Supplementary Information

Transmetalation from Magnesium NHCs – Convenient Synthesis of Chelating π-Acidic NHC Complexes

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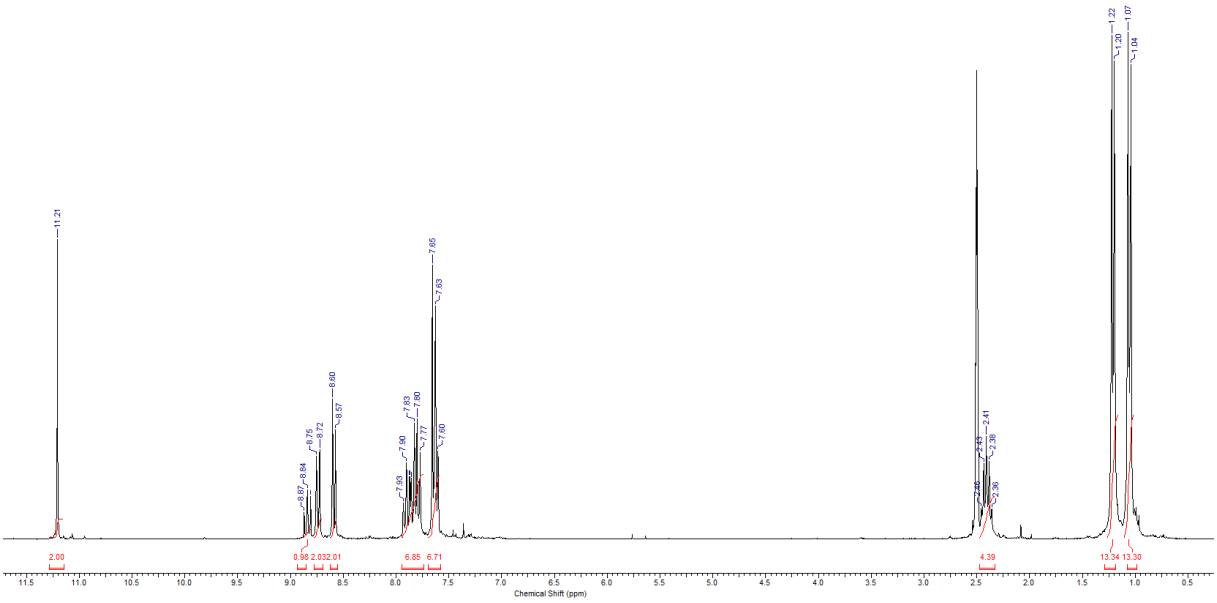

Figure S1. ^{1}H NMR spectrum of benzimidazolium salt $\mathbf{1}^{benz}$ (270 MHz, DMSO-D$_6$).

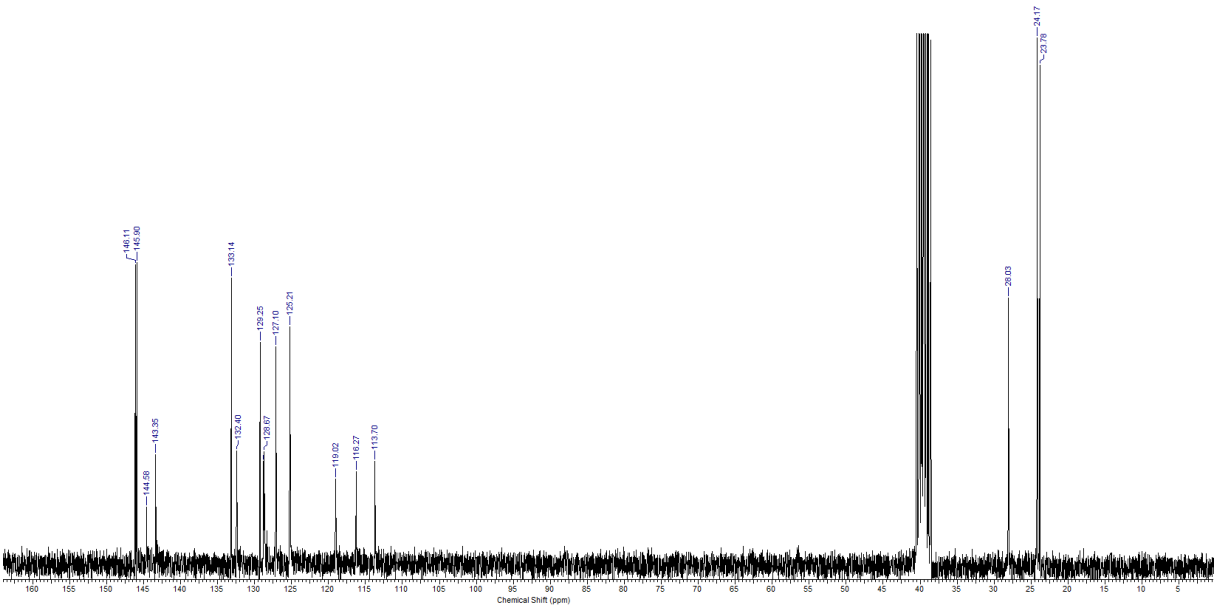

Figure S2. ^{13}C NMR spectrum of benzimidazolium salt $\mathbf{1}^{benz}$ (68 MHz, DMSO-D$_6$).

1.2. Proton and Carbon NMR Spectra of Free Carbene $\mathbf{2^{sa}}$

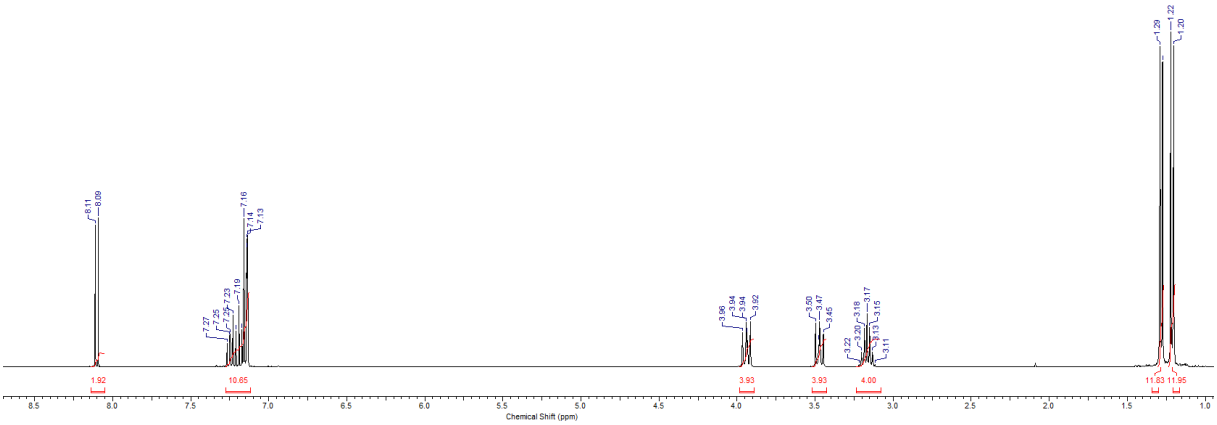

Figure S3. ^{1}H NMR spectrum of free carbene $\mathbf{2^{sa}}$ (400 MHz, C_6D_6).

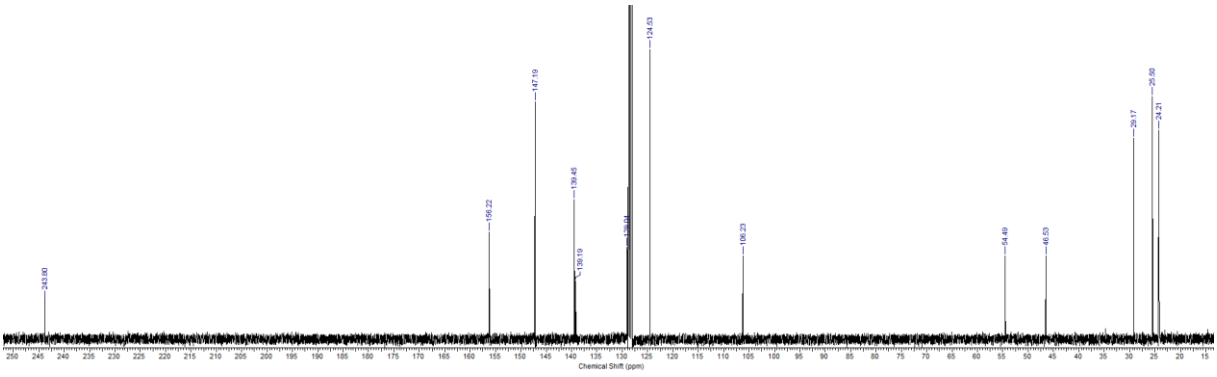

Figure S4. ^{13}C NMR spectrum of free carbene $\mathbf{2^{sa}}$ (101 MHz, C_6D_6).

1.3. Proton and Carbon NMR Spectra of Free Carbene $\mathbf{2^{benz}}$

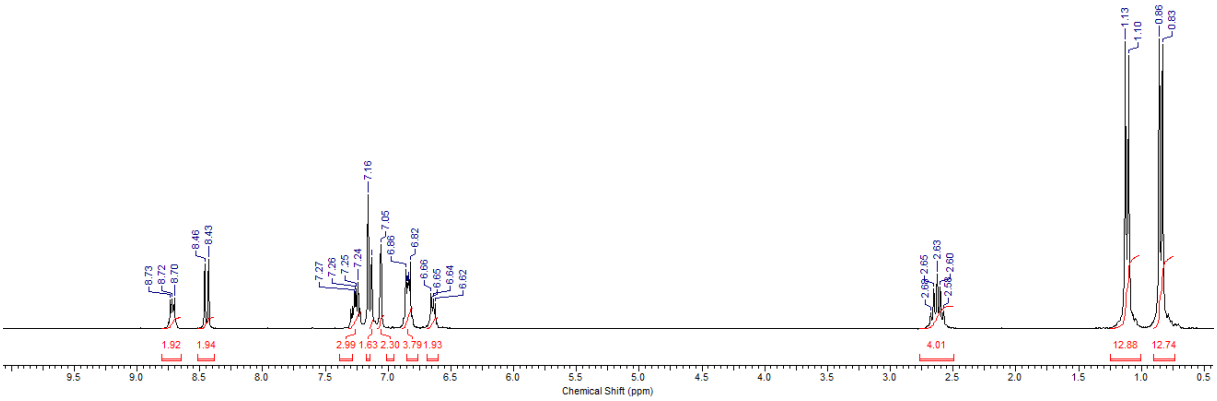

Figure S5. ^{1}H NMR spectrum of free carbene $\mathbf{2^{benz}}$ (270 MHz, C_6D_6).

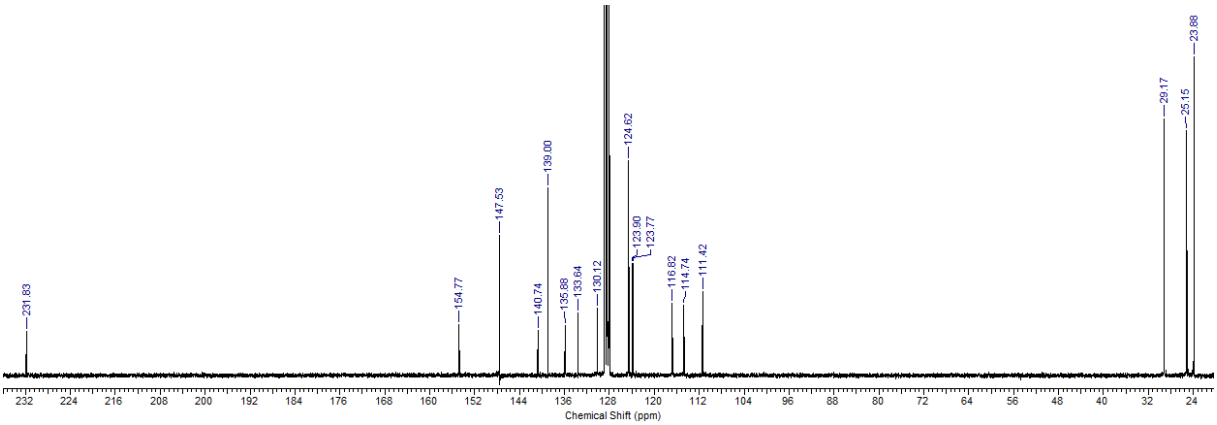

Figure S6. ^{13}C NMR spectrum of free carbene **2**^{benz} (68 MHz, C_6D_6).

1.4. Proton and Carbon NMR Spectra of Palladium Complex ***3***^{sa}

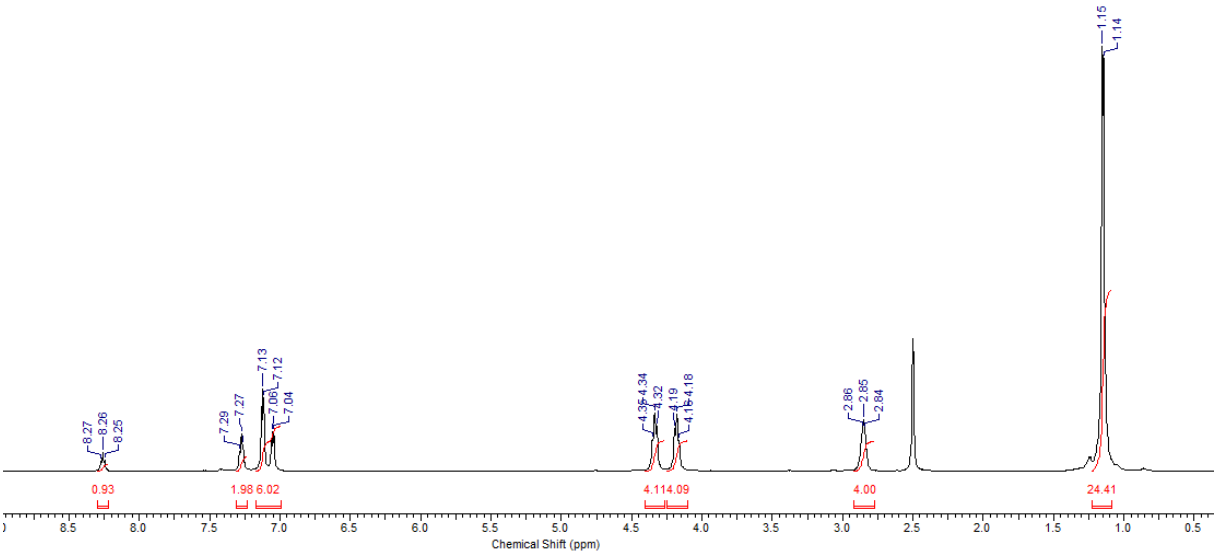

Figure S7. ^{1}H NMR spectrum of palladium complex **3**^{sa} (600 MHz, DMSO-D_6).

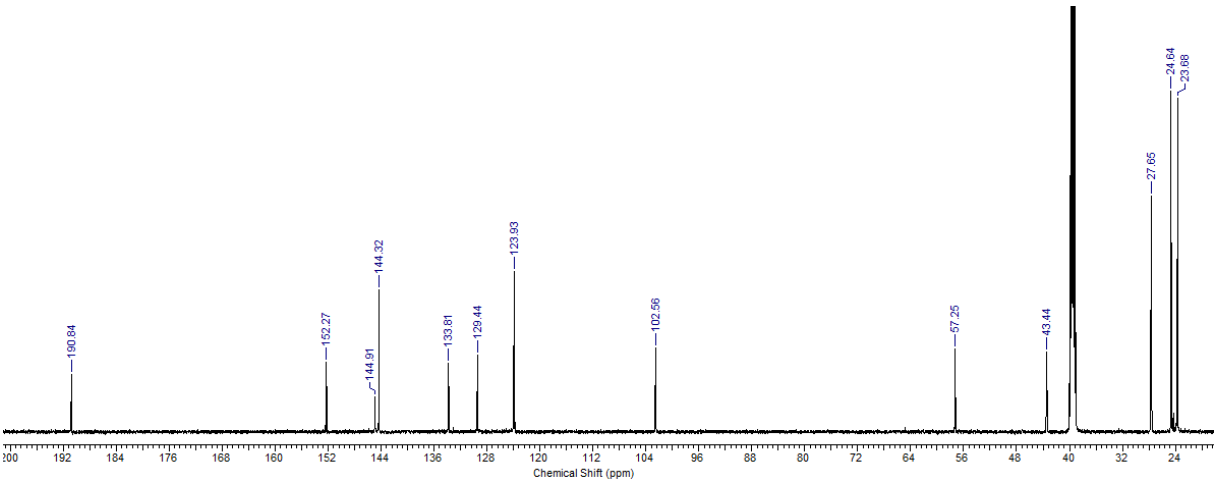

Figure S8. ^{13}C NMR spectrum of palladium complex **3**^{sa} (151 MHz, DMSO-D_6)

1.5. Proton and Carbon NMR Spectra of Palladium Complex ***3benz***

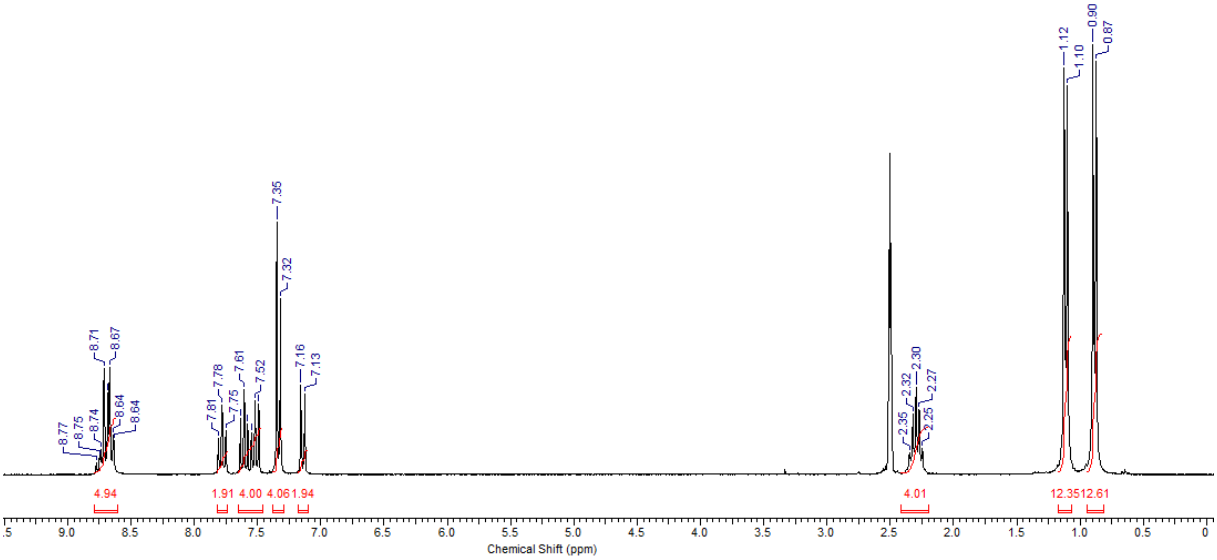

Figure S9. ^{1}H NMR spectrum of palladium complex **3benz** (270 MHz, DMSO-D$_6$).

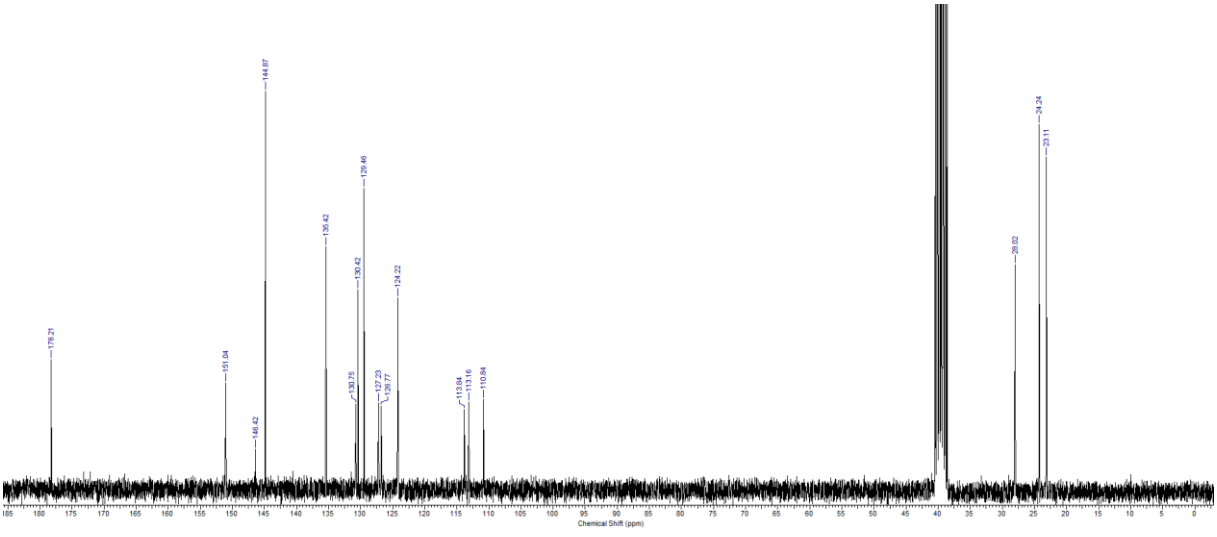

Figure S10. ^{13}C NMR spectrum of palladium complex **3benz** (68 MHz, DMSO-D$_6$).

1.6. Proton and Carbon NMR Spectra of Magnesium Complex ***4**^{sa}*

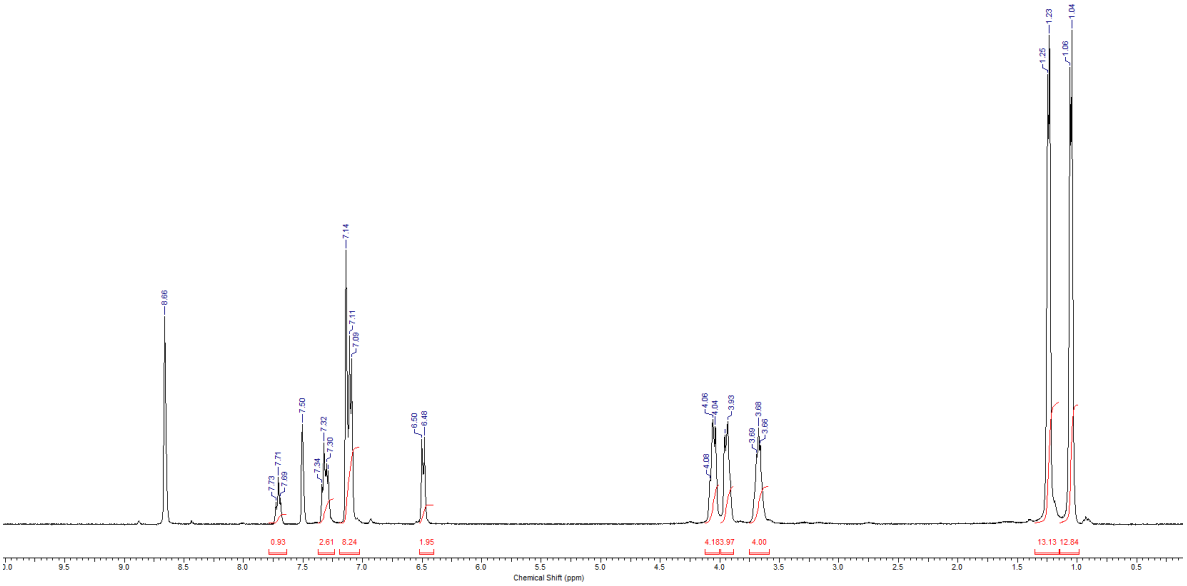

Figure S11. ^{1}H NMR spectrum of magnesium complex **4**^{sa} (400 MHz, pyridine-D_5).

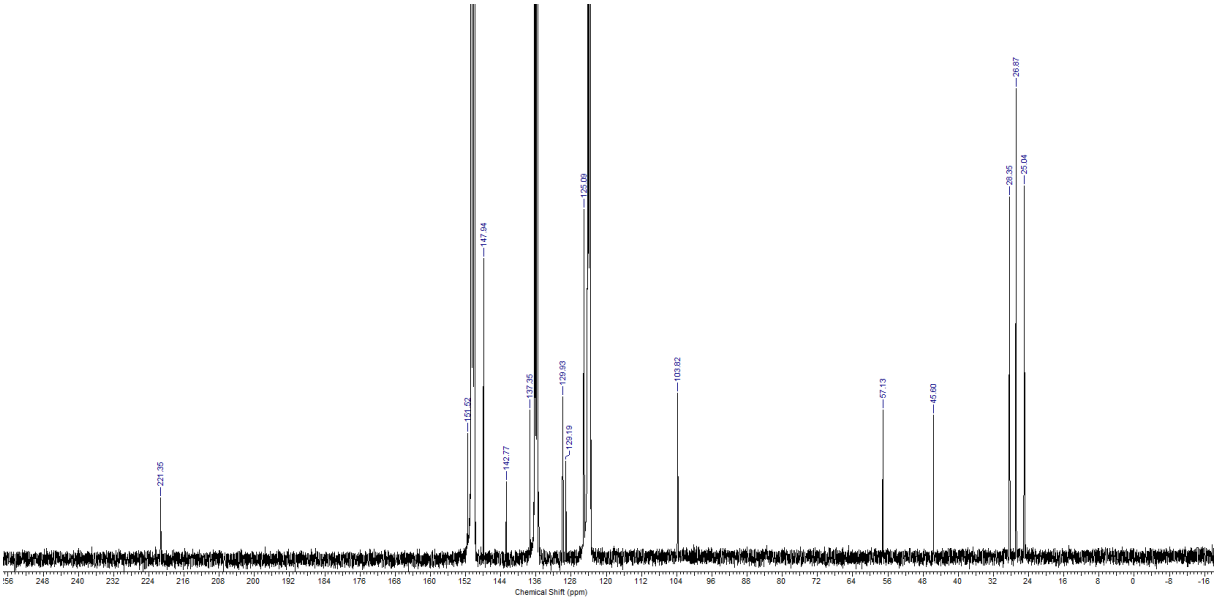

Figure S12. ^{13}C NMR spectrum of magnesium complex **4**^{sa} (101 MHz, pyridine-D_5).

1.7. Proton and Carbon NMR Spectra of Magnesium Complex ***4*** ^{benz}

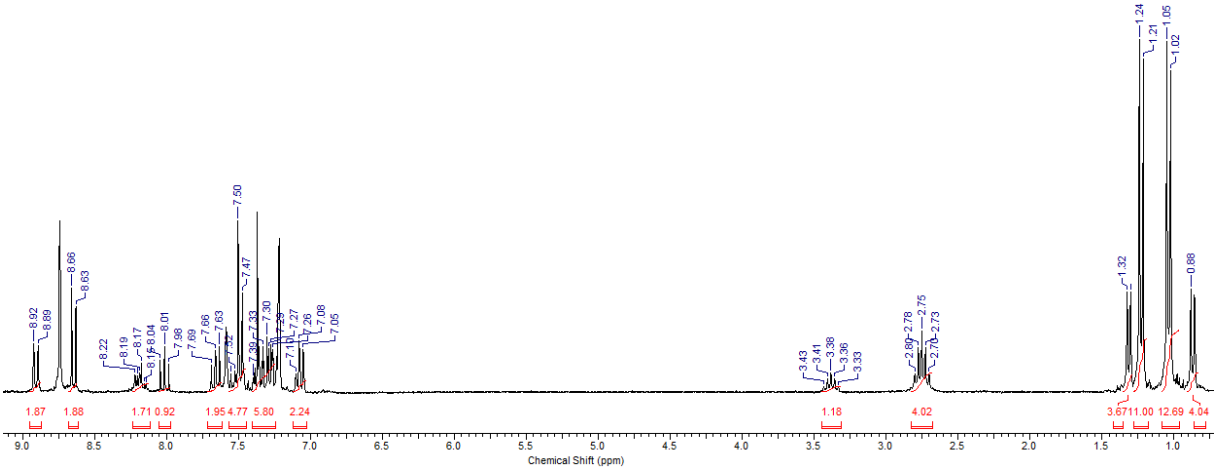

Figure S13. ^{1}H NMR spectrum of magnesium complex **4**^{benz} (270 MHz, pyridine-D$_5$).

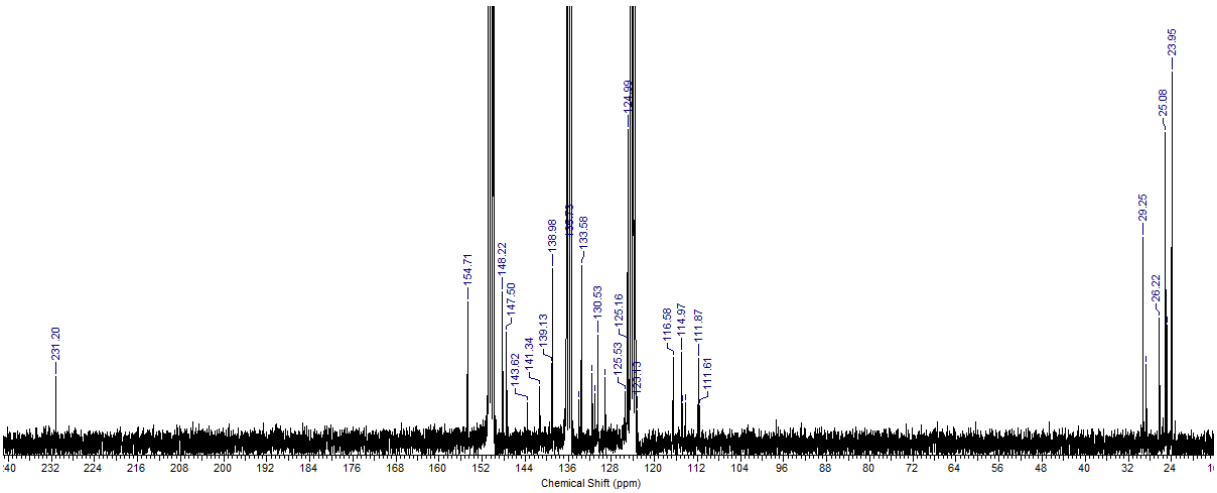

Figure S14. ^{13}C NMR spectrum of magnesium complex **4**^{benz} (68 MHz, pyridine-D$_5$).

1.8. The Impact of Magnesium Bromide on The Purity of The Palladium Complex

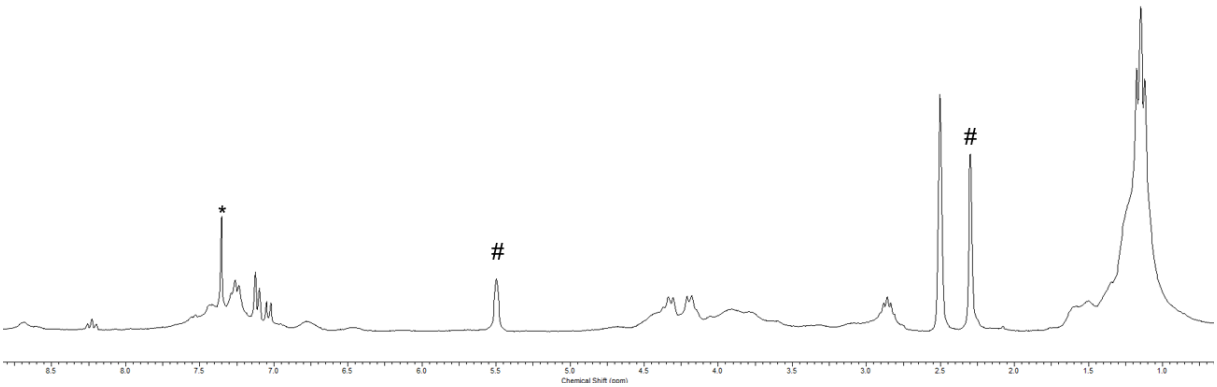

Figure S15. The crude ^{1}H NMR spectrum of the reaction of free carbene **2**^{sa} with [Pd(COD)Cl_2] (270 MHz, DMSO-D_6) indicates the formation of a mixture of products. The free carbene was dissolved in benzene and [Pd(COD)Cl_2] was added. The solvent was removed in vacuo until a solid was obtained. The solid was dissolved in DMSO-D_6 and analyzed by NMR spectroscopy. Marked signals are due to residual 1,5-cyclooctadiene (#) and benzene (*).

2. X-ray Crystallographic Data

CCDC-1906543 for **3**^{benz} and CCDC-1906542 for **4**^{sa} contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: ++33-1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

2.1. Palladium(II) Complex ***3***^{benz}

Single crystals of **3**^{benz} were obtained by slow evaporation of a saturated solution in CH_2Cl_2. The crystals were obtained as yellow platelets and the sample was coated with protective perfluoropolyalkylether oil. A suitable single crystal was selected, mounted on a MiTeGen micro mount and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data were collected at 100 K on a Bruker Kappa APEX 2 *IμS* Duo diffractometer equipped with QUAZAR focusing Montel optics using Mo$K\alpha$ radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects; semiempirical absorption corrections were performed on the basis of multiple scans using SADABS [1]. The structure was solved by direct methods (*SHELXT*) [2] and refined by full-matrix least-squares procedures on F^2 using *SHELXL 2014/6* [3]. *OLEX2* was used to prepare material for publication [4].

Identification code	**3**^{benz}
Empirical formula	$C_{43}H_{45}Br_2N_5Pd$
Formula weight [g mol^{-1}]	898.06
Temperature [K]	100
Crystal system	monoclinic
Space group	$P2_1/n$
***a* [Å]**	20.957(5)
***b* [Å]**	8.173(2)
***c* [Å]**	22.929(5)
α [°]	90
β [°]	106.623(3)
γ [°]	90
Volume [Å^3]	3763(2)
Z	4
ρ_{calc} [g cm^{-3}]	1.585
μ [mm^{-1}]	2.66
***F*(000)**	1816
Crystal size [mm^3]	0.16 x 0.08 x 0.02
Radiation, wavelength [Å]	MoK_α, λ = 0.71073

2Θ range for data collection [°]	2.32 to 52.00
Index ranges	-25 ≤ h ≤ 25, -9 ≤ k ≤ 10, -28 ≤ l ≤28
Reflections collected	46711
Independent reflections	7389 [R_{int} = 0.1164, R_{sigma} = 0.0882]
Data/restraints/parameters	7389/0/468
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ(I)]	R_1 = 0.0694, wR_2 = 0.1525
Final R indexes [all data]	R_1 = 0.1029, wR_2 = 0.1683
Largest diff. peak/hole [eÅ^{-3}]	1.57/-1.49

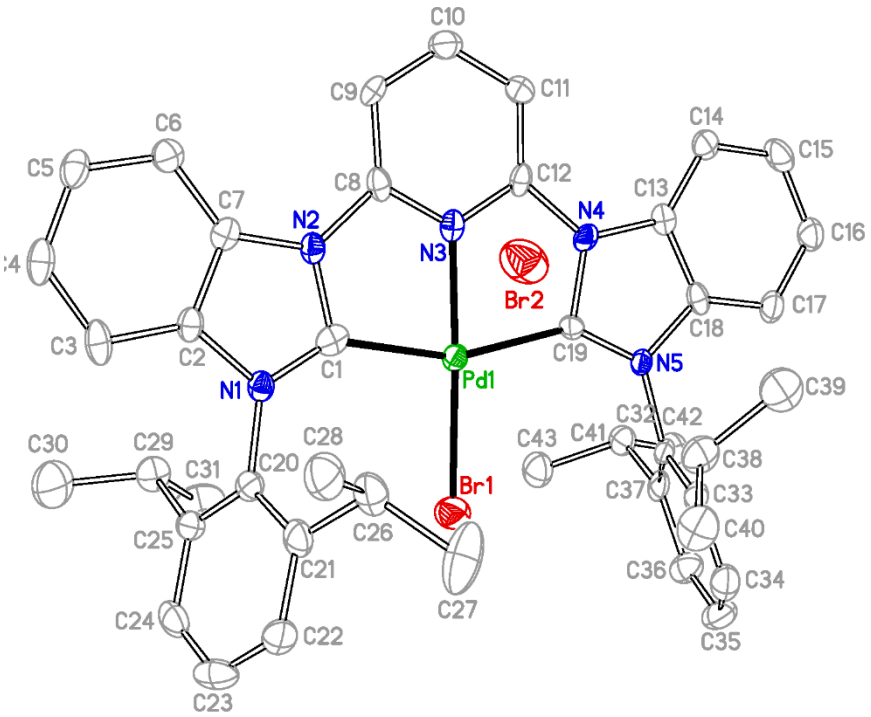

Figure S16.Thermal ellipsoid representation of the molecular structure of **3^{benz}** with the applied numbering scheme (50% probability level, hydrogen atoms omitted for clarity).

2.2. Magnesium Complex ***4^{sa}***

Single crystals of **4^{sa}** were obtained by vapor diffusion of pentane into a saturated solution of **4^{sa}** in pyridine. The crystals were obtained as colorless prisms and the sample was coated with protective perfluoropolyalkylether oil. A suitable single crystal was selected, mounted on a MiTeGen micro mount and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data were collected at 100 K on a Bruker Kappa Photon 2 $I\mu S$ Duo diffractometer equipped with QUAZAR focusing Montel optics using Mo$K\alpha$ radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects;

semiempirical absorption corrections were performed on the basis of multiple scans using SADABS [1]. The structure was solved by direct methods (*SHELXT*) [2] and refined by full-matrix least-squares procedures on F^2 using *SHELXL 2014/6* [3]. *OLEX2* was used to prepare material for publication [4]. The compound crystallized with two molecules of pyridine per formula unit.

Identification code	**4^{sa}**
Empirical formula	$C_{50}H_{60}Br_2MgN_8$
Formula weight [g mol^{-1}]	957.19
Temperature [K]	100
Crystal system	Monoclinic
Space group	$P2_1/n$
***a* [Å]**	19.0860(8)
***b* [Å]**	12.8472(6)
***c* [Å]**	20.6882(8)
α [°]	90
β [°]	111.643(1)
γ [°]	90
Volume [Å^3]	4715.1(3)
Z	4
ρ_{calc} [g cm^{-3}]	1.348
μ [mm^{-1}]	1.776
***F*(000)**	1992
Crystal size [mm^3]	0.15 x 0.13 x 0.08
Radiation, wavelength [Å]	MoK_α, λ = 0.71073
2Θ range for data collection [°]	3.65 to 59.21
Index ranges	-26 ≤ h ≤ 26, -17 ≤ k ≤ 17, -28 ≤ l ≤ 24
Reflections collected	186565
Independent reflections	13232 [R_{int} = 0.0639, R_{sigma} = 0.0290]
Data/restraints/parameters	13232/0/558
Goodness-of-fit on F^2	1.038
Final *R* indexes [I>=2σ(I)]	R_1 = 0.0307, wR_2 = 0.0623
Final *R* indexes [all data]	R_1 = 0.0474, wR_2 = 0.0680
Largest diff. peak/hole [eÅ^{-3}]	0.54/-0.40

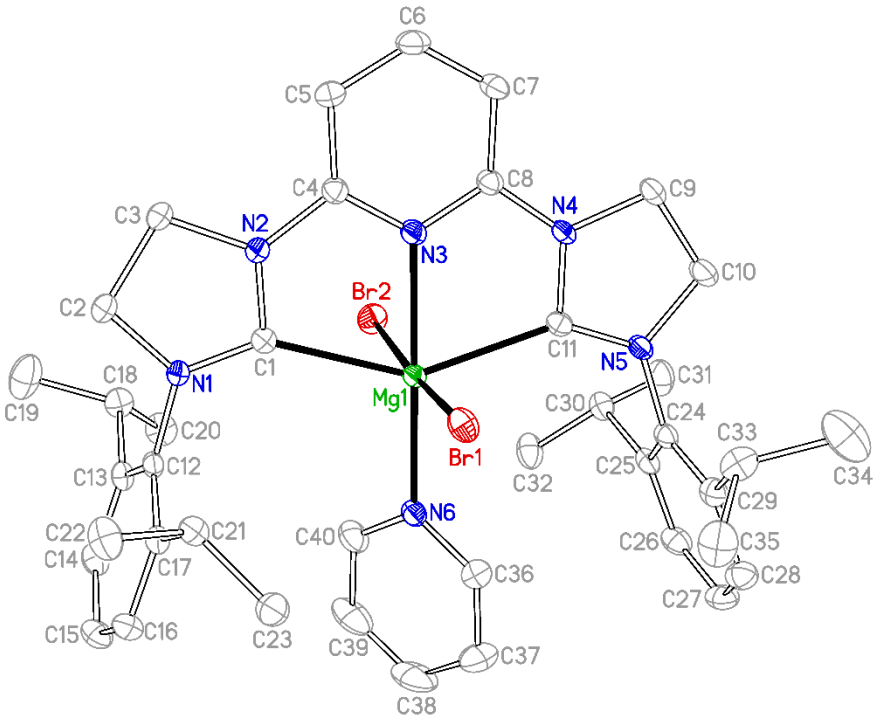

Figure S17. Thermal ellipsoid representation of the molecular structure of **4**^{sa} x 2 C_5H_6N with the applied numbering scheme (50% probability level, hydrogen atoms and solvent molecules omitted for clarity).

3. References

1. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J .Appl. Crystallogr.* **2015,** *48*, 3-10.
2. Sheldrick, G. M. SHELXT - integrated space-group and crystal-structure determination. *Acta Cryst.* **2015,** *A71*, 3-8.
3. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015,** *C71*, 3-8.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.