Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Recycling of Allylic Alkylation Pd Catalysts Containing Phosphine-Imidazoline Ligand in Ionic Liquids

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General Methods:

All reactions were carried out under an argon atmosphere using Standard Schlenk techniques. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra were recorded on a Varian Gemini spectrometer at 400 MHz. Chemical shifts were reported relative to tetramethylsilane for ^{1}H and ^{13}C{^{1}H} as internal reference, H_3PO_4 85% for ^{31}P{^{1}H}, and trichlorofluoromethane for ^{19}F{^{1}H} as external references. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. VG-Autospect equipment was used for FAB mass spectral analyses with 3-nitrobenzylalcohol as matrix. EI mass spectra were obtained on an HP 5989 A spectrometer at an ionizing voltage of 70eV. Conversion was measured by NMR spectrometry. The enantiomeric excesses was measured by HPLC (OD-H column)

General Procedure for Palladium-Catalysed Allylic Alkylation in Ionic Liquid; Thermal Conditions:

In an inerted Schlenk tube are introduced $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.84 mg, 5 µmol, 2mol%) and the phosphine-imidazoline ligand (0.011 mmol) in 2 mL of the corresponding IL. The resulting mixture is heated at 85°C for 20 minutes under nitrogen to preform the Pd complex. After cooling to rt, *rac*-1,3-diphenylprop-2-en-1-yl acetate (62.5 mg, 250 µmol), dimethyl malonate (750 µmol), BSA (185 µL, 750 µmol) and KOAc (0.5 mg, 2mol%) are successively added. Then, the reaction mixture was stirred at 45 ºC for 24 h. After cooling to rt, the products are extracted from the ionic liquid using dry degassed toluene (3 x 5mL), filtered over celite and the solvent removed. The conversion of the reaction was measured after removing the solvent by ^{1}H NMR of the crude mixture. Enantiomeric excesses were determined from the residue by HPLC[i] on a OD-H column (0.5 mL/min, n-hexane/isopropyl alcohol, 99:1): (*R*)-**PI** Rt=23 min, (*S*)-**PI** Rt=25 min.

Palladium-Catalysed Allylic Alkylation using ligand 3 in the IL 16; Thermal Conditions:

In an inerted Schlenk tube are introduced $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.84 mg, 5 µmol, 2mol%) and the ligand **3** (0.011 mmol) in 2 mL of [2,3-dmbim][BF_4] (**16**). The resulting mixture is heated at 85°C for 20 minutes under nitrogen to preform the Pd complex. After cooling to rt, *rac*-1,3-diphenylprop-2-en-1-yl acetate (62.5 mg, 250 µmol), dimethyl malonate (750 µmol), BSA (185 µL, 750 µmol) and KOAc (0.5 mg, 2mol%) are successively added. Then, the reaction mixture was stirred at 45 ºC for 24 h. After cooling to rt, the products are extracted from the ionic liquid using dry degassed toluene (3 x 5mL), filtered over celite and the solvent removed. The conversion of the reaction was measured after removing the solvent by ^{1}H NMR of the crude mixture. Product was purified by column chromatography hexane/ethyl acetate (4:1) obtaining 65 mg of product as yellow oil (Yield = 82 %)[ii]

General Procedure for Palladium-Catalysed Allylic Alkylation in Ionic Liquid; Microwave irradiation:

In an inerted Schlenk tube are introduced $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.84 mg, 5 µmol, 2mol%) and the phosphine-imidazoline ligand (0.011 mmol) in $[2,3\text{-dmbim}][BF_4]$ (2 mL). Then, *rac*-1,3-diphenylprop-2-en-1-yl acetate (62.5 mg, 250 µmol), dimethyl malonate (750 µmol), BSA (185 µL, 750 µmol) and KOAc (0.5 mg, 2mol%) are successively added. The resulting solution is then put under microwave (P=8 watts) for 1 hour. After cooling to rt, the products are extracted from the ionic liquid using dry degassed toluene (3 x 5mL), filtered over celite and the solvent removed. The ionic liquid is kept under vacuum for 3 hrs under stirring to remove the traces of organic solvent and reused for another bacth reaction by simply adding *rac*-1,3-diphenylprop-2-en-1-yl acetate (31 µL, 250 µmol, 1 eq.), dimethyl malonate (86 µL, 3 eq), BSA (152 µL, 3 eq.) and (0.5 mg, 2 mol %) KOAc.

Palladium-Catalysed Allylic Alkylation using ligand 3 in the Ionic Liquid 16; Microwave irradiation (One run):

In an inerted Schlenk tube are introduced $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.84 mg, 5 µmol, 2mol%) and the phosphine-imidazoline ligand **3** (0.011 mmol) in 2 mL of $[2,3\text{-dmbim}][BF_4]$ (**16**). Then, *rac*-1,3-diphenylprop-2-en-1-yl acetate (62.5 mg, 250 µmol), dimethyl malonate (750 µmol), BSA (185 µL, 750 µmol) and KOAc (0.5 mg, 2mol%) are successively added. The resulting solution is then put under microwave (P=8 watts) for 1 hour. After cooling to rt, the products are extracted from the ionic liquid using dry degassed toluene (3 x 5mL), filtered over celite and the solvent removed. The conversion of the reaction was measured after removing the solvent by ^1H NMR of the crude mixture. Product was purified by column chromatography hexane/ethyl acetate (4:1) obtaining 62 mg of product as yellow oil (Yield = 78 %)[iii]

Reactivity of ionic liquid with palladium precursors:

*Synthesis of complex **17**:*

Into a schlenk tube under nitrogen was introduced the palladium precursor $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (50 mg, 0.136 mmol) and the $[bmim][BF_4]$ (**13**) (0.5 mL). Then, KOAc (14 mg, 0.14 mmol) was introduced and the reaction mixture was heated at 45 ºC for 16 hours. After that, a ^1H NMR spectra was acquiered at room temperature observing the formation of a palladium-carbene complex **17**. The unreacted ionic liquid was removed by precipitation in a mixture of ethyl acetate/hexane (1:5) **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 6.82 (q, ^{4}J=1.6 Hz, 4H, CH), 5.38 (br, 1H, CH), 4.60 (br, 2H, CH_2), 4.07 (m, 4H, CH_2), 3.72 (s, 6H, CH_3), 3.22 (br, 2H, CH_2), 1.71 (m, 4H, CH_2), 1.24 (m, 4H, CH_2), 0.84 (t, ^{3}J=7.3 Hz, 6H, CH_3). **^{13}C-{^{1}H} NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 180.0 (NCN), 122.2 (CH), 120.9 (CH), 111.4 (CH), 63. 1 (CH_2), 51.0 (CH_2), 33.4 (CH_2), 20.0 (CH_2), 14.0 (CH_3).

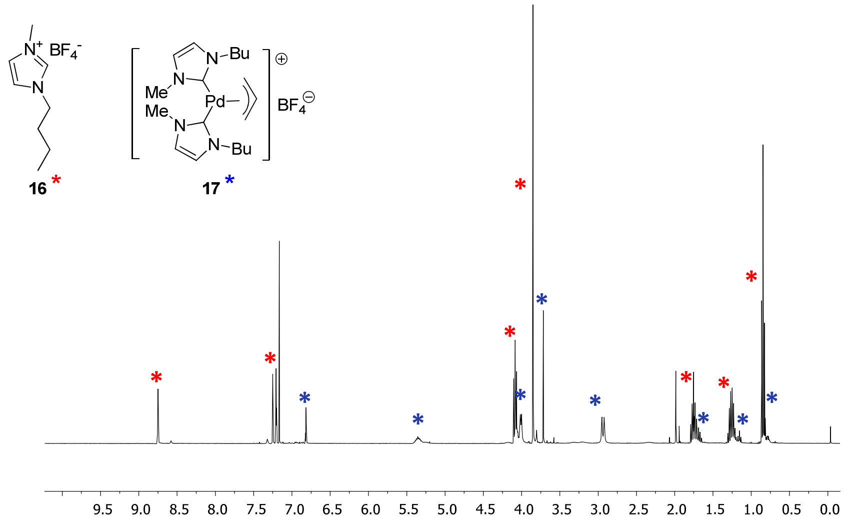


Figure 1. ^{1}H NMR spectra of reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with IL **13** and KOAc.

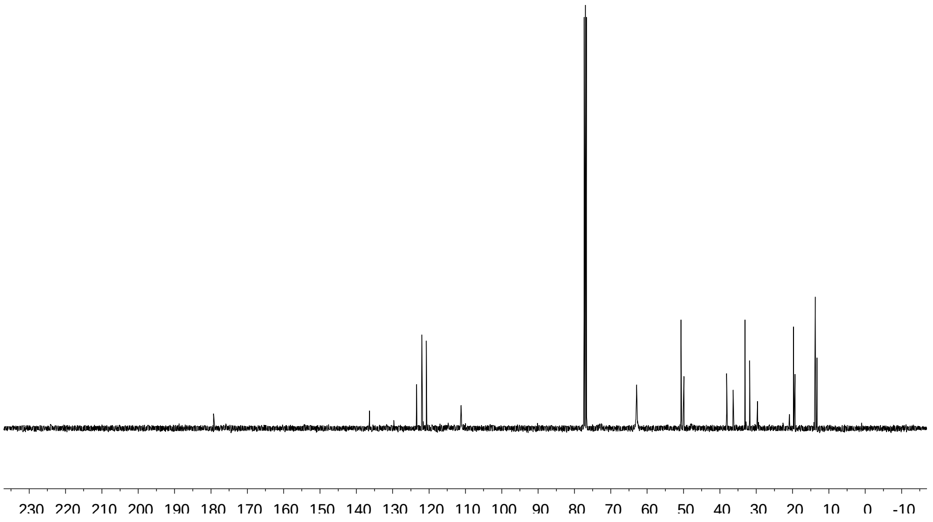


Figure 2. ^{13}C-{^{1}H} NMR spectra of reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with IL **13** and KOAc.

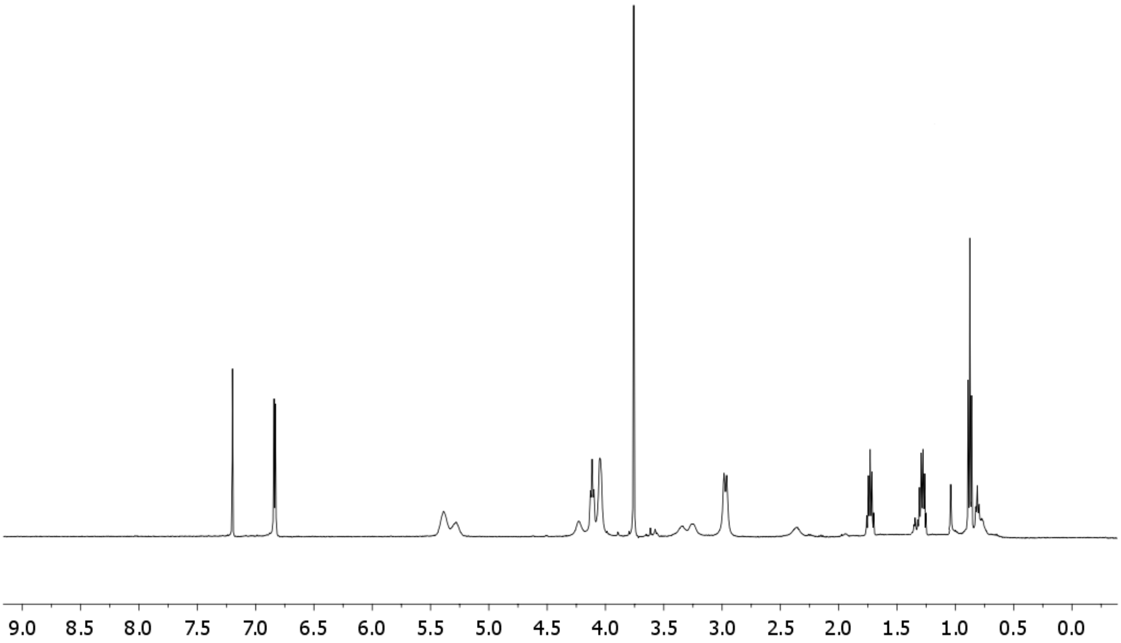


Figure 3. ^{1}H NMR spectra of reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with IL **13** and KOAc after cystallization in EtOAc/Hexane (1:5).

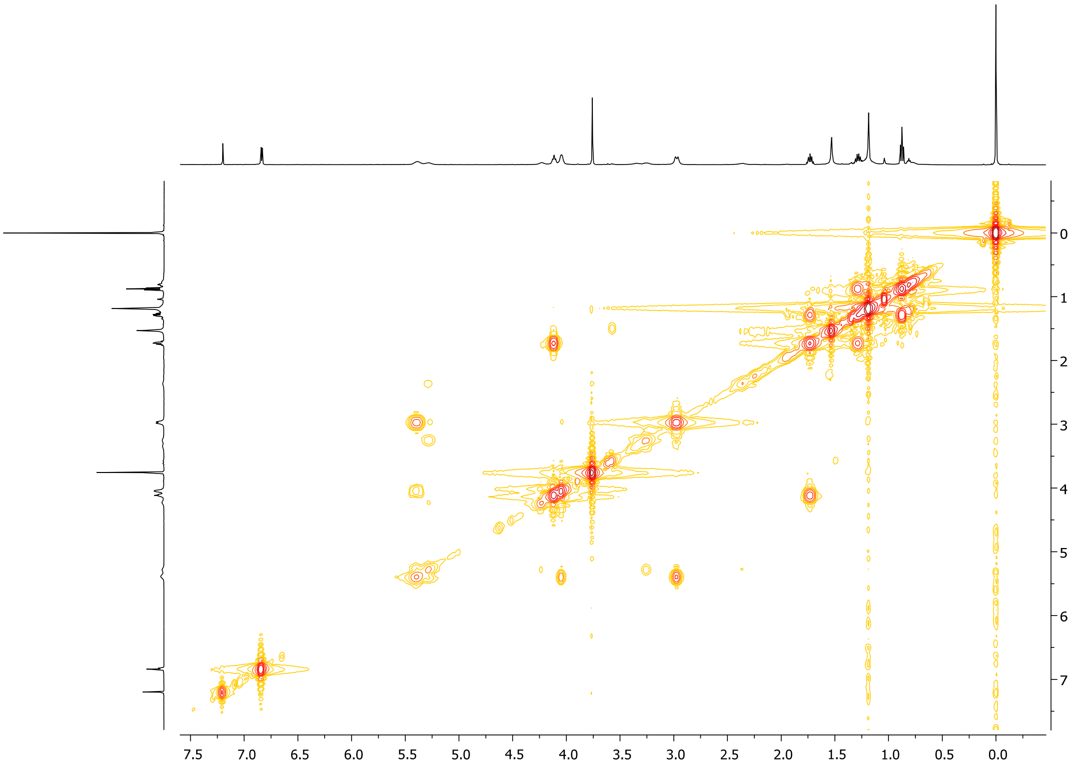


Figure 4. 2D COSY (^{1}H-^{1}H) NMR spectra of reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with IL **13** and KOAc.

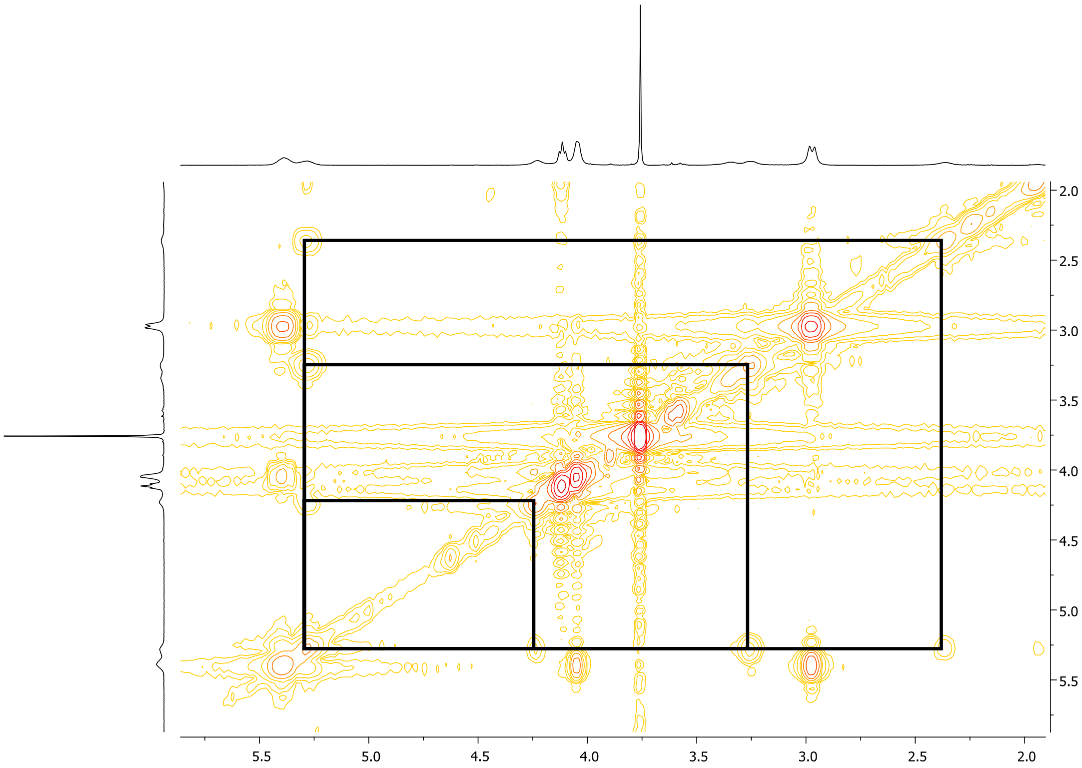


Figure 5. Expanded 2D COSY (^1H-^1H) NMR spectra of reaction of $[Pd(\eta^3-C_3H_5)Cl]_2$ with IL **13** and KOAc.

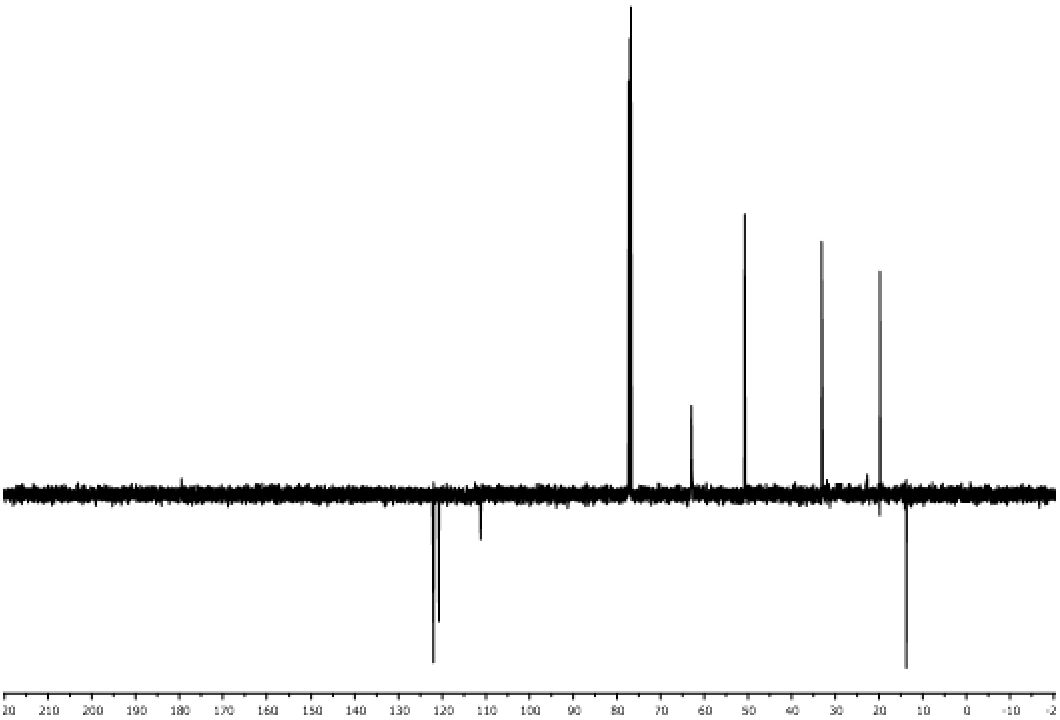


Figure 6. ^{13}C-$\{^1H\}$ NMR spectra of reaction of $[Pd(\eta^3-C_3H_5)Cl]_2$ with IL **13** and KOAc after crystallization with EtOAc/hexane (1:5).

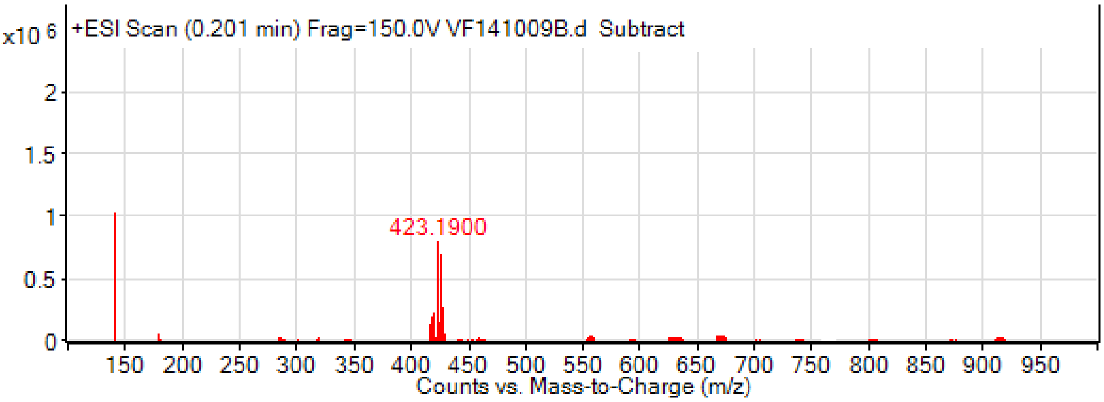
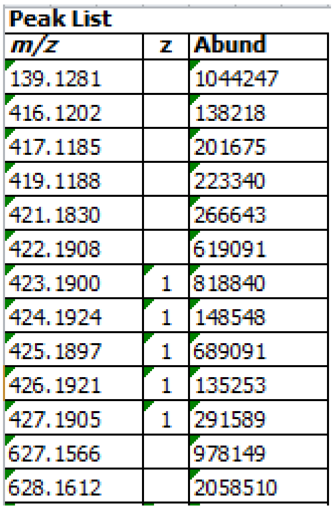


Figure 7. ESI-TOF chromatogram for complex **17**.

Table 1. ESI-TOF data for complex **17**.

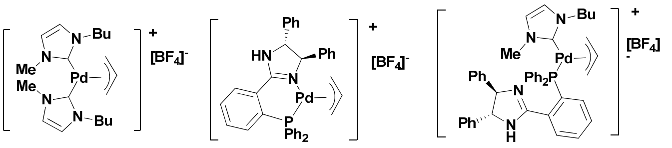


Peak List

m/z	z	Abund
139.1281		1044247
416.1202		138218
417.1185		201675
419.1188		223340
421.1830		266643
422.1908		619091
423.1900	1	818840
424.1924	1	148548
425.1897	1	689091
426.1921	1	135253
427.1905	1	291589
627.1566		978149
628.1612		2058510

*Reactivity of ligand **3** in IL **13** under basic conditions:*

Into a schlenk tube under nitrogen was introduced the palladium precursor [Pd(η^3-C_3H_5)Cl]$_2$ (50 mg, 0.136 mmol) and the phosphine-imidazoline ligand **3** (0.30 mmol) in [bmim][BF_4] (2 mL). Then, KOAc (14 mg, 0.14 mmol) was introduced and the reaction mixture was heated at 45 ºC for 16 hours. Then, the reacion crude was analysed by NMR and Mass spectroscopy observing a mixture of three different complexes as shown in Figure 8.



17 **18** **19**

Figure 8. Mixture of complexes formed by reaction of ligand **3** and [Pd(η^3-C_3H_5)Cl]$_2$ in ionic liquid **13** and KOAc.

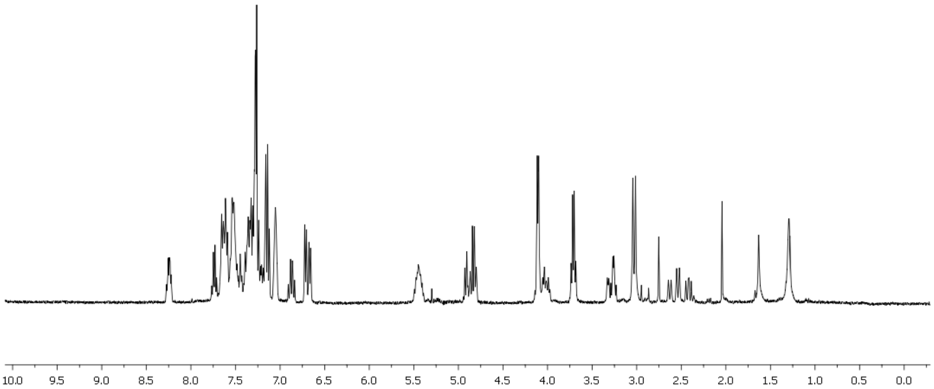


Figure 9. ^{1}H NMR of complex **18** at rt.

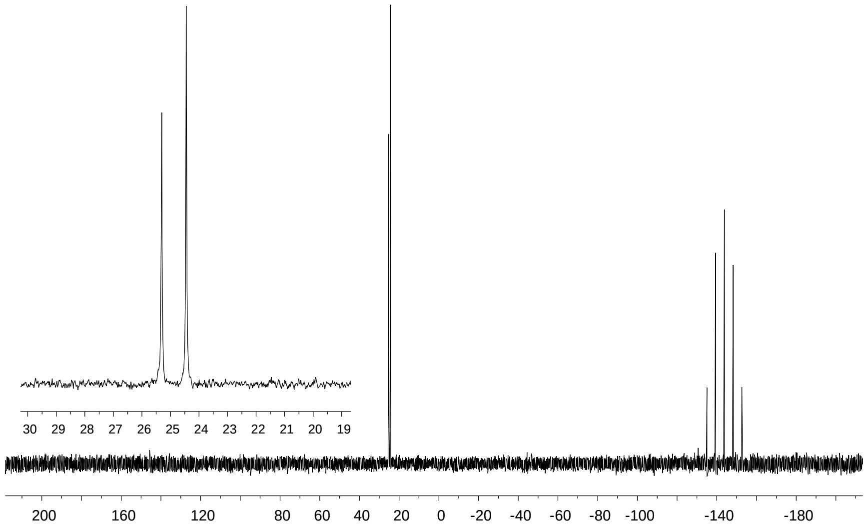
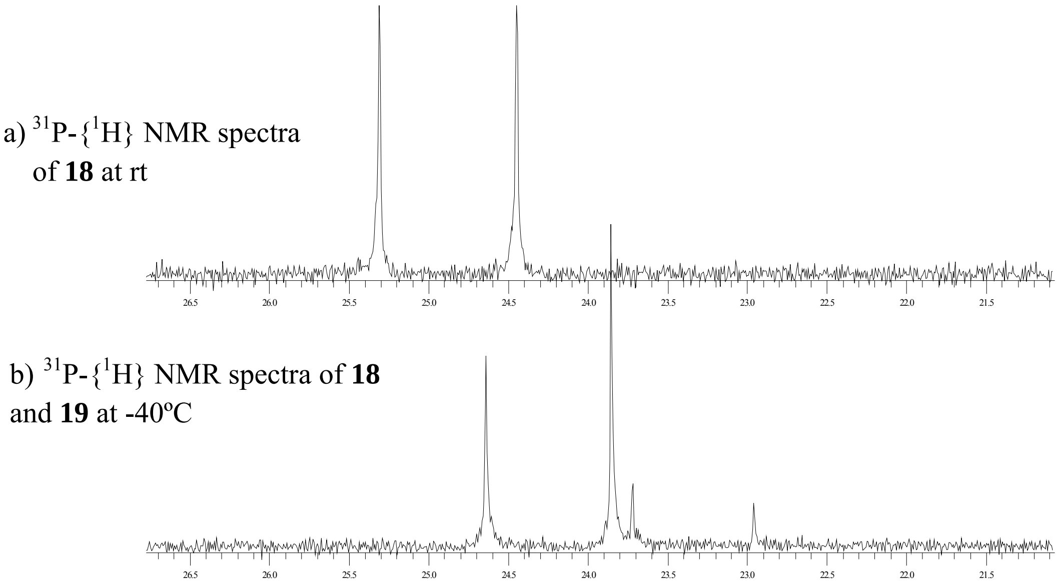


Figure 10. ^{31}P-{^{1}H} NMR of complex **18** at rt.

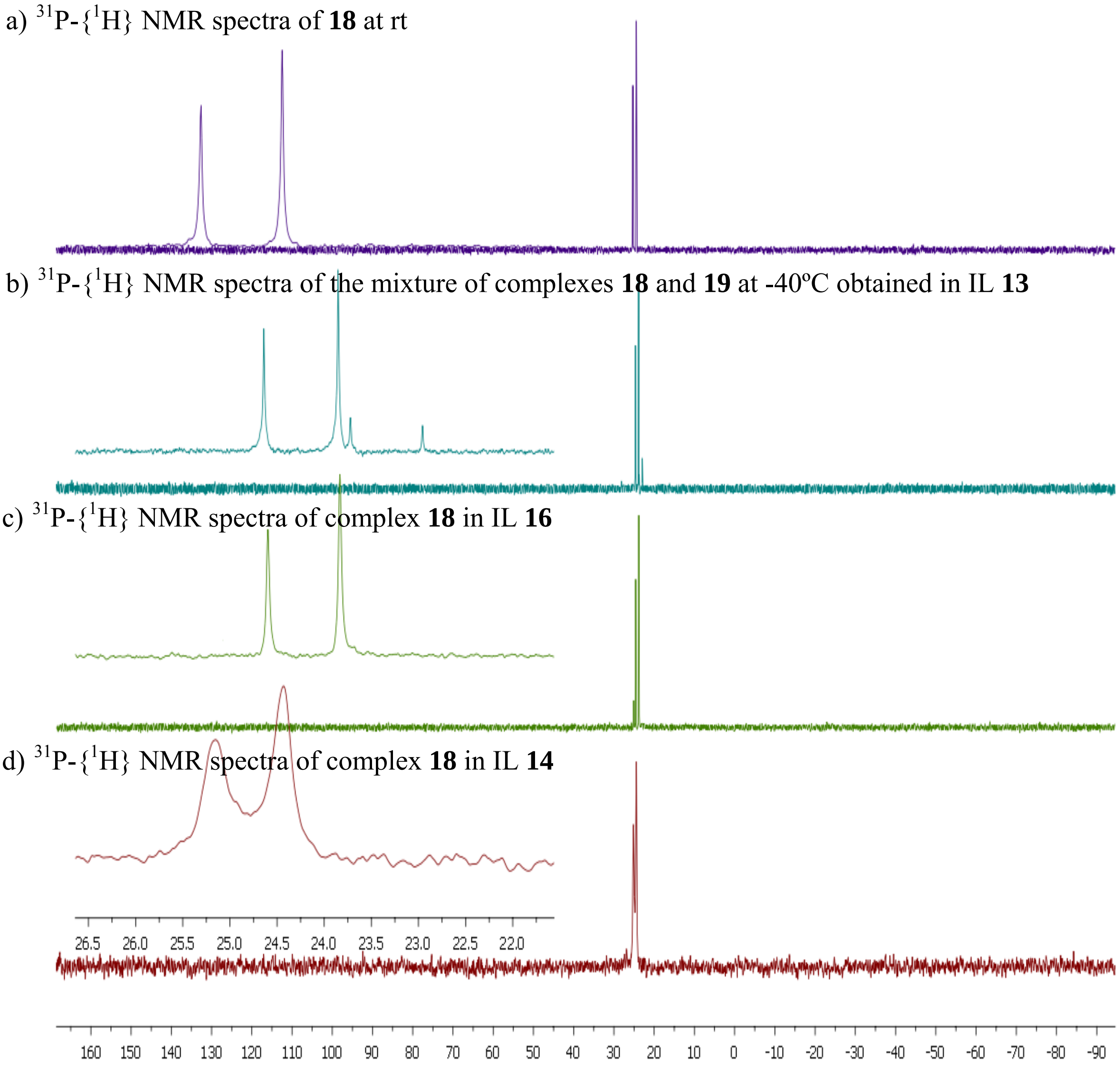

a) ^{31}P-{^{1}H} NMR spectra of **18** at rt

b) ^{31}P-{^{1}H} NMR spectra of **18** and **19** at -40ºC

Figure 11. ^{31}P-{^{1}H} NMR spectra: a) Isolated complex **18**; b) Complex mixture of **18** and **19** obtained by reaction of ligand **3** with [Pd(η^3-C_3H_5)Cl]$_2$ in ionic liquid **13** and KOAc.

*Reactivity of ligand **3** in ILs **13**, **14** and **16** under basic conditions:*

Into a schlenk tube under nitrogen was introduced the palladium precursor [Pd(η^3-C_3H_5)Cl]$_2$ (50 mg, 0.136 mmol) and the phosphine-imidazoline ligand **3** (0.30 mmol) in 2 mL of the corresponding ionic liquid (**13**, **14** or **16**). Then, KOAc (0.14 mg, 0.14 mmol) was introduced and the reaction mixture was heated at 45 ºC for 16 hours. Then, the reacion crude was analysed by NMR.



a) ^{31}P-{^{1}H} NMR spectra of **18** at rt

b) ^{31}P-{^{1}H} NMR spectra of the mixture of complexes **18** and **19** at -40ºC obtained in IL **13**

c) ^{31}P-{^{1}H} NMR spectra of complex **18** in IL **16**

d) ^{31}P-{^{1}H} NMR spectra of complex **18** in IL **14**

Figure 12. ^{31}P-{^{1}H} NMR spectra: a) ^{31}P-{^{1}H} NMR spectra of the isolated complex **18** at rt; b) ^{31}P-{^{1}H} NMR spectra of the mixture of complexes **18** and **19** at -40ºC obtained by reaction of ligand **3** and [Pd(η^3-C_3H_5)Cl]$_2$ in the IL **13**; c) ^{31}P-{^{1}H} NMR spectra of complex **18** obtained by reaction of ligand **3** and [Pd(η^3-C_3H_5)Cl]$_2$ in the IL **16**; d) ^{31}P-{^{1}H} NMR spectra of complex **18** obtained by reaction of ligand **3** and [Pd(η^3-C_3H_5)Cl]$_2$ in the IL **14**.

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[i] D. Popa, C. Puigjaner, M. Gómez, J. Benet-Buchholz, A. Vidal-Ferran, M. A. Pericàs, *Adv. Synth. Catal.* **2007**, *349*, 2265.

[ii] M. Zehnder, S. Schaffner, M. Neuburger, D. A. Plattner, *Inorg. Chim. Acta* **2002**, *337*, 287.

[iii] M. Zehnder, S. Schaffner, M. Neuburger, D. A. Plattner, *Inorg. Chim. Acta* **2002**, *337*, 287.