Electronic Supplementary Material (ESI)

Bimetallic Co/Al nanoparticles in ionic liquid: Synthesis and application to alkyne hydrogenation

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Ionic liquid

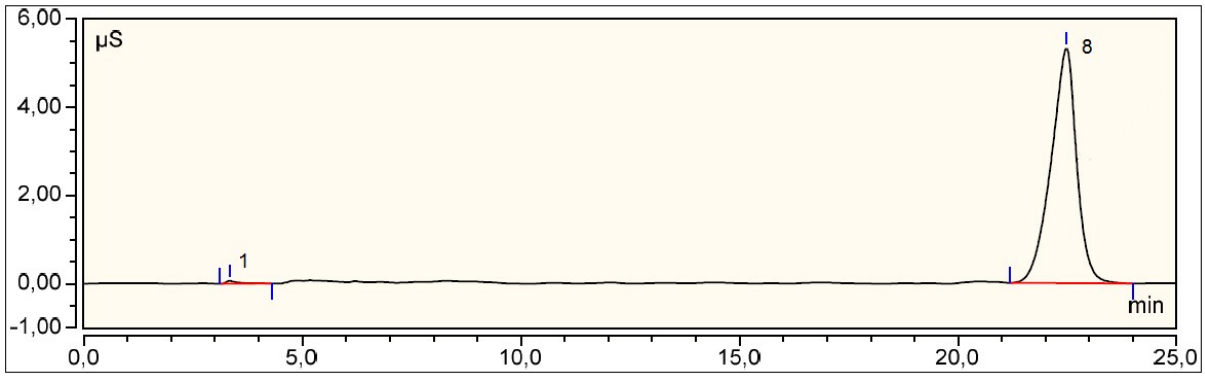


Fig. S1 Chromatogram of [BMIm]NTf_2. Column: AG 22/ AS 22, flowrate: 1.20 mL/min; eluent: 4.5 mmol·L^{-1} Na_2CO_3 und 1.4 mmol·L^{-1} $NaHCO_3$ and 30 vol.-% acetonitrile, run time: 25 min. 1 H_2O, 8 NTf_2^-.

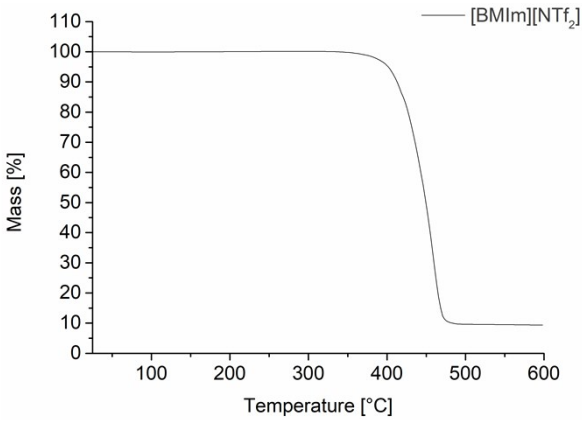


Fig. S2 TG curve of [BMIm]NTf_2. 25–600 °C, heating rate 5 K/min.

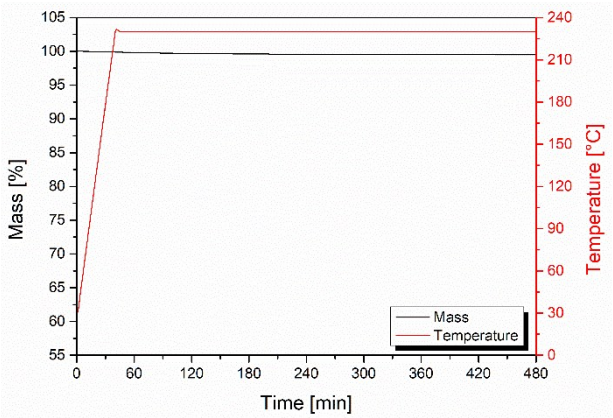


Fig. S3 TG curve of [BMIm]NTf_2. 25-230 °C, heating rate 5 K/min, isothermal step at 230 °C for 8 h (black: mass loss, red: temperature profile).

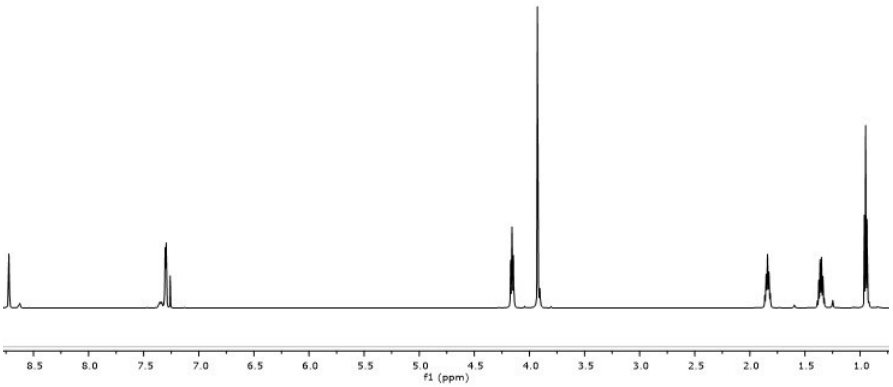


Fig. S4 ^{1}H-NMR of [BMIm]NTf$_2$ in $CDCl_3$ (7.26 ppm) after microwave irradiation to 230 °C for 30 min.

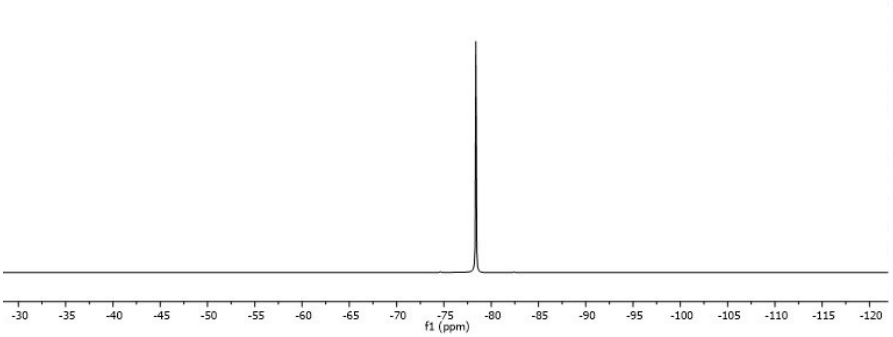


Fig. S5 ^{19}F-NMR of [BMIm]NTf$_2$ without solvent after microwave irradiation to 230 °C for 30 min.

Precursor

Table S1 Thermogravimetric analysis of [AlCp*]$_4$, $Co_2(CO)_8$, [$Me_2Al(^iPr_2$-MeAMD)] and [Co(^{i}Pr$_2$-MeAMD)$_2$].[a]

Precursor	Decomposition temperature [°C]
[AlCp*]$_4$	113
$Co_2(CO)_8$	75; 136
[$Me_2Al(^iPr_2$-MeAMD)]	95
[Co(^{i}Pr$_2$-MeAMD)$_2$]	83; 173

[a] See thermogravimetric diagrams in Fig. S6 below.

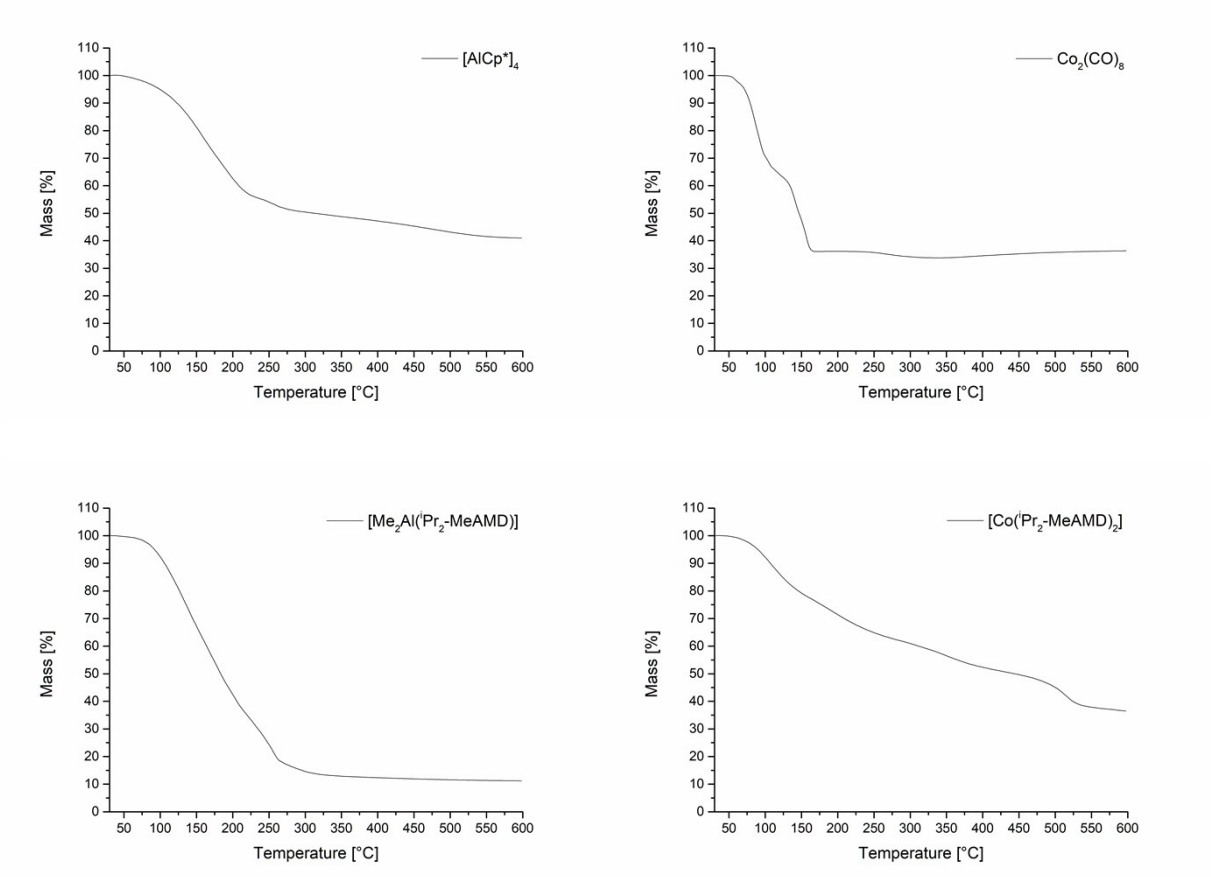
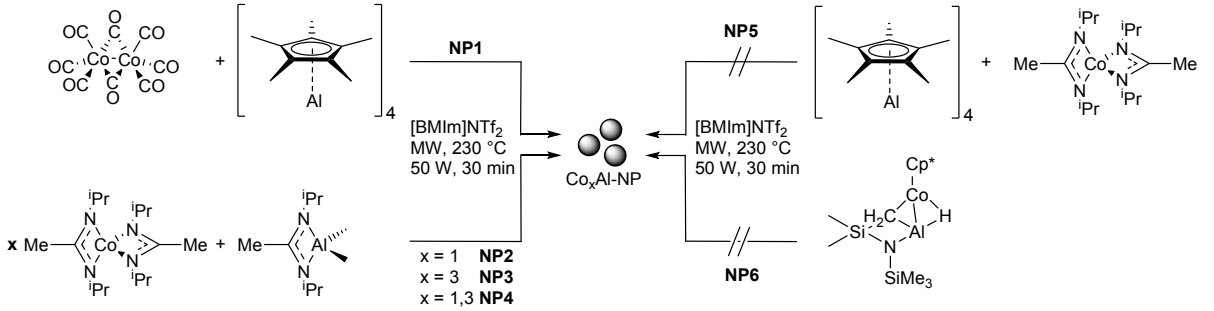


Fig. S6 TG curves of the precursors $[AlCp^*]_4$, $Co_2(CO)_8$, $[Me_2Al(^iPr_2\text{-}MeAMD)]$ and $[Co(^iPr_2\text{-}MeAMD)_2]$.

Nanoparticles



Scheme 1 Synthesis of Co/Al-NPs, from $Co_2(CO)_8$ and $[(AlCp^*)_4]$ (NP1), $[Co(^iPr_2\text{-}MeAMD)_2]$ and $[Me_2Al(^iPr_2\text{-}MeAMD)]$ in different molar ratio (NP2, NP3, NP4), $[Co(^iPr_2\text{-}MeAMD)_2]$ and $[(AlCp^*)_4]$ (NP5) and $[Cp^*Co(\mu\text{-}H)(Al(\kappa^2\text{-}(CH_2SiMe_2)NSiMe_3)(btsa))]$ (NP6) by microwave (MW) assisted thermal decomposition in $[BMIm]NTf_2$.

Table S2 Quantification cobalt against aluminum by EDX analysis.[a]

	EDX 1 Co:Al [at.-%]	EDX 2 Co:Al [at.-%]	EDX 3 Co:Al [at.-%]	EDX 4 Co:Al [at.-%]
CoAl (NP1)	45:55	33:67	50:50	58:42
CoAl (NP2)	30:70	39:61	25:75	--
Co_3Al (NP3)	85:15	84:16	77:23	--
CoAl/ Co_3Al (NP4)	57:43	--	--	--
Co@Al (NP5)	--	--	--	--
Co@Al (NP6)	39:61	88:12	1:99	--

[a] Quantification of $Co_{K\alpha1}$ and $Al_{K\alpha1}$.

Table S3 Quantification cobalt against aluminum by XPS analysis.

		Area	ASF[a,b]	at.-%
NP1	Cobalt[b,c]	23939.3	10003.9	41
	Aluminum[d,e]	3433.7	14673.9	59
NP2	Cobalt[b,c]	28258.6	11808.9	43
	Aluminum[d,e]	3607.7	15417.4	57
NP3	Cobalt[b,c]	51452.9	21501.4	75
	Aluminum[d,e]	1704.3	7283.21	25
NP4	Cobalt[b,c]	20598.3	8607.73	50
	Aluminum[d,e]	2029.5	8673.08	50

[a] The atomic sensitivity factor (F_{ASF}) is element specific.; $ASF = \frac{Area}{F_{ASF}}$. [b] The Co $2p^3/_2$ orbital were used for calculations. [c] F_{ASF} = 2.393. [d] The Al 2p orbital were used for calculations. [e] F_{ASF} = 0.234.

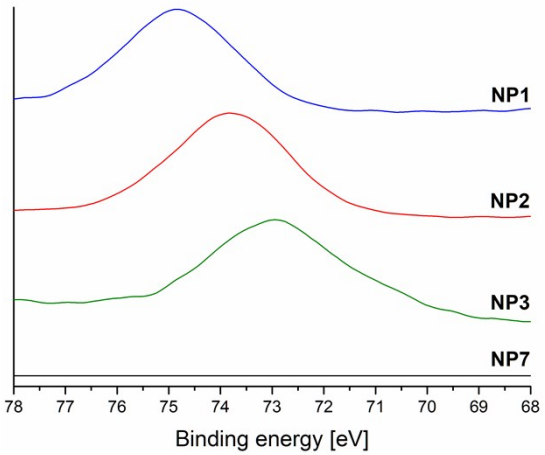


Fig. S7 Comparison of the HR-spectra of Al 2p of NP1 (blue), NP2 (red), NP3 (green) and Co-NPs (NP7) from 68 eV to 78 eV.

CoAl-NP (NP1)

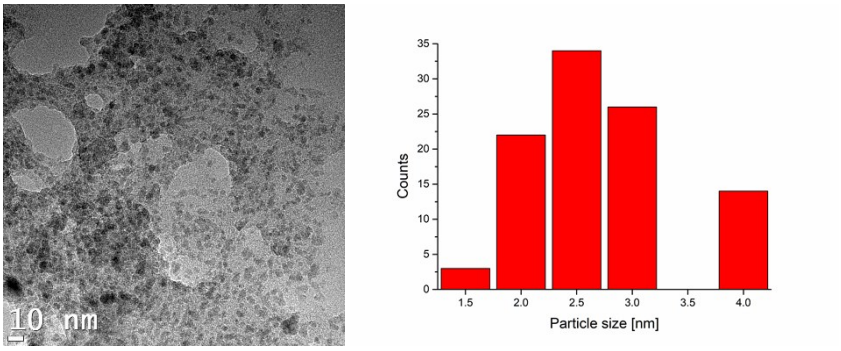


Fig. S8 Left, middle: TEM images of 0.5 wt.-% CoAl-NPs (NP1) from $Co_2(CO)_8$ and $[AlCp^*]_4$ in $[BMIm]NTf_2$; right: particle size histogram of NP1 in $[BMIm]NTf_2$.

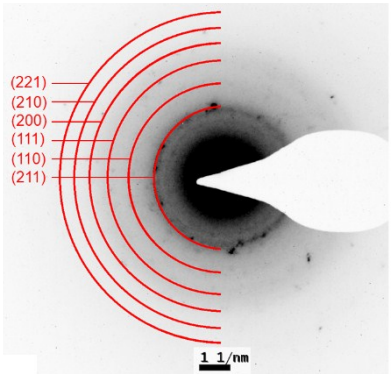


Fig. S9 SAED of 0.5 wt.-% CoAl-NPs (NP1) in $[BMIm]NTf_2$ from $Co_2(CO)_8$ and $[AlCp^*]_4$ (CoAl reference reflexes[1] in red, face centered cubic (fcc) structure with space group $Pm\bar{3}m$). Additional diffraction rings in the lower angle regime indicate an oxide species.

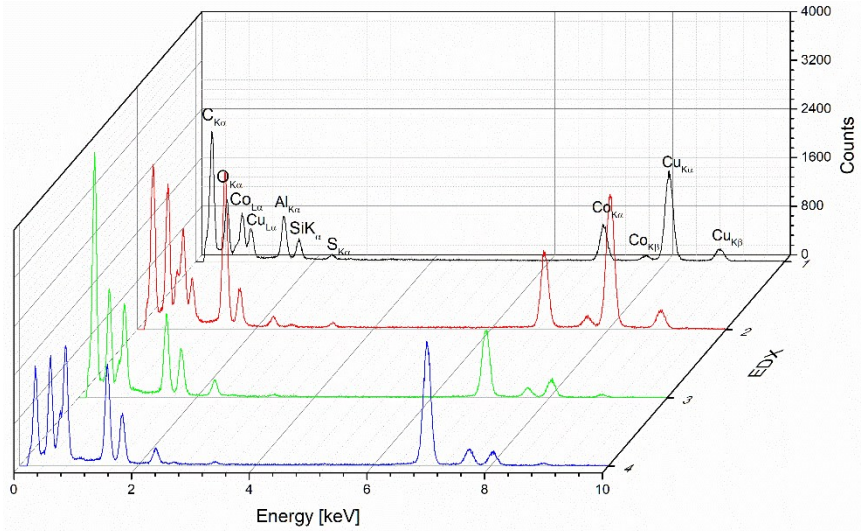


Fig. S10 EDX of 0.5 wt.-% CoAl-NPs (NP1) in $[BMIm]NTf_2$ from $Co_2(CO)_8$ and $[AlCp^*]_4$.

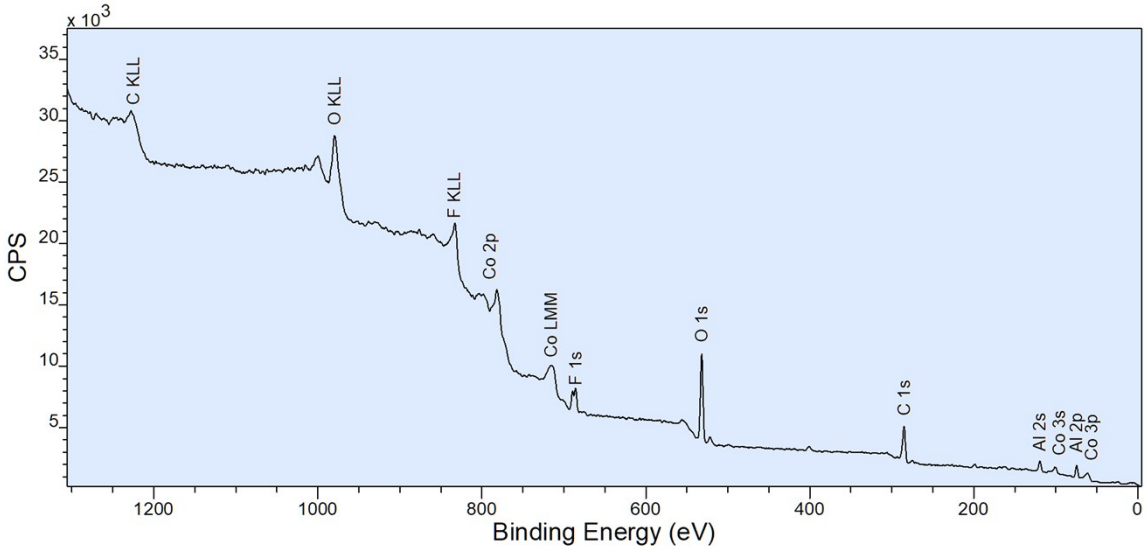


Fig. S11 XPS survey spectrum of 0.5 wt.-% CoAl-NPs (NP1) in $[BMIm]NTf_2$ from $Co_2(CO)_8$ and $[(AlCp^*)_4]$.

CoAl-NP (NP2)

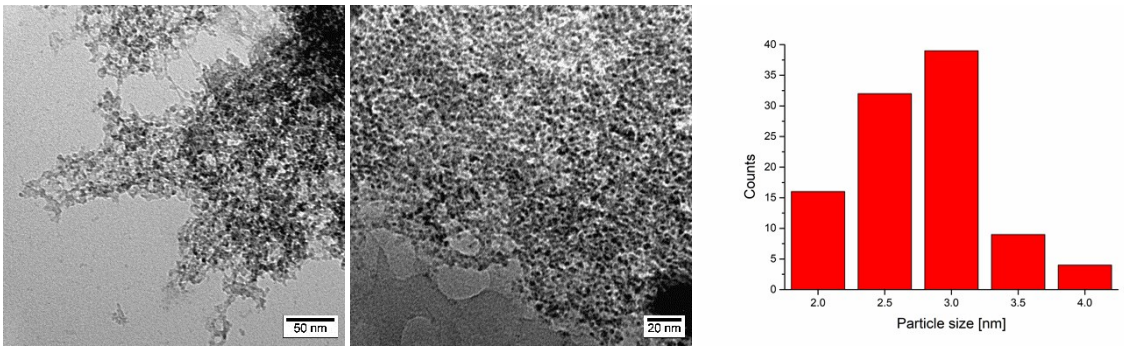


Fig. S12 Left, middle: TEM images of 1.0 wt.-% CoAl-NPs (NP2) from $[Co(^iPr_2\text{-MeAMD})_2]$ and $[Me_2Al(^iPr_2\text{-MeAMD})]$ in $[BMIm]NTf_2$; right: particle size histogram of NP2 in $[BMIm]NTf_2$.

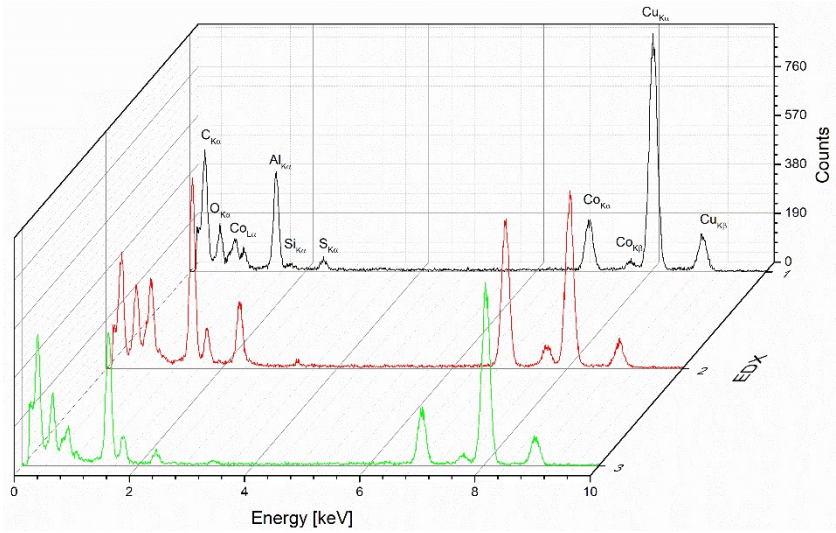


Fig. S13 EDX of 1.0 wt.-% CoAl-NPs (NP2) from $[Co(^iPr_2\text{-MeAMD})_2]$ and $[Me_2Al(^iPr_2\text{-MeAMD})]$ in $[BMIm]NTf_2$.

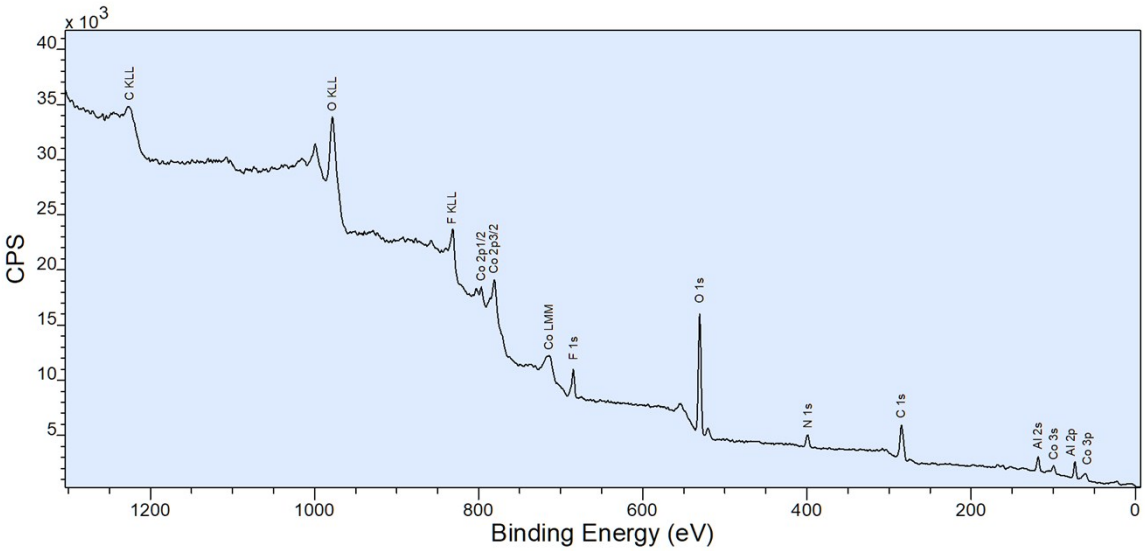


Fig. S14 XPS survey spectrum of 1.0 wt.-% CoAl-NPs (NP2) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me$_2$Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf$_2$.

Co$_3$Al-NP (NP3)

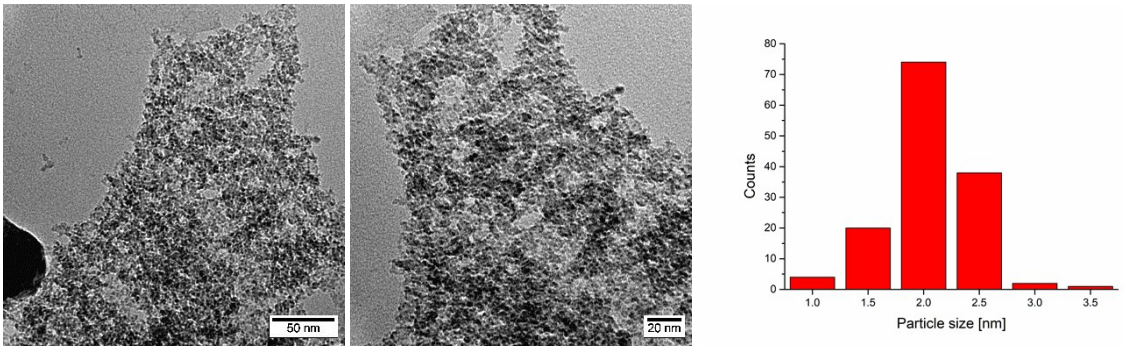


Fig. S15 Left, middle: TEM images of 1.0 wt.-% Co$_3$Al-NPs (NP3) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me$_2$Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf$_2$; right: particle size histogram of NP3 in [BMIm]NTf$_2$.

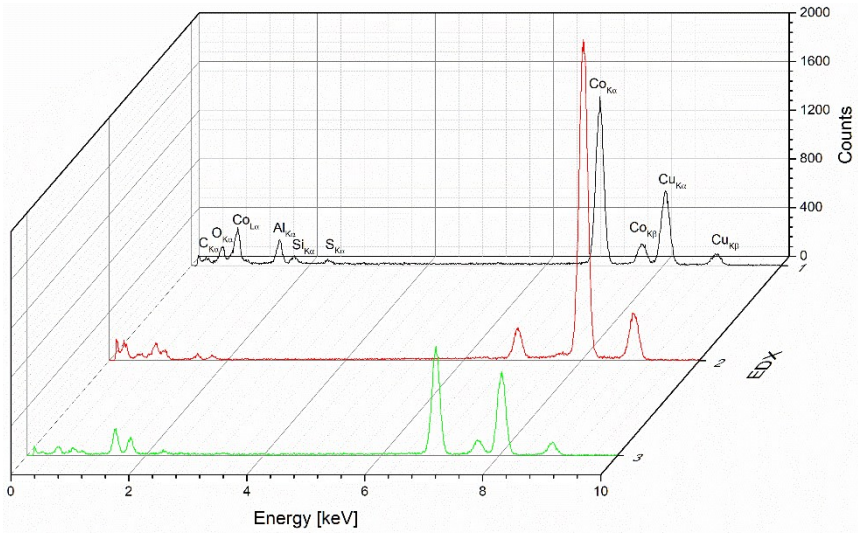


Fig. S16 EDX of 1.0 wt.-% Co$_3$Al-NPs (NP3) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me$_2$Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf$_2$.

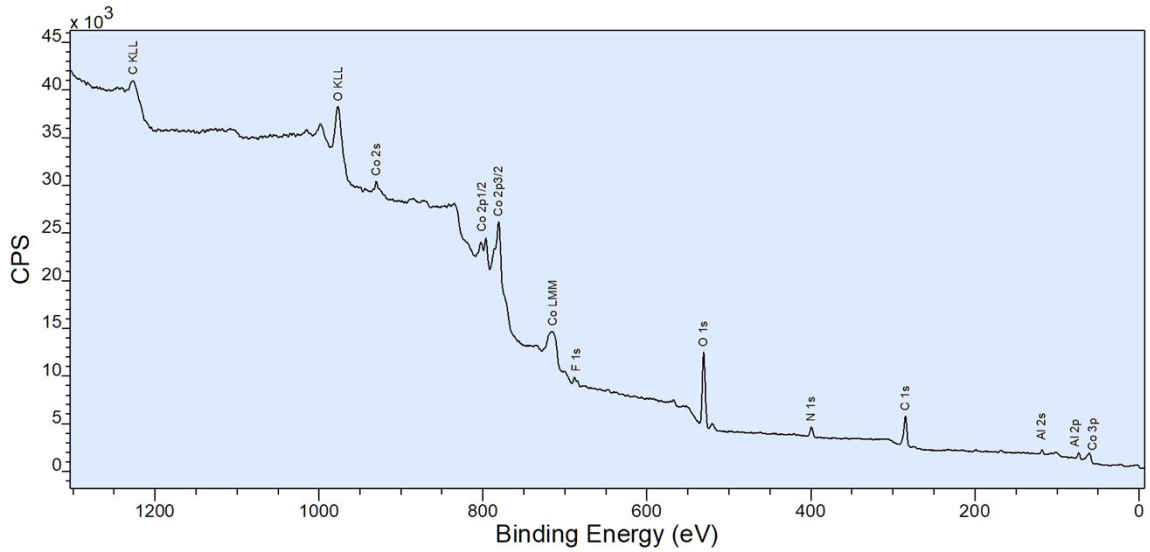


Fig. S17 XPS survey spectrum of 1.0 wt.-% Co_3Al-NPs (NP3) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me$_2$Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf$_2$.

CoAl/ Co_3Al-NP (NP4)

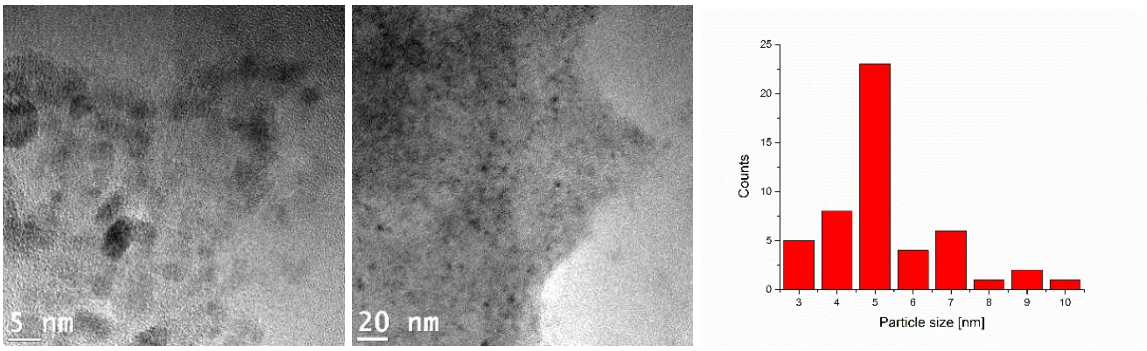


Fig. S18 Left, middle: TEM images of 0.5 wt.-% CoAl/ Co_3Al-NPs (NP4) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me$_2$Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf$_2$; right: particle size histogram of NP4 in [BMIm]NTf$_2$.

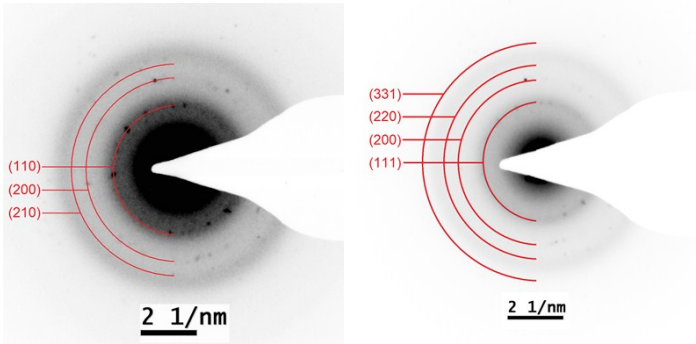


Fig. S19 SAED of 0.5 wt.-% CoAl/ Co_3Al-NPs (NP4) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me$_2$Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf$_2$; left: Co_3Al (Co_3Al reference reflexes[2] in red, face centered cubic (fcc) structure with space group $Pm\bar{3}m$); right: CoAl (CoAl reference reflexes[1] in red, face centered cubic (fcc) structure with space group $Pm\bar{3}m$).

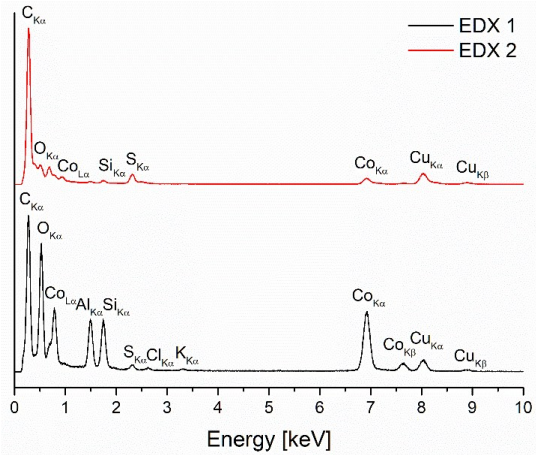


Fig. S20 EDX of 0.5 wt.-% CoAl/ Co_3Al-NPs (NP4) in [BMIm]NTf_2 from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [Me_2Al(^{i}Pr$_2$-MeAMD)] in [BMIm]NTf_2.

Co-NP@Al (NP5)

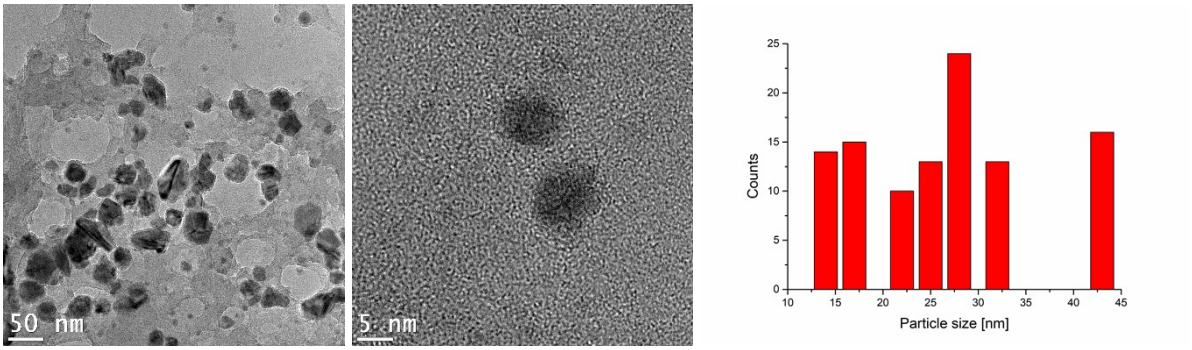


Fig. S21 Left, middle: TEM images of 0.5 wt.-% Co-NPs@Al (NP5) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [AlCp*]$_4$ in [BMIm]NTf_2; right: particle size histogram of NP5 in [BMIm]NTf_2.

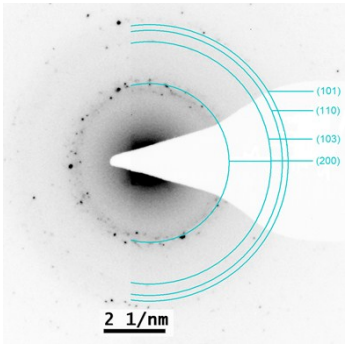


Fig. S22 SAED of 0.5 wt.-% Co-NPs@Al (NP5) from [Co(^{i}Pr$_2$-MeAMD)$_2$] and [AlCp*]$_4$ in [BMIm]NTf_2 (Co reference reflexes in blue from COD 9008492, hexagonal close packed (hcp) structure with space group $P6_3/mmc$).

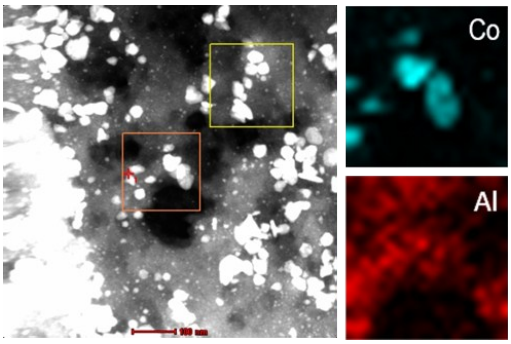


Fig. 23 HAADF-STEM image (middle) and EDX-mapping (right) of cobalt (blue) and aluminum (red) of NP5 obtained by thermal decomposition of [Co(^{i}Pr$_2$-MeAMD)$_2$] and [(AlCp*)$_4$] in [BMIm]NTf$_2$. The orange window in the HAADF-STEM image displays the area of EDX mapping.

Co-NP (NP6)

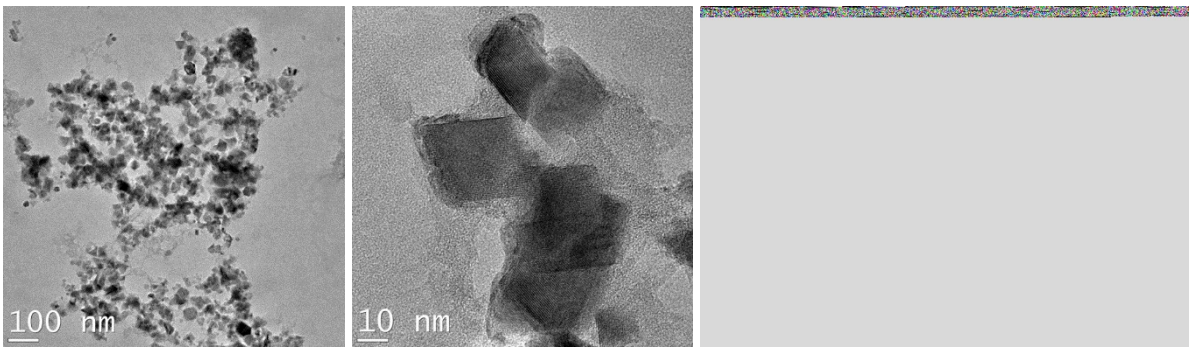


Fig. S24 Left, middle: TEM images of Co-NPs@Al (NP6) from [Cp*Co(μ-H)(Al(κ^2-(CH$_2$SiMe$_2$)NSiMe$_3$)(btsa))] in [BMIm]NTf$_2$; right: particle size histogram of NP6 in [BMIm]NTf$_2$.

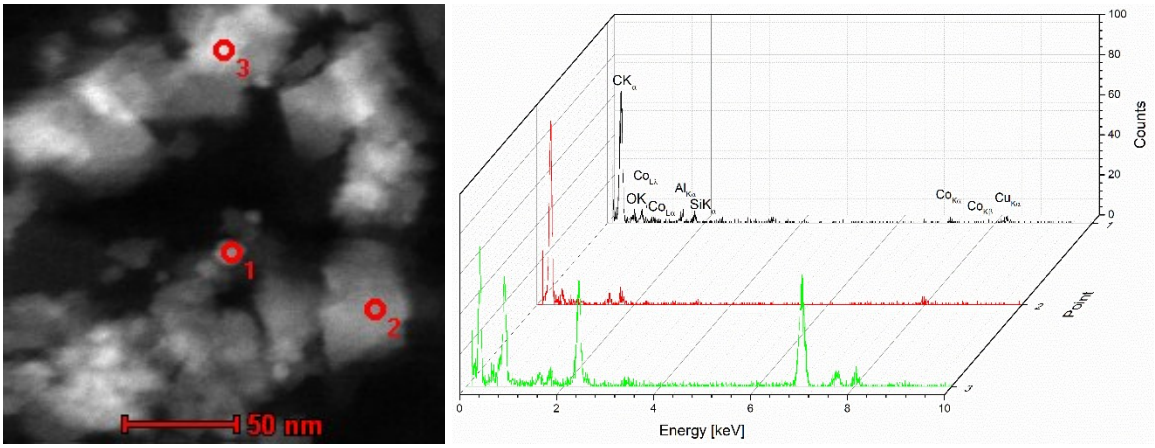


Fig. S25 HAADF-STEM image and point-EDX of 0.5 wt.-% Co-NP@Al (NP6) from [Cp*Co(μ-H)(Al(κ^2-(CH$_2$SiMe$_2$)NSiMe$_3$)(btsa))] in [BMIm]NTf$_2$.

Table S4 Quantification cobalt against aluminum by point-EDX (HAADF-STEM) analysis for Co-NP@Al (NP6).[a]

Point	Co [at.-%]	Al [at.-%]
1	100	0
2	100	0
3	97	3

[a] Quantification of Co$_{Kα1}$ and Al$_{Kα1}$.

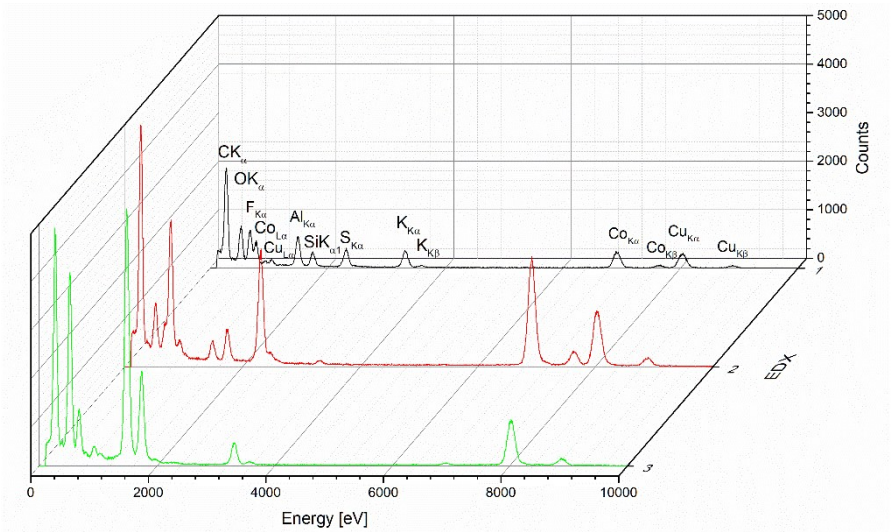


Fig. S26 EDX (TEM) of Co-NP@Al (NP6) from [Cp*Co(μ-H)(Al(κ^2-(CH_2SiMe_2)$NSiMe_3$)(btsa))] in [BMIm]NTf_2.

Co-NP (NP7)

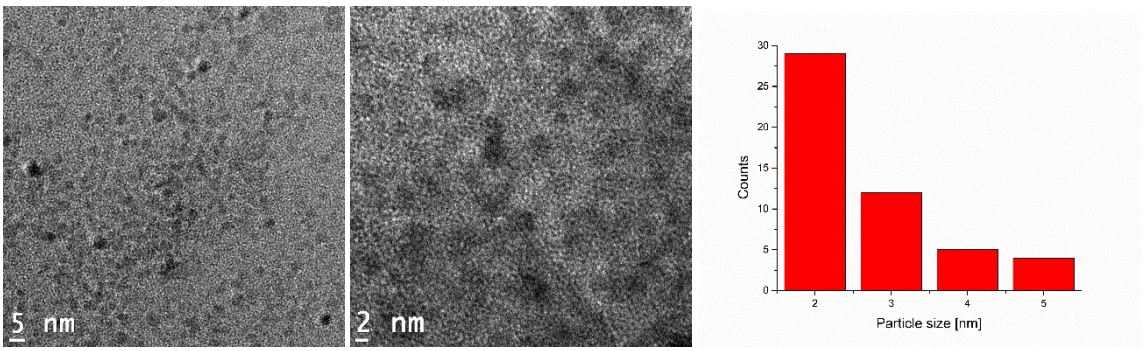


Fig. S27 Left, middle: TEM images of 1.0 wt.-% Co-NPs (NP7) from [Co(^{i}Pr_2-MeAMD)$_2$] in [BMIm]NTf_2; right: particle size histogram of NP7 in [BMIm]NTf_2.

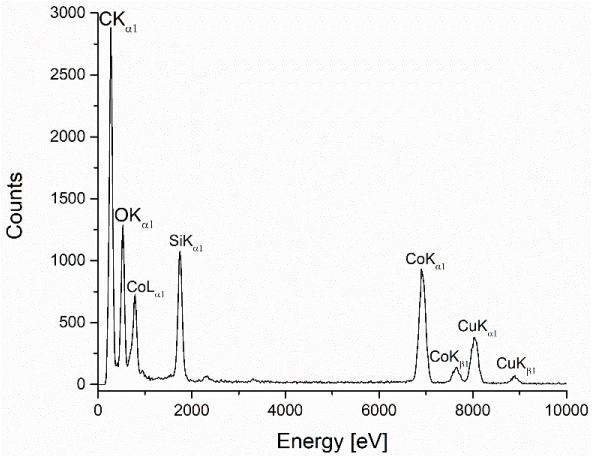
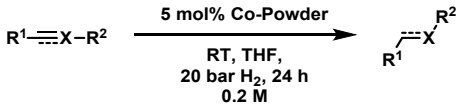
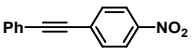


Fig. S28 EDX of Co-NPs (NP7) from [Co(^{i}Pr_2-MeAMD)$_2$] in [BMIm]NTf_2.

Hydrogenation reactions Co-, CoAl- and Co_3Al-NPs

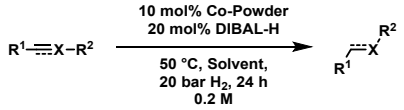
Table S5 First screening.



Entry	Substrate	Conversion [%]	Selectivity
1		0	-
2 [a]		0	-
3		0	-
4		0	-
5		0	-
6		0	-
7		0	-
8 [b,c]		0	-
9 [b]		0	-
10 [b,d]		0	-

Conditions: 0.1 mmol alkyne in 0.5 mL THF. Conversion determined/estimated by GC-MS. [a] Pre-activation with 5 mol% $PhSiH_3$; [b] Stirred without H_2 in glovebox for 24 h; [c] Solvent mixture: 0.3 mL THF and 0.2 mL 2-pentanol; [d] 100 mol% $PhSiH_3$.

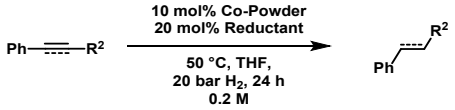
Table S6 Reduction with DIBAL-H. Reaction screening.



Entry	Solvent	Catalyst	Substrate	Conversion [%]
1	THF	Co-powder 20 mol% DIBAL-H		<5
2				<5
3				20[a]
4				<5[a]
5				20[b] (5[c])
6	Hexane	Co-powder 20 mol% DIBAL-H		<5
7				<5
8				20[a]
9				<5[a]
10				<5
11	0.1 mL hexane	0.1 mL Co-NP-IL		0
12				0
13				0
14				0[d]
15				0

Conditions: 0.1 mmol alkyne in 0.5 mL Solvent. Yield and isomer ratio determined/estimated by GC-MS. [a] Reduction with DIBAL-H [b] Alkene; [c] Alkane; [d] Hydrolysis during work up.

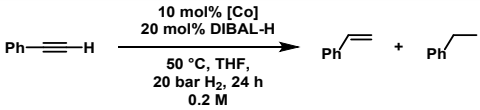
Table S7 Reduction with different reductants. Hydrogenation screening.



Entry	Substrate	Reductant	Conversion [%]
1		NaH	<5
2		$LiAlH_4$	<1
3		DIBAL-H	10
4		NaH	<1
5		$LiAlH_4$	0
6		$NaCNBH_3$	0

Conditions: 0.1 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-MS.

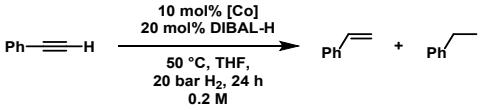
Table S8 Reduction with DIBAL-H, Co-powder/IL. Hydrogenation screening.



Entry	Catalyst system	Conversion [%]	Selectivity
1	Co-powder, 0.5 mL THF, DIBAL-H	20[a]	Hydrogenation
2	Co-powder, 0.5 mL hexane, DIBAL-H	15[a]	Hydrogenation
3	0.1 mL Co-IL, 0.4 mL hexane	0	-
4	0.1 mL Co-IL, 0.4 mL hexane, DIBAL-H	20	Hydrogenation + Trimerization

Conditions: 0.1 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-MS. [a] Also alkane.

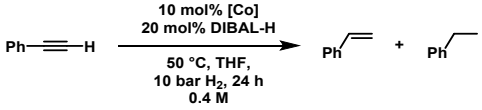
Table S9 Hydrogenation phenylacetylene with Co-powder.



Entry	Reaction	Yield Product [%]	Selectivity
1	Hydrogenation	27 (alkene)	(3% alkane) (8% trimerization)
2[a]		<1 (alkene)	(no trimerization)
3[b]		4 (alkene)	(23% trimerization)
4[c]		12 (alkene)	(no trimerization)
5[d]	Isomerization	63 / 19 / 2 (9% alkane)	-
6	Trimerization	9 (alkene)	no trimerization
7[a]		-	no trimerization
8[b]		29 (trimerization)	29/1 (ratio of isomers)
9[c]		16 (alkene)	no trimerization

Conditions: 0.1 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-MS. [a] 0.1 mL Co-NP-IL + 0.3 mL Hexane; [b] 0.1 mL Co-NP-IL + 0.3 mL hexane + 50 µL 1M DIBAL-H; [c] 0.4 mL hexane + 50 µL 1M DIBAL-H; [d] Isomerization of allylbenzene: SM/E/Z. Trimerization Yield with regard to starting material.

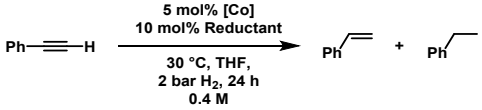
Table S10 Hydrogenation phenylacetylene with Co-, CoAl- and Co_3Al-NPs.



Entry	[Co]	Reductant	Yield product [%]	Selectivity
1	Co	DIBAL-H	34% alkene + 4% alkane + SM	(8% Trimerization)
2	CoAl		2% alkene + 96% alkane	Hydrogenation Trimerization <1%
3	Co_3Al		3% alkene + 96% alkane	Hydrogenation Trimerization <1%
4	CoAl	-	2% alkene + SM	Hydrogenation
5	Co_3Al		3% alkene + SM	Hydrogenation

Conditions: 0.2 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-FID.

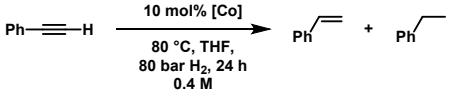
Table S11 Hydrogenation phenylacetylene with CoAl-, Co_3Al-NPs and different reductant.



Entry	[Co]	Reductant	Yield product [%]	Selectivity
1	CoAl	DIBAL-H	4% alkene + 91% alkane	Hydrogenation Trimerization <2%
2	Co_3Al		2% alkene + 97% alkane	Hydrogenation
3	CoAl	$LiAlH_4$	1% alkene + 70% alkane	Hydrogenation
4	Co_3Al		1% alkene + 63 % alkane	Hydrogenation
5	CoAl	BH_3·THF	5% alkene + <1% alkane	Hydrogenation
6	Co_3Al		7% alkene + <1% alkane	Hydrogenation
7	CoAl	NaH	<1% alkene + <1% alkane	Hydrogenation
8	Co_3Al		<1% alkene + <1% alkane	Hydrogenation

Conditions: 0.2 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-FID.

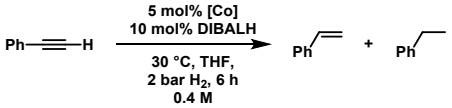
Table S12 Hydrogenation phenylacetylene with CoAl- and Co_3Al-NPs (without DIBAL-H).



Entry	[Co]	Yield product [%]	Selectivity
1	Co	1% alkene	-
2	CoAl	56% alkene + 43% alkane	Hydrogenation
3	Co_3Al	85% alkene + 15% alkane	Hydrogenation

Conditions: 0.2 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-FID.

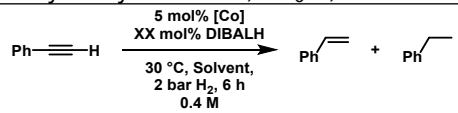
Table S13 Hydrogenation substrates with CoAl-, Co_3Al-NPs and reductant.



Entry	[Co]	Substrate	Yield product [%]	Selectivity
1	CoAl	Ph-CC-H	55% alkene + 6% alkane	Hydrogenation
2	Co_3Al		72% alkene + 9% alkane	Hydrogenation
3	CoAl	Ph-CC-Me	19% *Z*-alkene + 2% *E*-alkene + 2% alkane	Hydrogenation
4	Co_3Al		24% *Z*-alkene + 2% *E*-alkene + 3% alkane	Hydrogenation
5	CoAl	Ph-$(CH_3)C=CH_2$	3% alkane	Hydrogenation
6	Co_3Al		6% alkane	Hydrogenation
7	CoAl	Ph-N=CH-Ph	Decomposition	Hydrogenation
8	Co_3Al		Decomposition	Hydrogenation
9[a]	CoAl	Ph-CC-H	33% alkene+ 3% alkane	Hydrogenation
10[a]	Co_3Al		80% alkene + 14% alkane	Hydrogenation

Conditions: 0.2 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-FID. [a] [BMIm]NTf_2/THF (0.2 mL/0.5 mL) as solvent.

Table S14 Hydrogenation phenylacetylene CoAl, Co_3Al, reductant amount, solvent screening.



Entry	[Co]	Solvent	DIBAL-H [mol%]	Yield product [%]	Selectivity
1	CoAl	THF	10	25% alkene + 3% alkane	Hydrogenation
2	Co_3Al		10	56% alkene + 7% alkane	Hydrogenation
3	CoAl		5	10% alkene + 1% alkane	Hydrogenation
4	Co_3Al		5	8% alkene + 1% alkane	Hydrogenation
5	CoAl		1	1% alkene	Hydrogenation
6	Co_3Al		1	1% alkene	Hydrogenation
7	CoAl	Toluene	10	11% alkene+ 1% alkane	Hydrogenation
8	Co_3Al			12% alkene + 1% alkane	Hydrogenation
9	CoAl	MTBE	10	63% alkene + 9% alkane	Hydrogenation
10	Co_3Al			79% alkene + 14% alkane	Hydrogenation

Conditions: 0.2 mmol alkyne in 0.5 mL solvent. Yield and isomer ratio determined/estimated by GC-FID.

References

1 S. N Hosseini, T. Mousavi, F. Karimzadeh and M. H. Enayati, J. Mater. Sci. Technol., 2011, **27**, 601–606.

2 M. Ellner, S. Kek and B. Predel, *J. Alloys Compd.,* 1992, **189**, 245–248.