H, H_{ar}), 8.01 (d, ³J_{H,H} = 9.2 Hz, 1H, H_{ar}), 7.42 (d, ³J_{H,H} = 16.0 Hz, 1H, H_{ar}), 7.35 (td, ³J_{H,H} = 7.0 Hz, ⁴J_{H,H} = 1.0 Hz, 1H, H_{ar}). ¹³C NMR (126 MHz, DMSO-*d*₆, δ): 143.5–143.2 (m, C_{ar}F), 141.5–41.1 (m, C_{ar}F), 138.5–138.3 (m, C_{ar}F), 136.6–136.4 (m, C_{ar}F), 129.9 (NCN), 128.8 (C_{ar}), 125.9 (C_{ar}), 124.6 (C_{ar}), 119.0 (C_{ar}), 118.4 (C_{ar}), 115.2 (C_{ar}) 131.23 (t, ¹J_{C,F} = 15.9 Hz, CF). ¹⁹F NMR (376 MHz, DMSO-*d*₆, δ): –70.16 (d, ¹J_{P,F} = 711.3 Hz, 6F), –146.25 (m, 2F), –149.71 (t, 1F, ³J_{F,F} = 23.1 Hz), –160.73 (m, 2F). ³¹P NMR (162 MHz, DMSO-*d*₆, δ): –144.22 (h, ¹J_{P,F} = –711.3 Hz, 1P).

4a. Yield: 82% (182.3 mg, 0.30 mmol) – C₂₂H₂₇N₃O₃Si₂ calcd. C 43.99 H 4.53 N 6.99; found C 44.37 H 4.65 N 7.01. ¹H NMR (500 MHz, CD₂Cl₂, δ): 8.00 (d, ³J_{H,H} = 7.8 Hz, 1H, H_{ar}), 7.83 (d, ³J_{H,H} = 8.4 Hz, 2H, H_{ar}), 7.67 (d, ³J_{H,H} = 8.6 Hz, 3H, H_{ar}), 7.36 (d, ³J_{H,H} = 9.4 Hz, 1H, H_{ar}), 6.87 (dd, ³J_{H,H} = 8.9 Hz, 6.6 Hz, 1H, H_{ar}), 6.52 (t, ³J_{H,H} = 7.0 Hz, 1H, H_{ar}), 2.48–1.68 (m, 6H, SiCH₂), 0.25 (s, 6H, SiCH_{3,eq}), –0.43 (s, 6H, SiCH_{3,ax}). ¹³C NMR (126 MHz, CD₂Cl₂, δ): 177.9 (NCN), 144.6 (C_{ar}), 133.2 (C_{ar}), 132.7 (C_{ar}), 129.3 (C_{ar}), 129.0 (C_{ar}), 128.5 (C_{ar}), 125.5 (C_{ar}), 123.6 (C_{ar}), 118.3 (C_{ar}), 117.6 (C_{ar}), 112.5 (C_{ar}), 112.2 (C_{ar}), 111.6 (CN), 41.4 (CH₂CHSi, ¹J_{Pt,C} = 158.8), 35.9 (CH₂CHSi, ¹J_{Pt,C} = 121.0), 1.4 (SiCH_{3,eq}), –2.3 (SiCH_{3,ax}). ¹⁹⁵Pt NMR (86 MHz, CD₂Cl₂, δ): –5339. UV–Vis: $\lambda_{\max} = 371$ nm, $\epsilon = 5941$ M^{–1} cm^{–1}. IR (solid): $\tilde{\nu} = 3007$ w, 2955 w, 2921 w, 2230.7 w, 1652 w, 1606 m, 1523 m, 1392 w, 1347 m, 1335 m, 1298 m, 1243 m, 1086 m, 1016 w, 982 m.

4b. Yield: 78% (185.6 mg, 0.29 mmol) – C₂₂H₂₇F₃N₂O₃Si₂ calcd. C 41.05 H 4.23 N 4.35; found C 40.91 H 4.33 N 4.36. ¹H NMR (400 MHz, CD₂Cl₂, δ): 8.05 (d, ³J_{H,H} = 8.3 Hz, 1H, H_{ar}), 7.82 (d, ³J_{H,H} = 7.9 Hz, 2H, H_{ar}), 7.74–7.61 (m, 3H, H_{ar}), 7.40 (d, ³J_{H,H} = 9.3 Hz, 1H, H_{ar}), 6.90 (dd, ³J_{H,H} = 9.3, 6.4 Hz, 1H, H_{ar}), 6.55 (t, ³J_{H,H} = 7.3 Hz, 1H, H_{ar}), 2.49–1.73 (m, 6H, SiCH₂), 0.27 (s, 6H, SiCH_{3,eq}), –0.45 (s, 6H, SiCH_{3,ax}). ¹³C NMR (126 MHz, CD₂Cl₂, δ): 177.3 (NCN), 144.1 (C_{ar}), 132.5 (C_{ar}), 130.3 (CCF₃, ²J_{C,F} = 35.3 Hz), 129.0 (C_{ar}), 126.3 (C_{ar}), 125.6 (C_{ar}), 124.2 (CF₃, ¹J_{C,F} = 270.9 Hz),

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