Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Data

Zero-valent ML_2 complexes of group 10 metals supported by terphenyl phosphanes. Synthesis of elusive Ni(0) bis-phosphane

M. Trinidad Martín,[a] Mario Marín,[a] Raquel J. Rama,[a] Eleuterio Álvarez,[b] Celia Maya,[b] Francisco Molina,[c] M. Carmen Nicasio*[a]

[a] *Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo 1203, 41071 Sevilla, Spain*

[b] *Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Avenida Américo Vespucio 49, 41092 Sevilla, Spain*

[c] *Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21071 Huelva, Spain*

mnicasio@us.es

Table of contents

1. General considerations.

All preparations and manipulations were carried out under oxygen-free nitrogen, using conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. Dimethyterphenyl phosphanes $PMe_2Ar^{Ph}{}_2$[1] and $PMe_2Ar^{Dtbp}{}_2$,[1b] $Pd(CH_2SiMe_3)_2(cod)$,[2] $PtCl_2(cod)$,[3] and $Ni(cod)_2$[4] were synthesized following described procedures. Reagents were purchased from commercial suppliers and used without further purification. Solution NMR spectra were recorded on a Bruker Avance DPX-300, Avance DRX-400 and Avance DRX-500 MHz spectrometer. The ^1H and ^{13}C resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to TMS, while ^{31}P was referenced to external H_3PO_4. Elemental analyses were performed by the Servicio de Microanálisis of the Instituto de Investigaciones Químicas (IIQ). X-ray diffraction studies were accomplished at Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla (CITIUS), at Instituto de Investigaciones Químicas (IIQ) and at Centro de Investigación en Química Sostenible (CIQSO) de la Universidad de Huelva.

2. Synthesis of M(PMe$_2$Ar')$_2$ (Ar' = terphenyl group) complexes 1-4.

2.1. Synthesis of Pd(PMe$_2$Ar^{Dtbp2})$_2$, 1.

In a nitrogen-filled glove box, a solution of the PMe_2Ar^{Dtbp2} phosphane (51.4 mg, 0.10 mmol) dissolved in the minimum amount of hexane was added to a solution of $Pd(CH_2SiMe_3)_2(cod)$ (19.5 mg, 0.05 mmol) dissolved in hexane. The resulting yellow solution was kept in the fridge at -20 °C, furnishing complex **1** as yellow crystals. Yield: 40.0 mg (70 %).

^1H NMR (400 MHz, C_6D_6, 298 K): δ 8.16 (m, 8H, *o*-Dtbp), 7.52 (t, 4H, $^4J_{HH}$ = 1.8 Hz, *p*-Dtbp), 7.38-7.35 (m, 4H, *m*-C_6H_3), 7.25-7.21 (m, 2H, *p*-C_6H_3), 1.40 (s, 72H, $C(CH_3)_3$), 0.94 (t, 12H, J_{app} = 1.4 Hz, PCH_3).

$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 298 K): δ 150.9 (*m*-Dtbp), 146.6 (t, J_{app} = 4 Hz, *o*-C_6H_3), 144.3 (*ipso*-Dtbp), 138.6 (t, J_{app} = 7 Hz, *ipso*-C_6H_3), 131.8 (t, J_{app} = 2 Hz, *m*-C_6H_3), 127.5 (*p*-C_6H_3), 126.0 (*o*-Dtbp), 120.4 (*p*-Dtbp), 35.3 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 20.0 (t, J_{app} = 10 Hz, PCH_3).

---

[1] (a) B. Buster, A. A. Diaz, T. Graham, R. Khan, M. A. Khan, D. R. Powell and R. J. Wehmschulte, *Inorg. Chim. Acta*, 2009, **362**, 3465; (b) M. Marín, J. J. Moreno, C. Navarro-Gilabert, E. Álvarez, C. Maya, R. Peloso, M. C. Nicasio and E. Carmona, *Chem. Eur. J.* 2019, ***25***, 260.

[2] Y. Pan and G. B. Young, *J. Organomet. Chem.*, 1999, ***577***, 257.

[3] E. Costa, P.G. Pringle, M. Ravetz and Richard J. Puddephatt, *Inorg. Synth.*, 1997, ***31***, 284.

[4] J. W. Wielandt and D. Ruckerbauer, *Inorg. Synth.*, 2010, ***35***, 120.

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ −12.8.

Anal. Calcd. for $C_{72}H_{102}P_2Pd$: C, 76.13; H, 9.05. Found: C, 76.08; H, 9.17.

2.2. Synthesis of Pt(PMe$_2$Ar^{Dtbp2})$_2$, 2.

A solution of KOH (16.8 mg, 0.3 mmol) in methanol (1 mL) was added to a suspension of Pt(COD)Cl_2 (44.4 mg, 0.15 mmol) in toluene (1 mL) cooled at -5 ºC. To the resulting mixture, a solution of the phosphane PMe$_2$Ar^{Dtbp2} (154.2 mg, 0.3 mmol) in toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 24 h. Methanol was added to precipitate the product, which was then filtered, washed with methanol and dried under vacuum to afford complex **2** as a yellowish solid. Yield: 146.7 mg (80%).

^1H NMR (400 MHz, C_6D_6, 298 K): δ 9.00 (b, 8 H, *o*-Dtbp), 7.53 (t, $^4J_{HH}$ = 1.7 Hz, 4 H, *p*-Dtbp), 7.39 (b d, $^3J_{HH}$ = 7.1 Hz, 4 H, *m*-C_6H_3), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, *p*-C_6H_3)1.41 (s, 72H, C(CH_3)$_3$), 1.08 (t, 12H, J_{app} = 2.3 Hz, PCH_3).

$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 298 K): δ 150.8 (*m*-Dtbp), 146.8 (t, J_{app} = 4 Hz, *o*-C_6H_3), 144.0 (*ipso*-Dtbp), 137.2 (t, J_{app} = 16 Hz, *ipso*-C_6H_3), 132.0 (*m*-C_6H_3), 127.5 (*p*-C_6H_3), 126.3 (*o*-Dtbp), 120.5 (*p*-Dtbp), 35.3 (*C*(CH$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 20.7 (t, J_{app} = 17 Hz, P*C*H$_3$).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ 14.2 ($^1J_{PPt}$ = 3794Hz).

Anal. Calcd. for $C_{72}H_{102}P_2Pt$: C, 70.62; H, 8.42. Found: C, 70.65; H, 8.68.

2.3. Synthesis of Ni(PMe$_2$Ar^{Ph2})$_2$, 3.

In a nitrogen-filled glove box, a solution of the phosphane PMe$_2$Ar^{Ph2} (116 mg, 0.4 mmol) in THF (1 mL) was added to a solution of Ni(cod)$_2$ (56 mg, 0.2 mmol) in THF (1 mL). The resulting dark red solution was stirred for 5 minutes and pentane was added to precipitate complex **3** was as a dark red solid. The title compound was obtained as dark red crystals after recrystallization in pentane:diethyl ether (2:1) mixtures at -20 °C. Yield: 94.8 mg (74%).

^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.13-7.17 (m, 4H, *p*-C_6H_5), 7.02 (t, 2H, $^3J_{HH}$ = 6.8 Hz, *p*-C_6H_3), 6.91 (d, 4H, $^3J_{HH}$ = 6.9 Hz, *m*-C_6H_3), 6.82-6.88 (m, 16H, *o*-C_6H_5, *m*-C_6H_5), 0.91 (t, 12H, J_{app} = 1.8 Hz, PCH_3).

^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 147.6 (t, J_{app} = 7 Hz, *o*-C_6H_3), 136.8 (t, J_{app}= 15 Hz, *ipso*-C_6H_3), 132.4 (*ipso*-C_6H_5), 129.1 (*o*-C_6H_5), 127.6 (*m*-C_6H_3), 124.2 (*p*-C_6H_5), 123.3 (*p*-C_6H_3), 119.1 (*m*-C_6H_5), 17.4 (t, J_{app} = 10 Hz, P*C*H_3).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ 2.2.

Anal. Calcd. for $C_{40}H_{40}P_2Ni$: C, 75.14; H, 5.99. Found: 75.34; H, 6.37.

2.4. Ni(PMe₂Ar^Dtbp2)₂, 4.

A Fischer-Porter vessel containing a mixture of Ni(cod)$_2$ (14 mg, 0.05 mmol) and PMe$_2$Ar^{Dtbp2} (52 mg, 0.1 mmol) in toluene (10 mL) was charged with H_2 (4 bar) and stirred at 50 °C for 3 hours. After that time, the H_2 atmosphere was discharged and volatiles removed under reduced pressure. The solid residue was extracted in pentane and filtered through a silica pad. Concentration and cooling at −20 °C rendered the sought product as reddish brown crystals. Yield: 12 mg (43%).

^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.19 (br s, 4H, *p*-Dtbp), 7.11 (d, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_3), 6.98-6.93 (m, 10 H, *p*-C_6H_3, *o*-Dtbp), 1.31 (s, 72 H, C(C*H*$_3$)$_3$), 1.09 (br s, 12 H, PC*H*$_3$).

$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 298 K): δ 150.4 (*o*-*C*$_6H_3$, *m*-Dtbp), 149.3 (*o*-*C*$_6H_3$), 140.2 (t, J_{app} = 16 Hz, *ipso*-*C*$_6H_3$), 129.6 (*ipso*-Dtbp), 129.1 (*m*-*C*$_6H_3$), 124.5 (*p*-*C*$_6H_3$), 120.3 (*o*-Dtbp), 118.1 (*p*-Dtbp), 35.0 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 17.1 (P*C*H$_3$).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ −4.3 (s).

Anal. Calcd. for $C_{72}H_{102}P_2Ni$: C, 79.47; H, 9.45. Found: C, 79.39; H, 9.37.

Selected NMR data obtained for complex **5**:

^1H NMR (300 MHz, C_6D_6, 298 K): δ 8.01-7.03 (m, 7H, C*H*), 6.05 (br s, 2H, *m*-C_6H_3), 3.03 (m, 2H, C*H*(COE)), 1.94-2.07 (m, 2H, C*H*$_2$(COE)), 1.76-1.90 (m, 4H, C*H*$_2$(COE)),1.49 (s, 18H, C(C*H*$_3$)$_3$), 1.42 (s, 18H, C(C*H*$_3$)$_3$), 1.27 (d, 12H, $^2J_{HP}$ = 5.4Hz, PC*H*$_3$).

$^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ 8.16 (s).

3. Variable temperature NMR studies

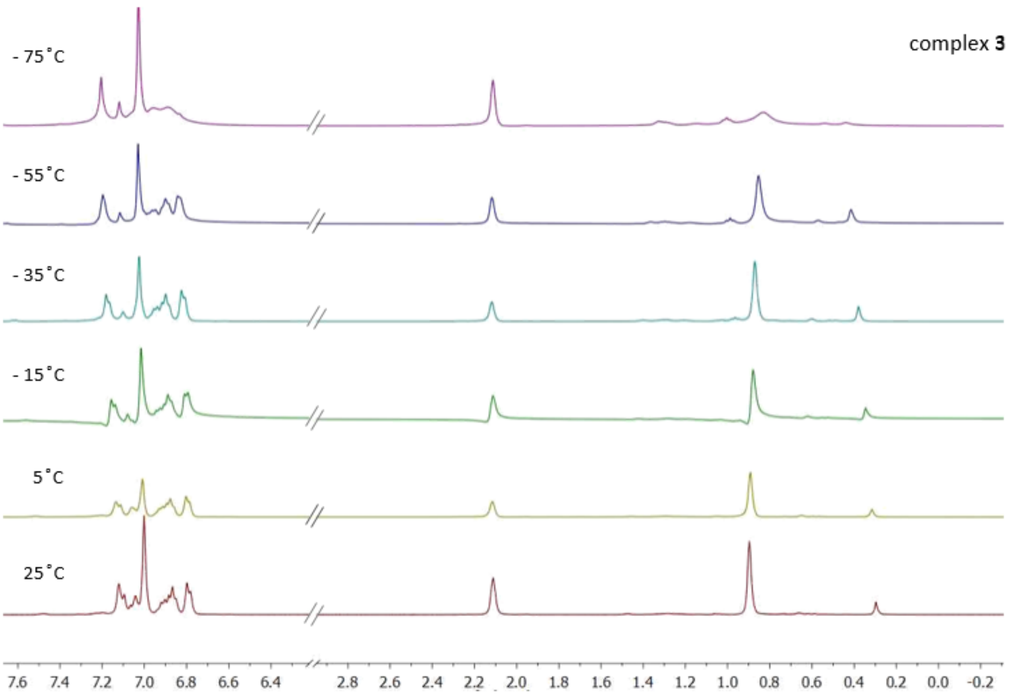


Figure S1. VT-^{1}H NMR spectra of **3** in toluene-d$_8$

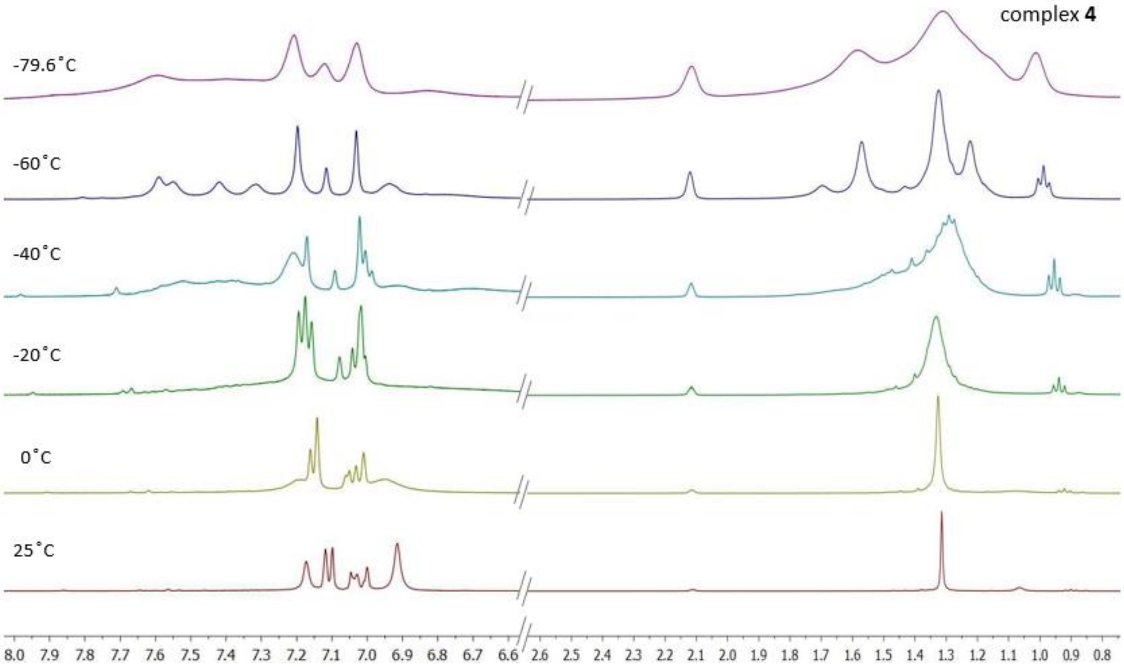
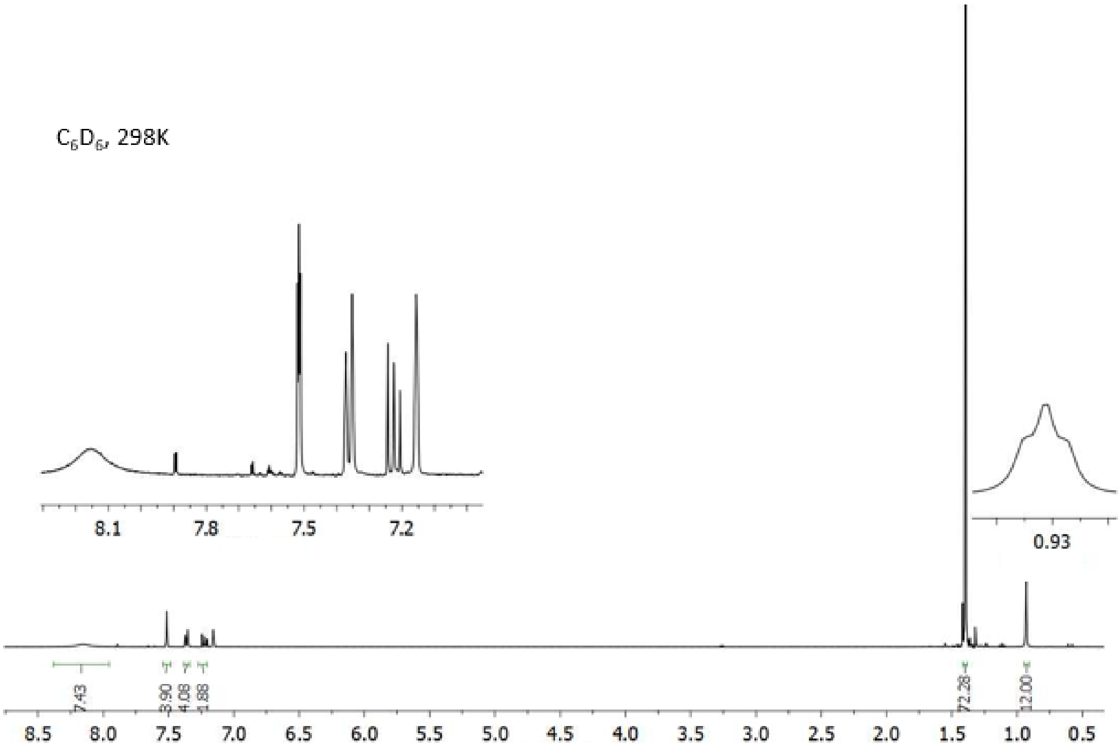


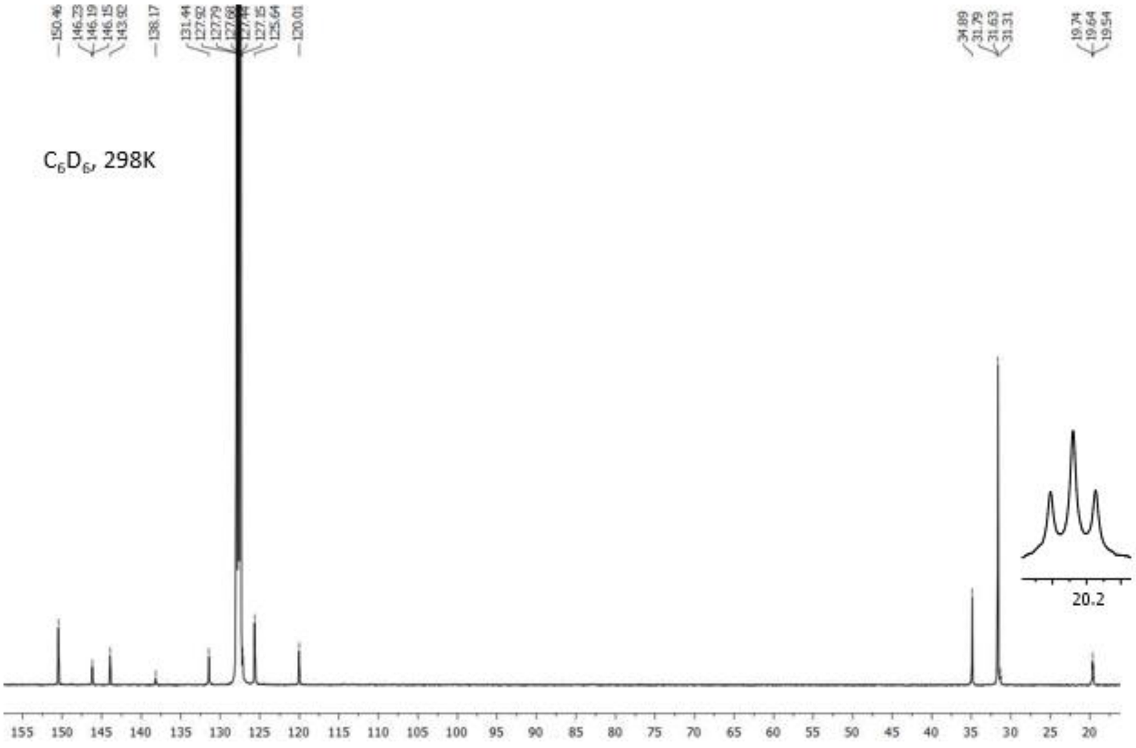
Figure S2. VT-^{1}H NMR spectra of **4** in toluene-d$_8$

4. NMR Spectra of compounds 1-5

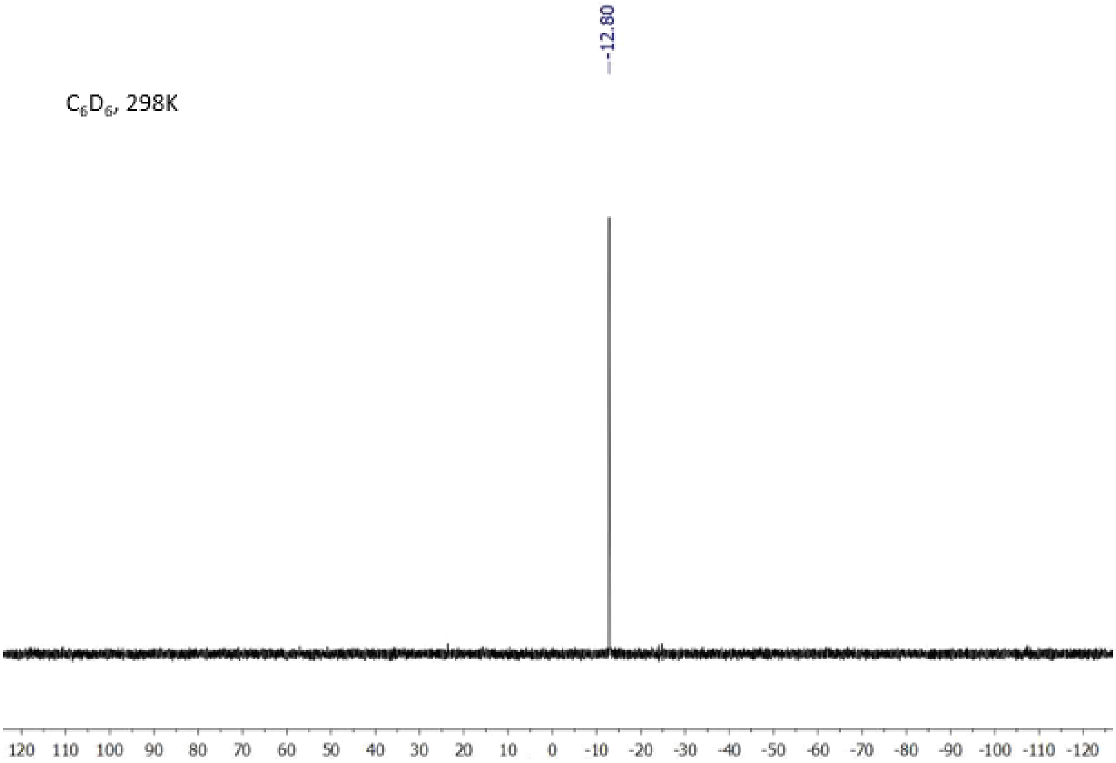
^{1}H NMR spectrum of Pd(PMe$_2$Ar^{Dtbp2})$_2$, 1·



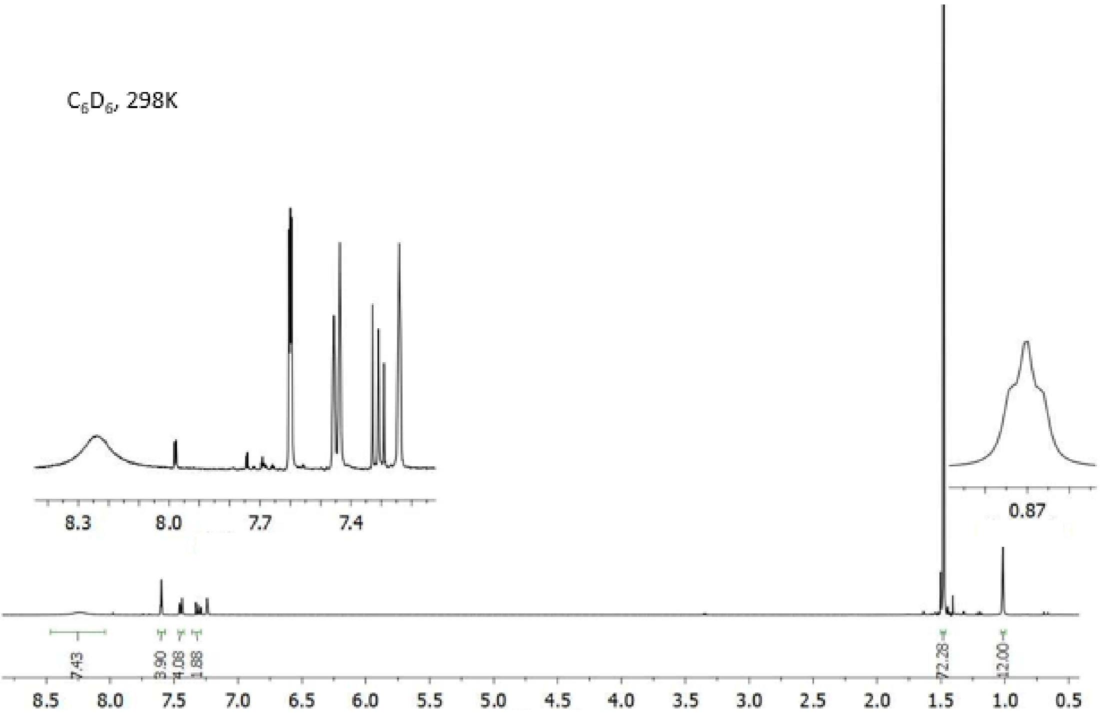
^{13}C{^{1}H} NMR spectrum of Pd(PMe$_2$Ar^{Dtbp2})$_2$, 1·



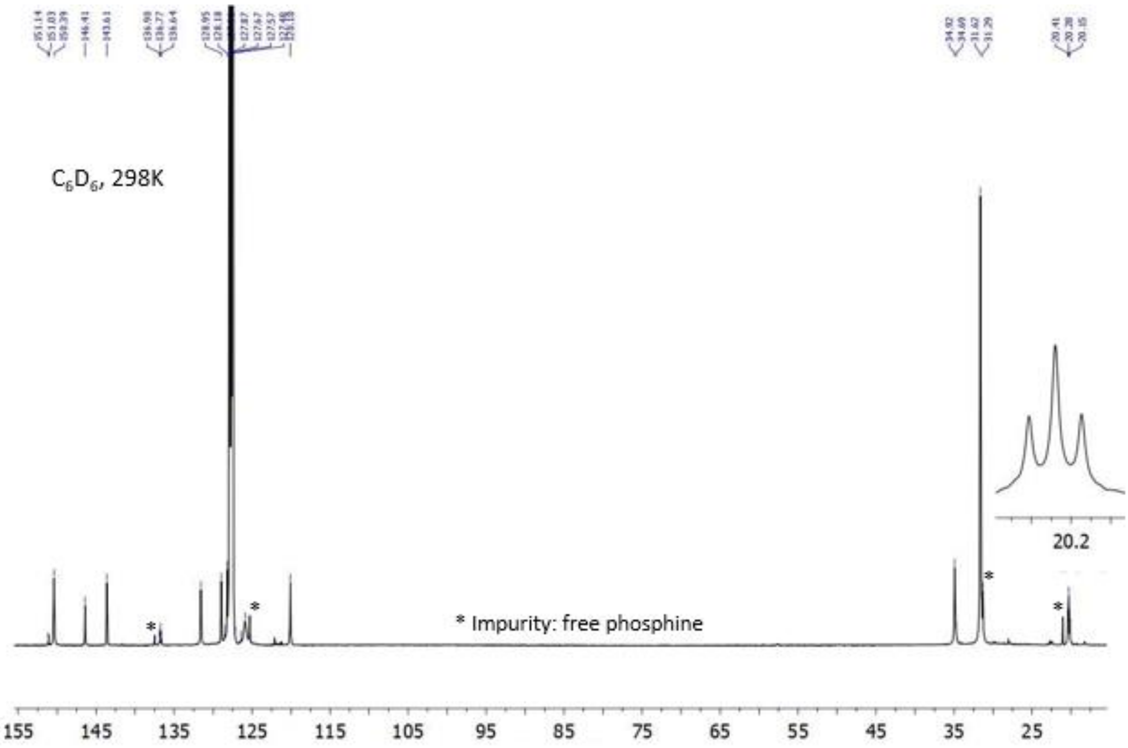
$^{31}P\{^1H\}$ NMR spectrum of $Pd(PMe_2Ar^{Dtbp2})_2$, 1·.



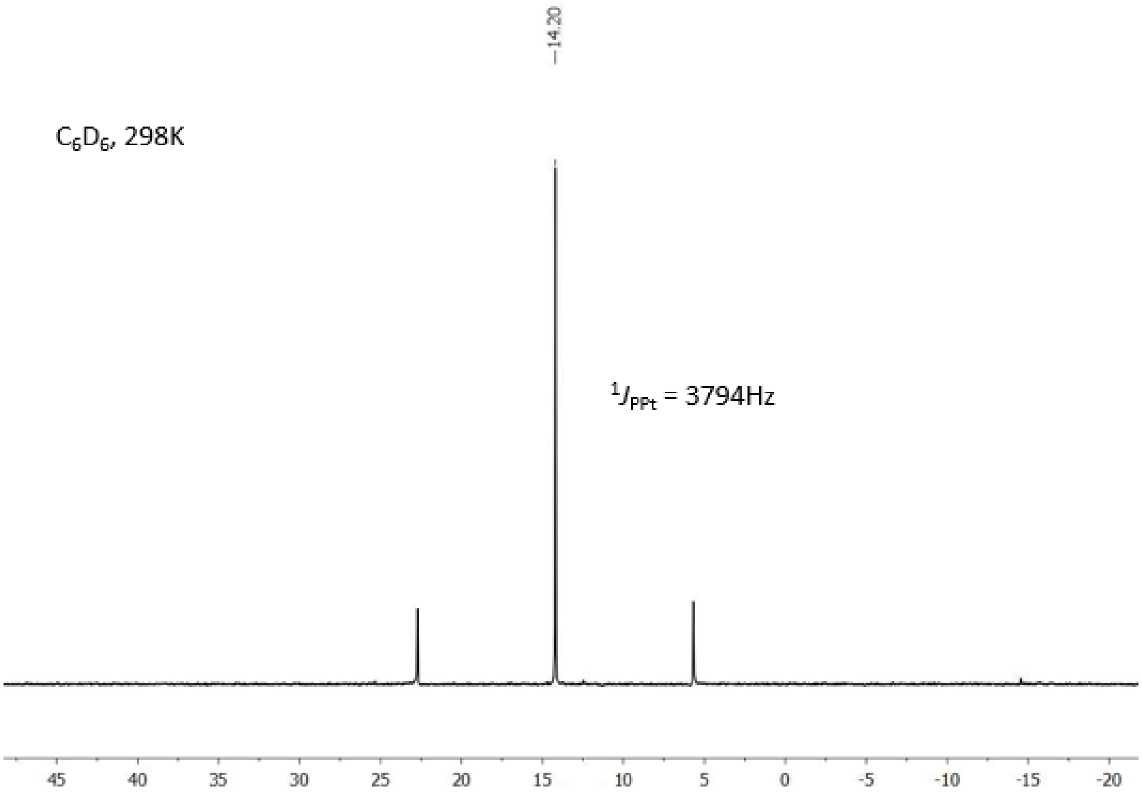
^{1}H NMR spectrum of Pt(PMe$_2$Ar^{Dtbp2})$_2$, 2·



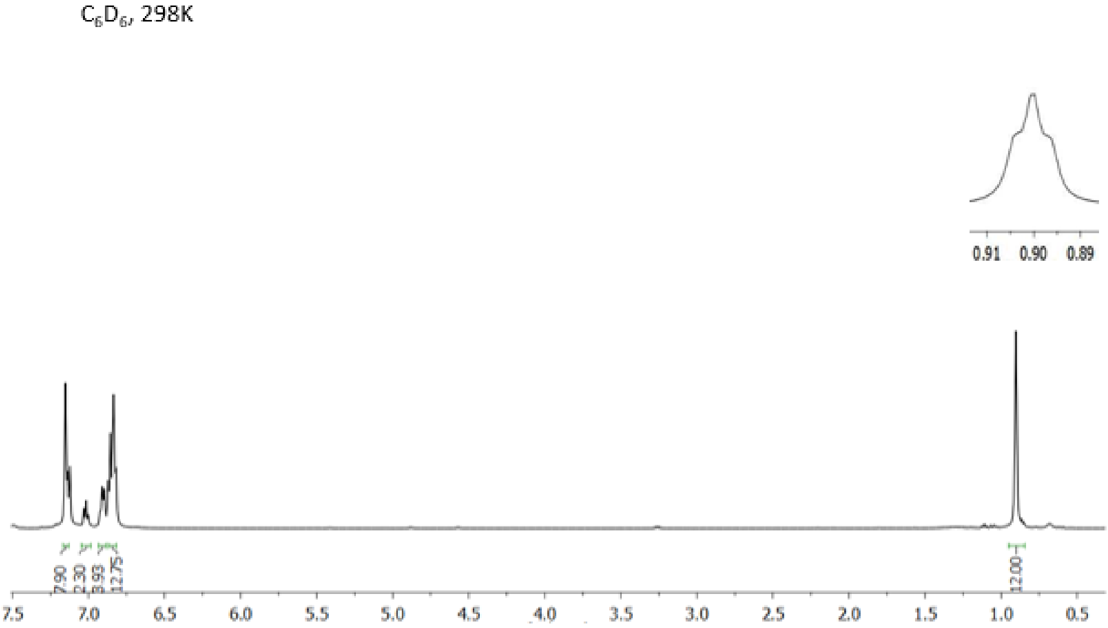
^{13}C{^{1}H} NMR spectrum of Pt(PMe$_2$Ar^{Dtbp2})$_2$, 2·



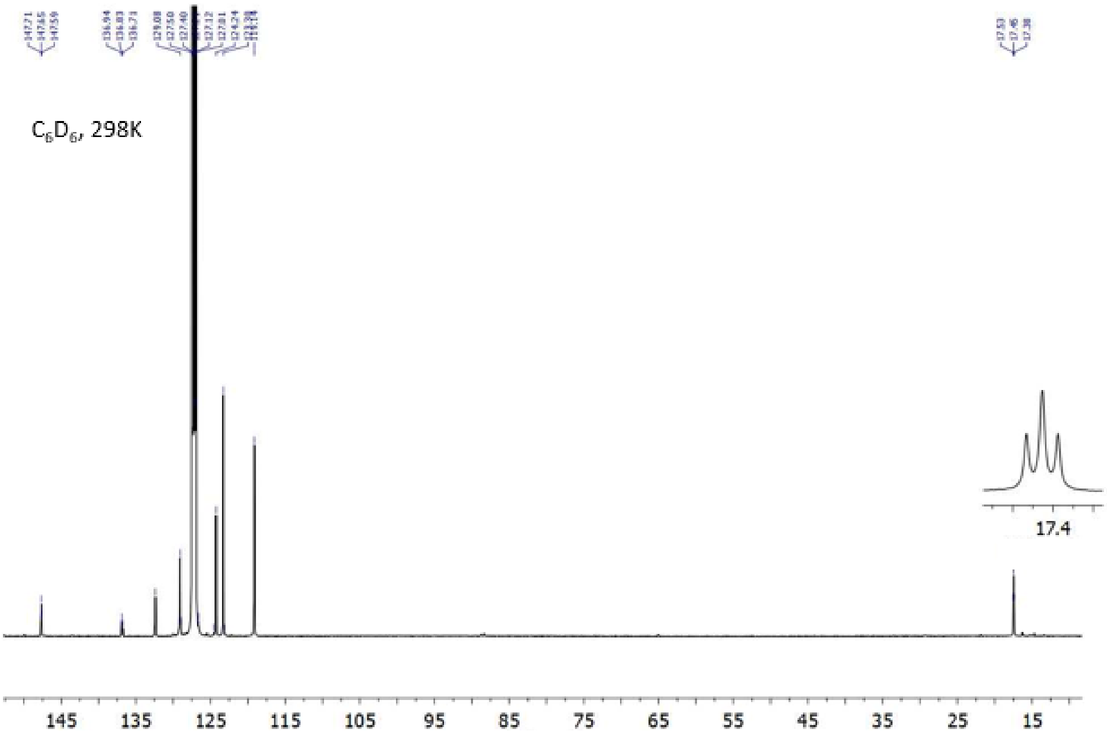
^{31}P{^{1}H} NMR spectrum of Pt(PMe$_2$Ar^{Dtbp2})$_2$, 2·.



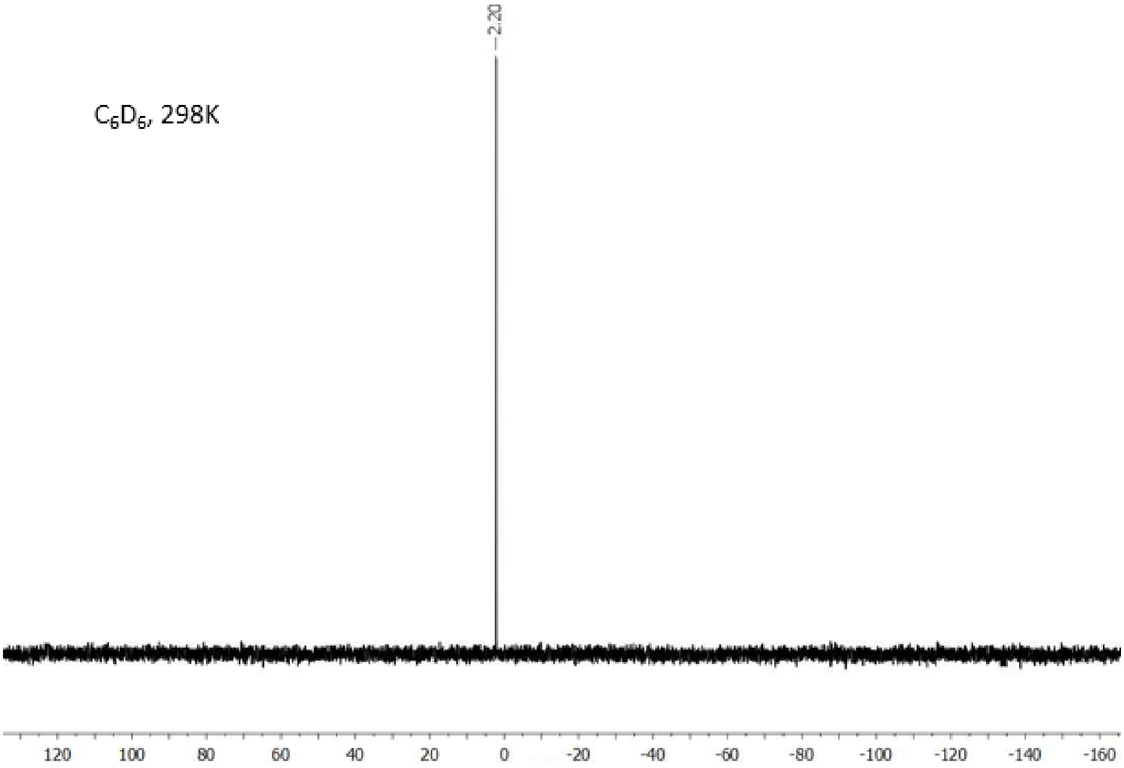
^{1}H NMR spectrum of Ni(PMe$_2$Ar^{Ph2})$_2$, 3·



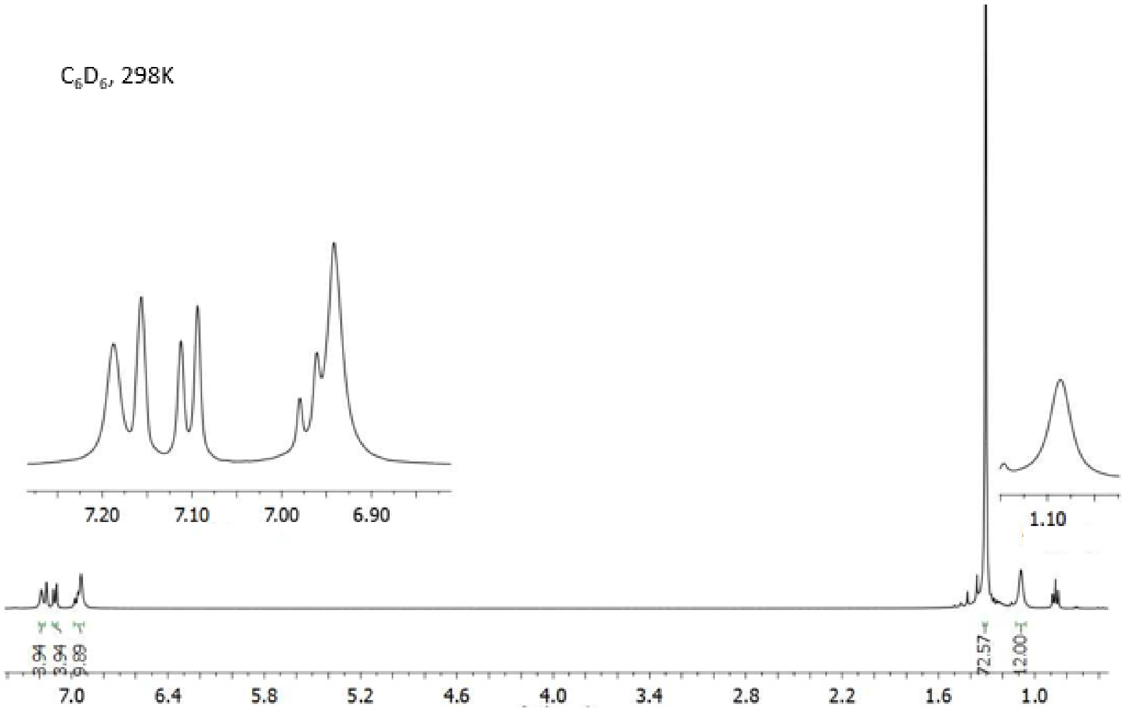
$^{13}C\{^{1}H\}$ NMR spectrum of Ni(PMe$_2$Ar^{Ph2})$_2$, 3·



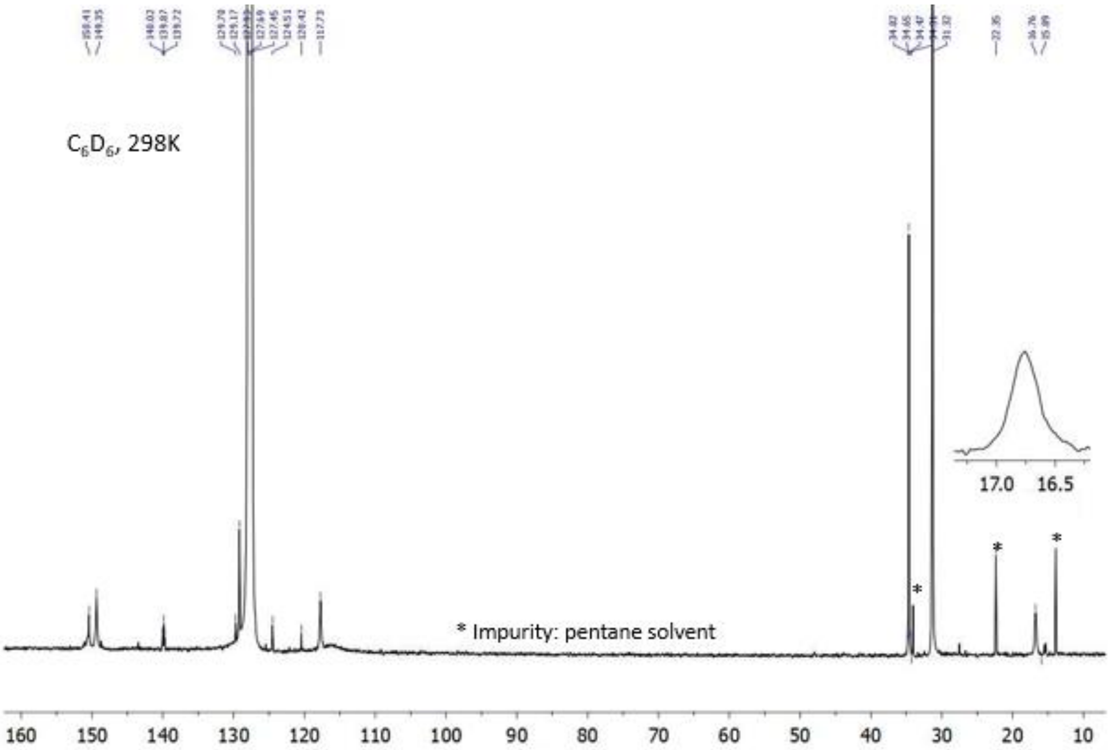
$^{31}P\{^{1}H\}$ NMR spectrum of Ni(PMe$_2$Ar^{Ph2})$_2$, 3·



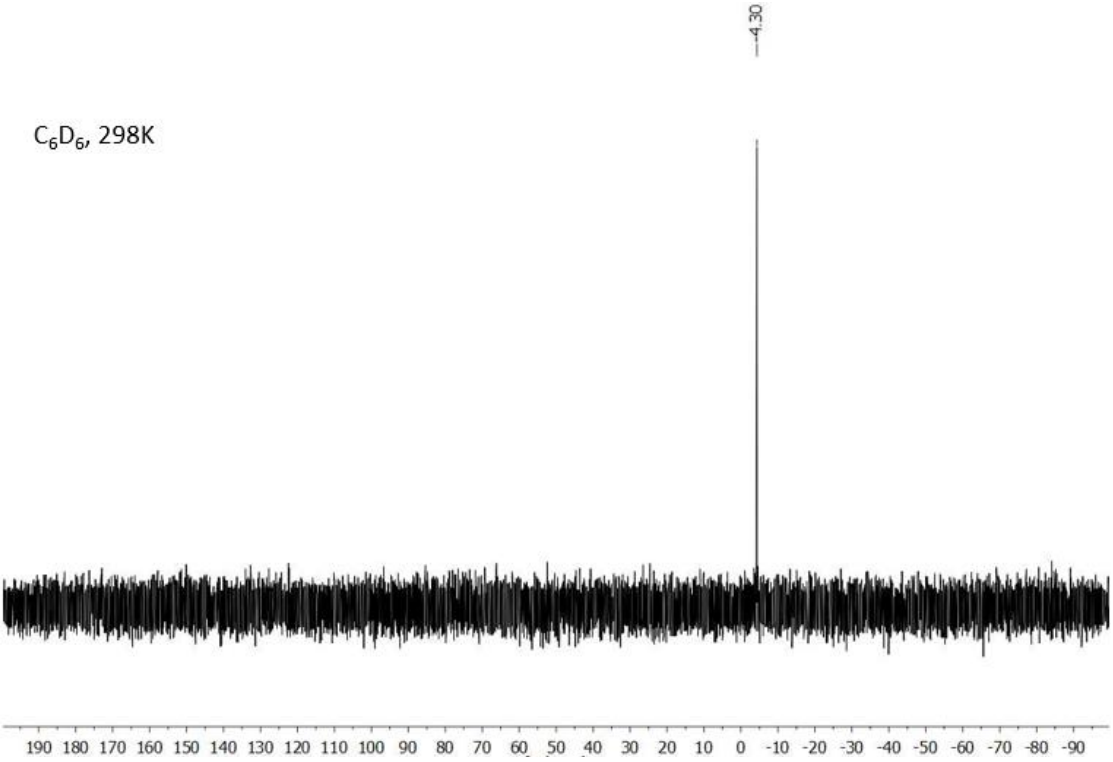
^{1}H NMR spectrum of Ni(PMe$_2$Ar^{Dtbp2})$_2$, 4·



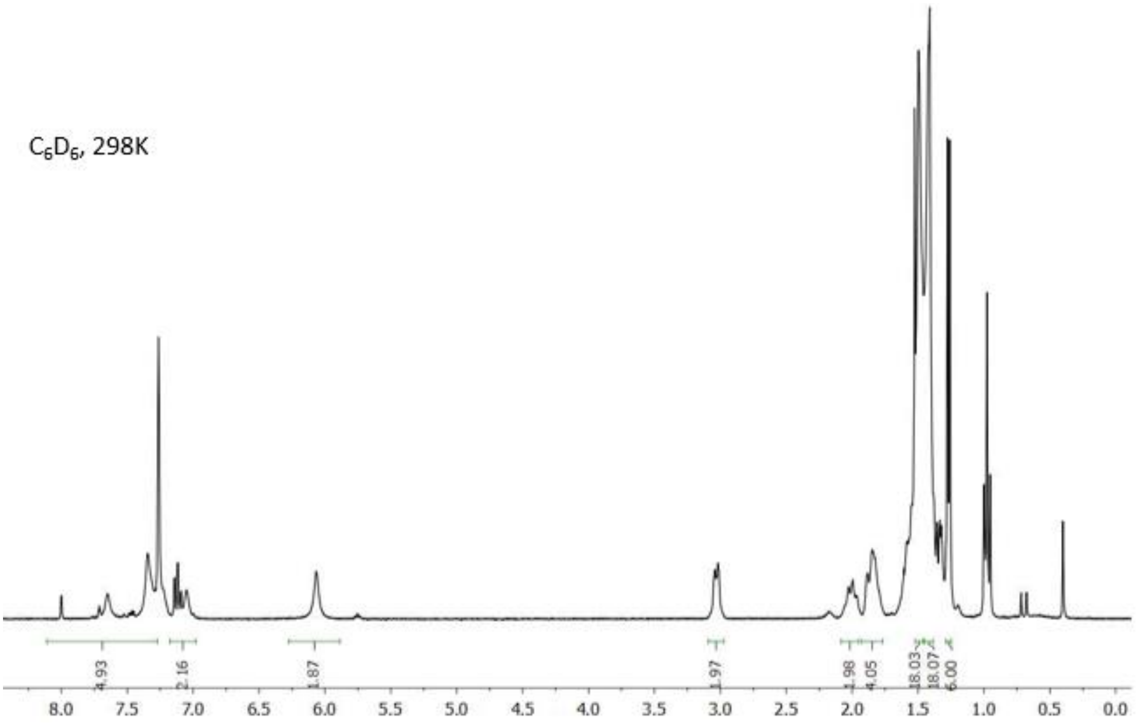
$^{13}C\{^{1}H\}$ NMR spectrum of Ni(PMe$_2$Ar^{Dtbp2})$_2$, 4·



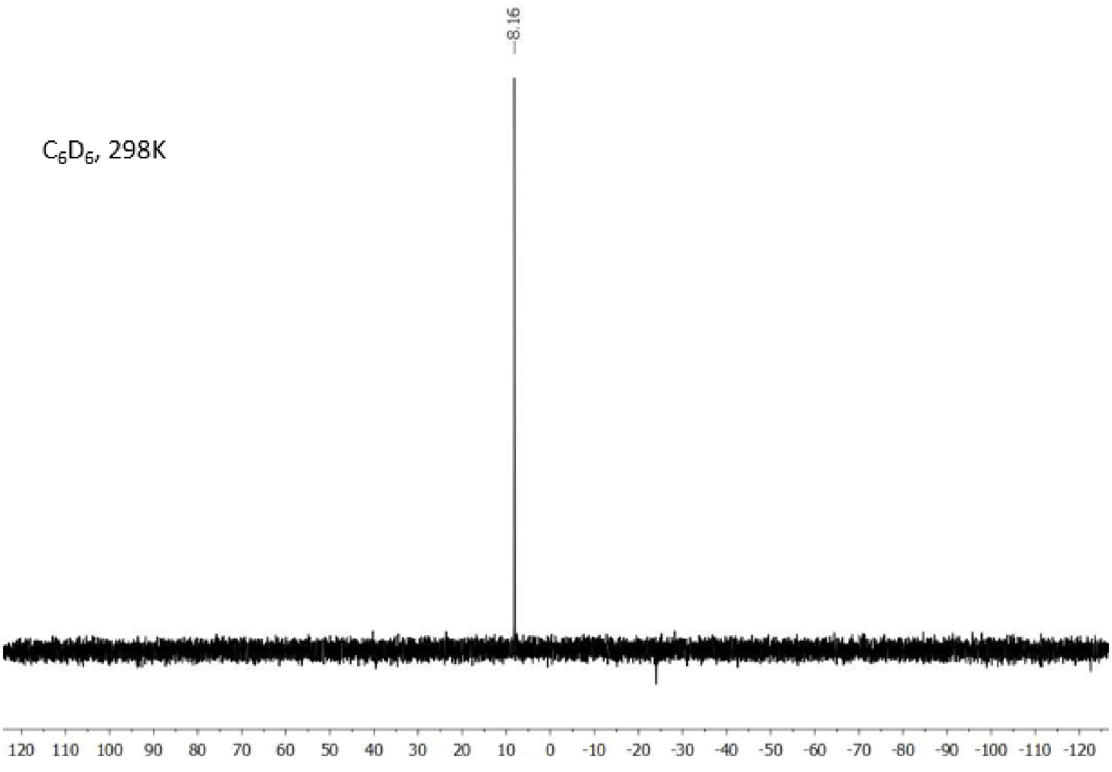
$^{31}P\{^1H\}$ NMR spectrum of Ni(PMe$_2$Ar^{Dtbp2})$_2$, 4·



^{1}H NMR spectrum of Ni(PMe$_2$Ar$^{\mathrm{Dtbp2}}$)(COE), 5·



^{31}P{^{1}H} NMR spectrum of Ni(PMe$_2$Ar$^{\mathrm{Dtbp2}}$)(COE), 5·



5. X-ray structural characterization of new complexes 1-5.

Single crystals for X-ray diffraction analyses were grown by slow evaporation of a solution of the complex in a solvent (hexane for complex **1**, pentane for complexes **2**, **4** and **5** and pentane:diethyl ether (2:1) for complex **3**) cooled to -20 ºC. Crystals of suitable size were coated with perfluoropolyether and mounted on a glass fibre and fixed in cold nitrogen stream to the goniometer head. Data collection have been performed on three diffractometers: a Bruker-Nonius X8 Apex-II CCD diffractometer, using a graphite monochromator Mo K_α radiation (λ=0.71073 Å) and fine-sliced ω and ϕ scans (scan widths 0.30° to 0.50°) under a flow of cold nitrogen (used with **1**, **4** and **5**) supplied by a Bruker Cryo-Flex low-temperature device, a Bruker-AXSX8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator Ag K_α radiation (λ=0.56086 Å) with a Bruker Cryo-Flex low-temperature device (used with **3**) and a Bruker D8 QUEST diffractometer equipped with a Photon II detector, using Mo K_α radiation (λ=0.71073 Å, micro focus sealed X-ray tube) with an Oxford Cryosystems low-temperature device (Cryostream 800), (used with **2**). Data obtained were reduced (SAINT) and corrected for absorption effects by the multiscan method (SADABS).[5] The structures were solved by direct methods (SIR2002,[6] SHELXS) and refined against all F^2 data by full-matrix least squares techniques (SHELXL-2018/3) minimizing $w[F_o^2-F_c^2]^2$.[7] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and allowed to ride on their carrier atoms with the isotropic temperature factors U_{iso} fixed at 1.2 times (1.5 times for methyl groups) of the U_{eq} values of the respective carrier atoms. The modelling of the observed disorders for some moieties of the structures required some geometric restraints (DFIX instruction), the ADP restraint SIMU and the rigid bond restraint DELU and RIGU were used in order to obtain more reasonable geometric and ADP values of the disordered atoms. It was also useful to restraint the anisotropic U-values of these atoms to behave more isotropically (ISOR instruction). A search for solvent accessible voids in **1** and **4** using PLATON,[8] showed some small volumes of potential solvents impossible to model even with the most severe restraints. The corresponding CIF data represent *SQUEEZE*[9] treated structures with the solvent molecules handling as a diffuse contribution to the overall scattering, without

---

[5] a) Bruker APEX2; Bruker AXS, Inc.; Madison, WI, 2007. (b) Bruker Advanced X-ray solutions. SAINT and SADABS programs. Bruker AXS Inc. Madison, WI, 2004.

[6] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna. SIR2002: the Program. *J. Appl. Crystallogr.* 2003, **36**, 1103.

[7] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 11.

[8] A. L. Spek, Single-crystal Structure Validation with the Program *PLATON*. *J. Appl. Crystallogr*. 2003, **36**, 7.

[9] P. v. d. Sluis, A. L. Spek, BYPASS: An Effective Method for the Refinement of Crystal Structures Containing Disordered Solvent Regions. *Acta Crystallogr.*, *Sect. A*. 1990, **46**, 194.

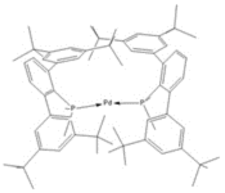
specific atom position and excluded from the structural model. The *SQUEEZE* results were appended to the CIF. A summary of cell parameters, data collection, structures solution, and the refinement of crystal structures are provided below. The corresponding crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 2060332 (**1**), 2060333 (**2**), 2060334 (**3**), 2060335 (**4**) and 2060336 (**5**). The data can be obtained free of charge via: https://www.ccdc.cam.ac.uk/structures/

Table S1. *Crystal data and structure refinement for **1**, and **2***

Identification code	**1**	**2**
Empirical formula	$C_{72}H_{102}P_2Pd$	$C_{72}H_{102}P_2Pt$, C_5H_{12}
Formula weight	1135.87	1296.71
Temperature	193(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Unit cell dimensions	a = 17.7569(6) Å b = 23.7286(9) Å c = 17.7374(7) Å α = 90° β = 101.795(2)° γ = 90°	a = 17.6217(14) Å b = 23.6025(18) Å c = 17.6699(14) Å α = 90° β = 101.514(3)° γ = 90°
Volume	7315.8(5) Å^3	7201.3(10) Å^3
Z	4	4
Density (calculated)	1.031 Mg/m^3	1.196 Mg/m^3
Absorption coefficient	0.332 mm^{-1}	2.032 mm^{-1}
F(000)	2440	2736
Crystal size	0.30 x 0.25 x 0.20 mm^3	0.16 x 0.13 x 0.06 mm^3
Theta range for data collection	1.452 to 25.249°	2.359 to 34.374°
Index ranges	-21<=h<=21, -28<=k<=28, -21<=l<=21	-27<=h<=27, -37<=k<=37, -28<=l<=28
Reflections collected	73134	146020
Independent reflections	6613 [R(int) = 0.0348]	15094 [R(int) = 0.0740]
Completeness to theta = 22.00°	99.9 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6924	0.1065 and 0.0645
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6613 / 222 / 415	15094 / 120 / 462
Goodness-of-fit on F^2	0.858	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1432	R1 = 0.0348, wR2 = 0.0836
R indices (all data)	R1 = 0.0570, wR2 = 0.1515	R1 = 0.0453, wR2 = 0.0906
Largest diff. peak and hole	1.544 and -0.471 e.Å^{-3}	1.873 and -0.935 e.Å^{-3}

Table S2. *Crystal data and structure refinement for **3**, **4** and **5**.*

Identification code	**3**	**4·**	**5**
Empirical formula	$C_{40}H_{38}NiP_2$	$C_{72}H_{102}NiP_2$	$C_{44}H_{65}NiP$, C_5H_{12}
Formula weight	639.35	1088.18	755.78
Temperature	173(2) K	193(2) K	193(2) K
Wavelength	0.56086 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	Iba2	$P\bar{1}$
Unit cell dimensions	a = 10.7226(8) Å b = 11.7463(9) Å c = 13.7443(11) Å α = 73.245(4)° β = 75.828(4)° γ = 69.982(3)°	a = 23.3099(10) Å b = 16.9037(7) Å c = 18.5008(8) Å α = 90° β = 90° γ = 90°	a = 9.8419(6) Å b = 12.7335(7) Å c = 19.0020(12) Å α = 104.668(2)° β = 99.269(2)° γ = 92.692(2)°
Volume	1536.8(2) Å^3	7289.8(5) Å^3	2264.1(2) Å^3
Z	2	4	2
Density (calculated)	1.386 Mg/m^3	0.992 Mg/m^3	1.109 Mg/m^3
Absorption coefficient	0.405 mm^{-1}	0.345 mm^{-1}	0.494 mm^{-1}
F(000)	672	2368	828
Crystal size	0.22 x 0.17 x 0.13 mm^3	0.25 x 0.20 x 0.10 mm^3	0.30 x 0.25 x 0.20 mm^3
Theta range for data collection	1.616 to 22.130°	2.202 to 25.250°	2.106 to 25.249°
Index ranges	-14<=h<=14, -15<=k<=15, -18<=l<=18	-27<=h<=17, -20<=k<=19, -13<=l<=22	-11<=h<=11, -15<=k<=15, -22<=l<=22
Reflections collected	26793	41221	30889
Independent reflections	7618 [R(int) = 0.0576]	5011 [R(int) = 0.0690]	8209 [R(int) = 0.0253]
Completeness to theta = 22.00°	98.7 %	99.8 %	100.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7447 and 0.6390	0.7448 and 0.5872	0.7461 and 0.6940
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7618 / 0 / 404	5011 / 37 / 358	8209 / 68 / 476
Goodness-of-fit on F^2	0.883	1.052	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1211	R1 = 0.0518, wR2 = 0.1326	R1 = 0.0511, wR2 = 0.1431
R indices (all data)	R1 = 0.0690, wR2 = 0.1435	R1 = 0.0623, wR2 = 0.1384	R1 = 0.0600, wR2 = 0.1499
Largest diff. peak and hole	0.453 and -0.942 e.Å^{-3}	0.439 and -0.336 e.Å^{-3}	1.216 and -0.638 e.Å^{-3}



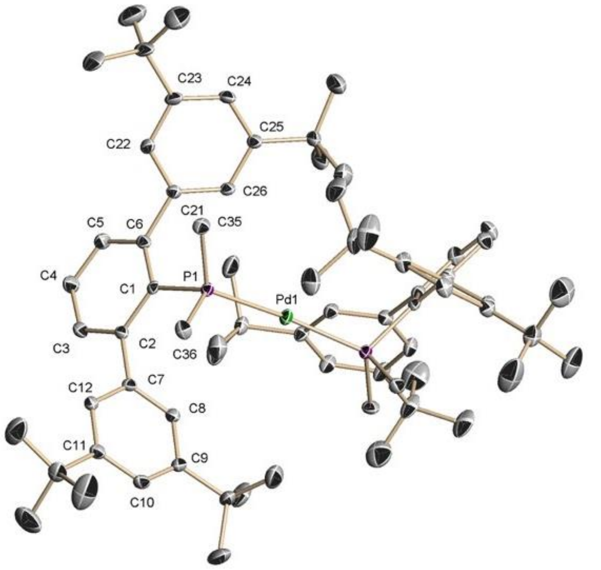


Figure S3. Molecular structure of Pd(PMe$_2$Ar^{Dtbp2})$_2$, **1.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pd-P 2.2701(7), P-Pd-P 171.49(4).