Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Base assisted C-C coupling between carbonyl and polypyridyl ligands in Ru-NADH type carbonyl complex

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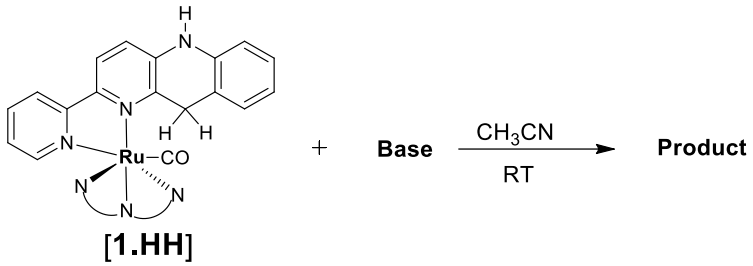
Table S1. Treatment of different bases on [**1**·**HH**][a]



Entry	Base	Amount of base (equiv.)	Product
1	Et_3N	6	No product
2	DABCO	6	No product
3	Proton sponge	6	No product
4	$PhCOONBu_4$	3	Base adduct
5	DBN	3	New five membered metallacycle

[a]All the reactions were carried out with 2mM [**1**.**HH**]$(PF_6)_2$ in 5 mL CH_3CN.

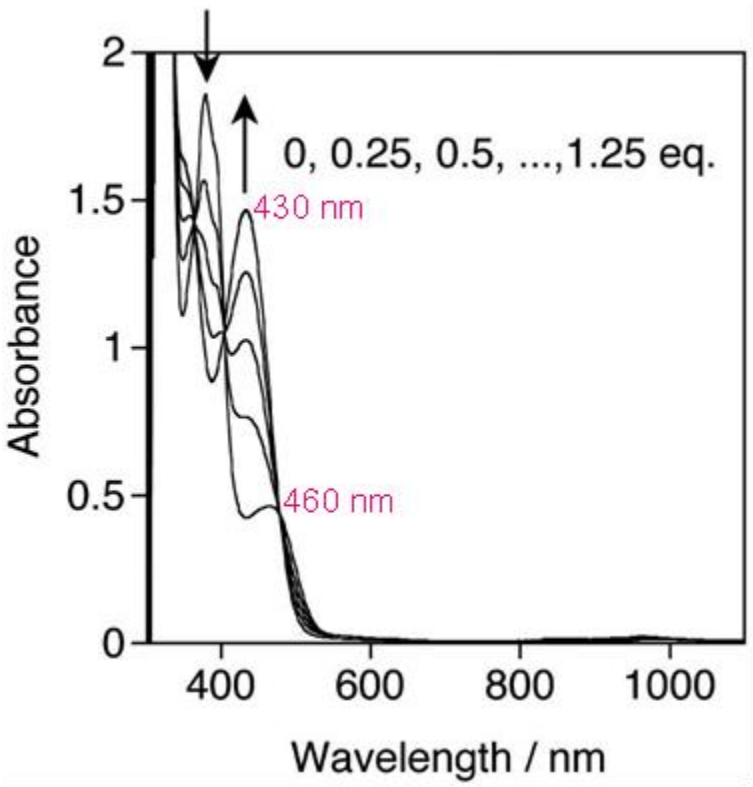


Figure S1. UV changes of the $[Ru(tpy)(pbn)(CO)]^{2+}$ complex (**1**) after addition of various amount of $Na_2S_2O_4$.

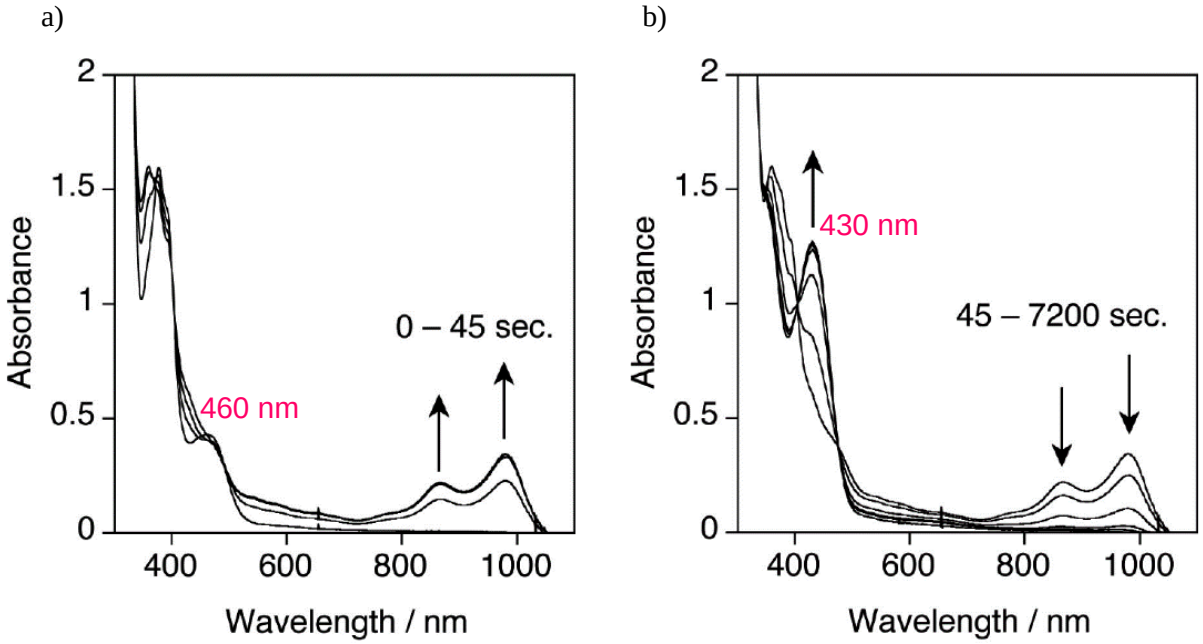


Figure S2. UV changes of the $[Ru(tpy)(pbn)(CO)]^{2+}$ complex (**1**) after irradiation with light (λ > 420 nm) in CH_3CN:TEOA = 99:1 observed in a) 45 sec and b) 7200 sec.

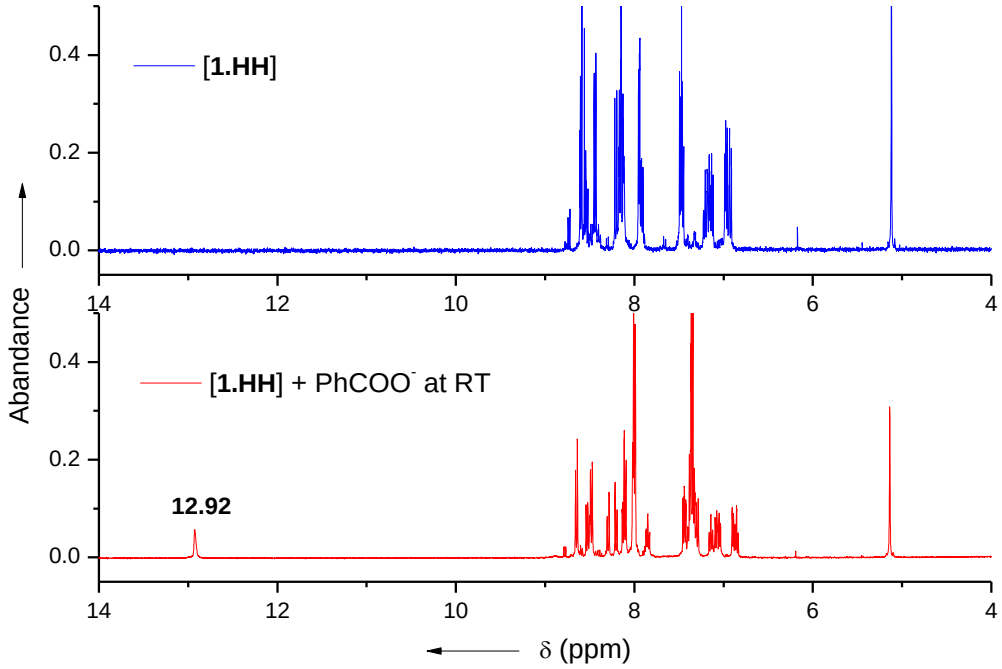


Figure S3. ^1H NMR spectral changes after addition of $PhCOONBu_4$ (red) to $[Ru(tpy)(pbnHH)(CO)]^{2+}$ complex [**1**.**HH**] (blue).

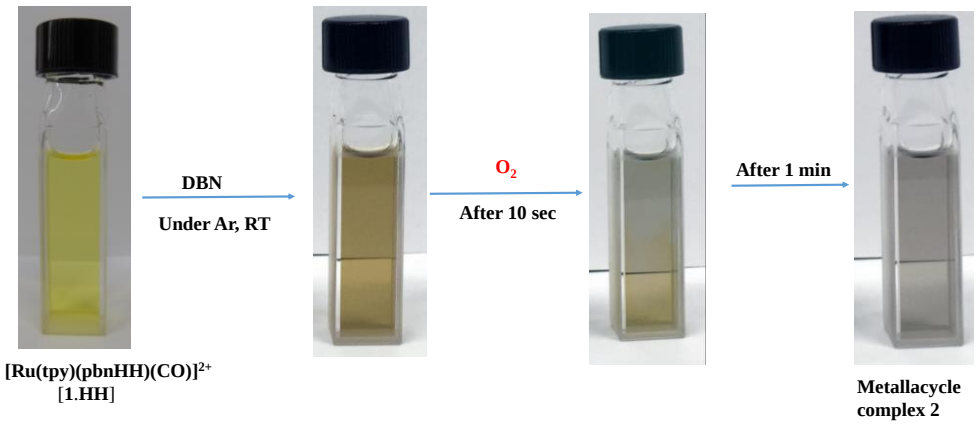


Figure S4. Visual colour changes of [**1**.**HH**] after addition of DBN followed by O_2.

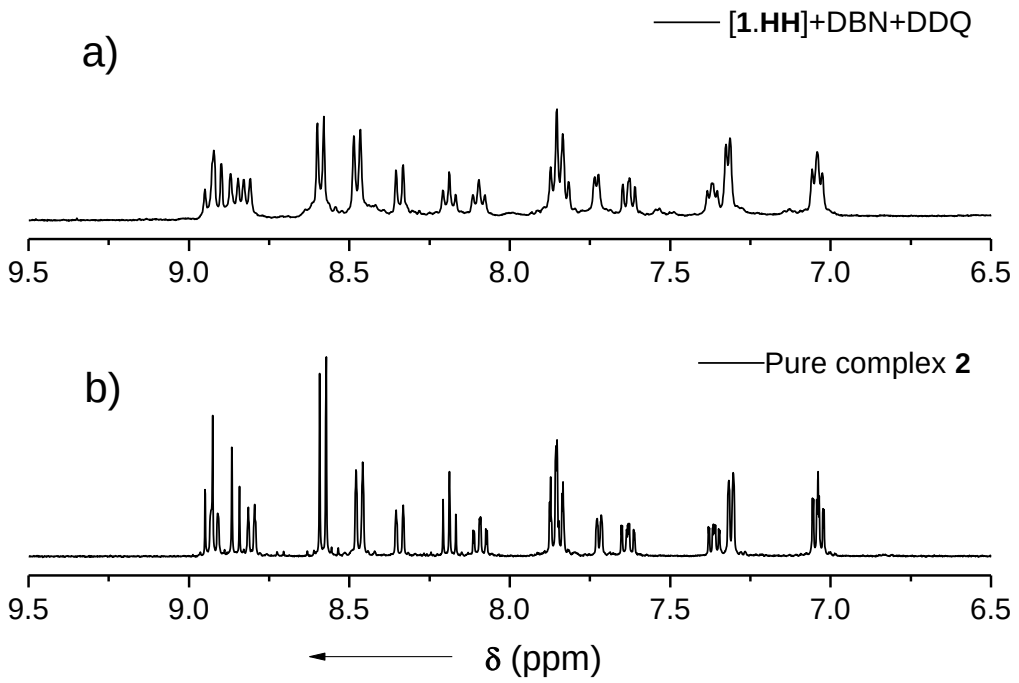


Figure S5. ^{1}H NMR spectrum of (a) the reaction mixture after addition of DBN (3 equiv. with respect to [**1**.**HH**]) to [**1**.**HH**] followed by DDQ (2 equiv. with respect to [**1**.**HH**]) under argon atmosphere; (b) pure complex **2**.

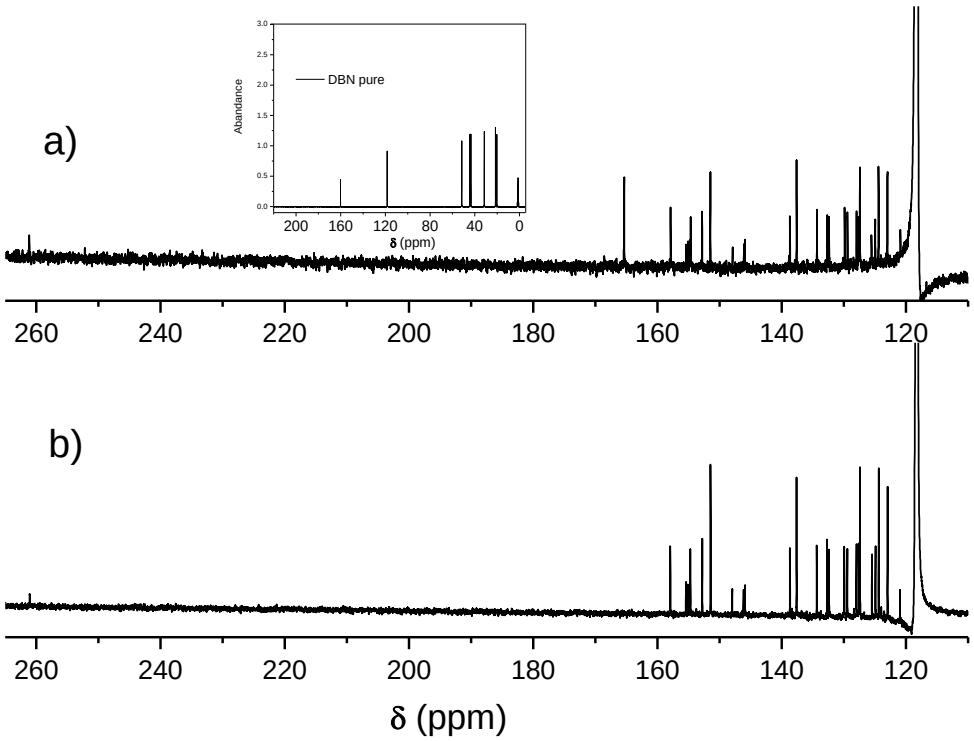


Figure S6. ^{13}C NMR spectrum of (a) the reaction mixture after addition of DBN (3 equiv. with respect to [**1**.**HH**]) to [**1**.**HH**] followed by DDQ (2 equiv. with respect to [**1**.**HH**]) under argon atmosphere; (b) pure complex **2**. Inset is the ^{13}C NMR spectrum of pure DBN.

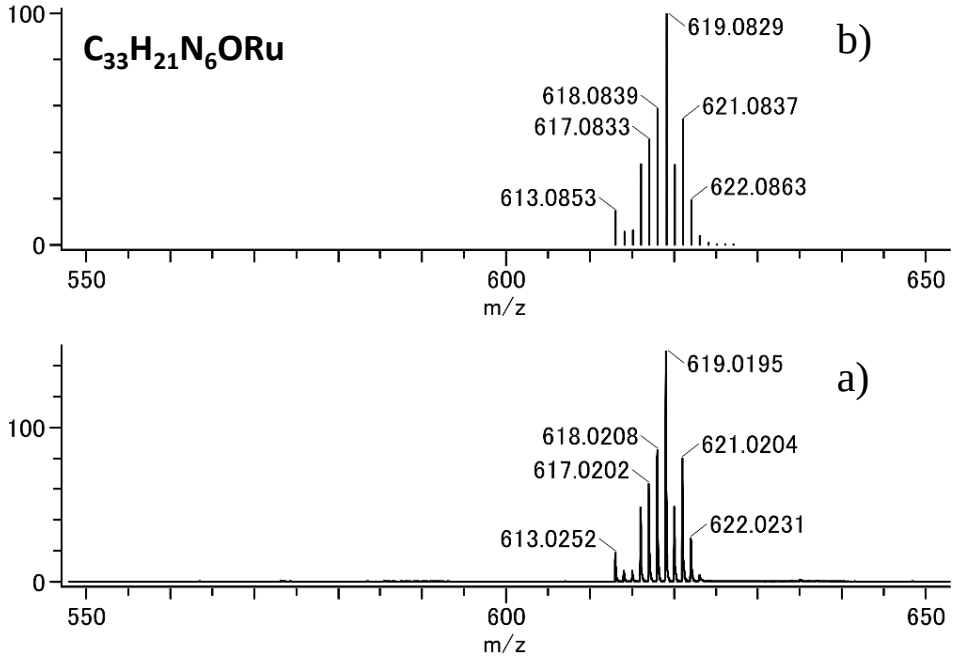


Figure S7. a) Observed ESI-MS spectrum of the metallacycle **2** obtained by the reaction of $[Ru(tpy)(pbnHH)(CO)]^{2+}$ with DBN base in CH_3CN under air; b) Calculated one.

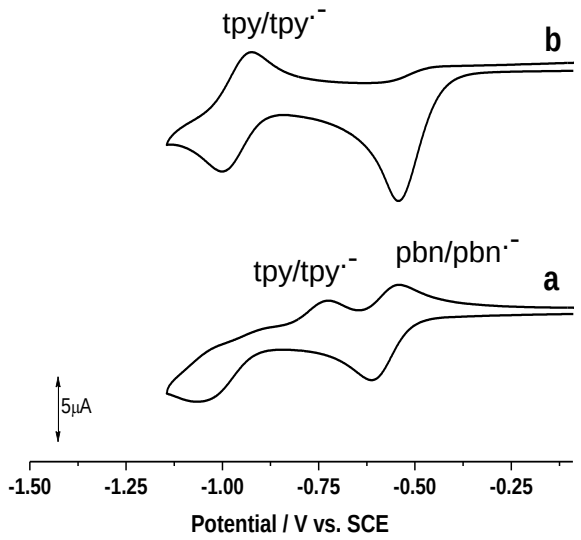


Figure S8: Cyclic voltammograms (CV) of $[Ru(tpy)(pbn)(CO)]^{2+}$ (**1**) in the absence (a) and presence (b) of 5 equiv. of AcOH, 1mM in Ar-purged CH_3CN with 0.1 MBu_4NPF_6 as the supporting electrolyte at a scan rate ν = 50 mVs^{-1}. The curves in the CV were assigned by comparing with literature data.[1,2,3] In the absence of proton (a), **1** undergoes successive one electron reduction by [pbn]/[pbn$^{-\cdot}$] and [tpy]/[tpy$^{-\cdot}$] redox couples. However, in the presence of proton (b), two electron reduction occurs at the pbn moiety of **1** to form $[Ru(tpy)(pbnHH)(CO)]^{2+}$ [**1**.**HH**].[1,2]

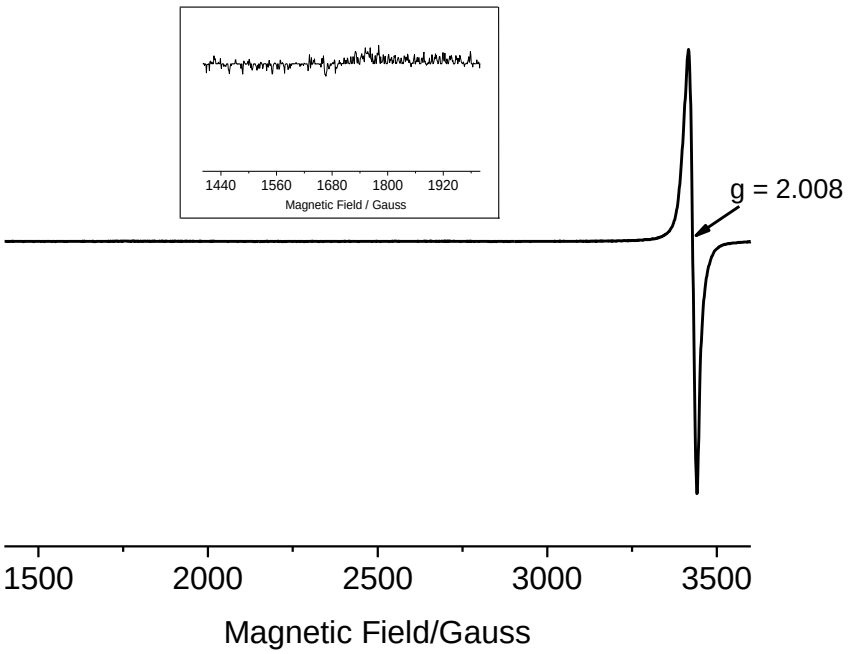


Figure S9. EPR spectrum obtained upon the addition of 3.0 equiv. of DBN to a CH_3CN solution of [**1**.**HH**] (1 mM) at 5 K.

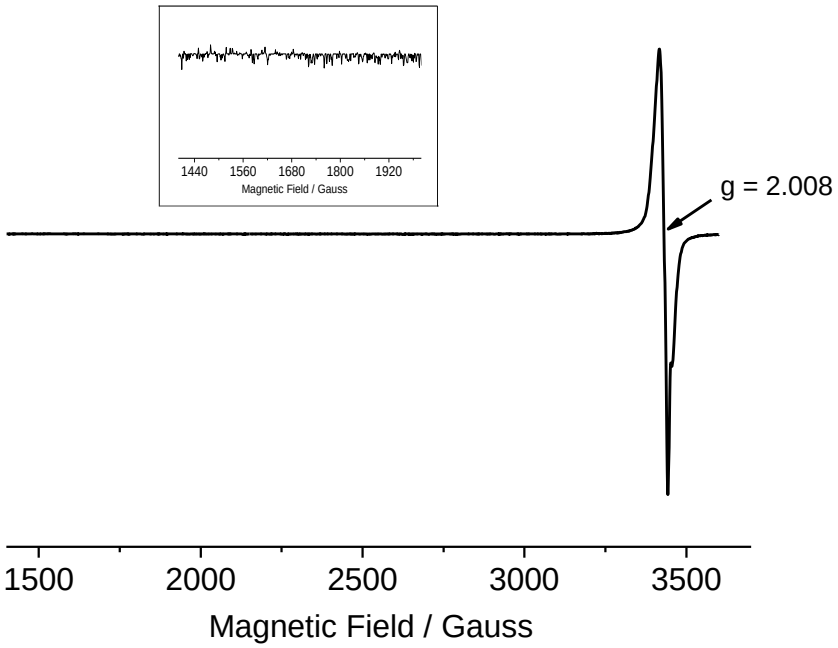


Figure S10. EPR spectrum obtained upon the addition of 3.0 equiv. of DBN to a CH_2Cl_2 solution of [**1**.**HH**] (0.5 mM) at 5 K.

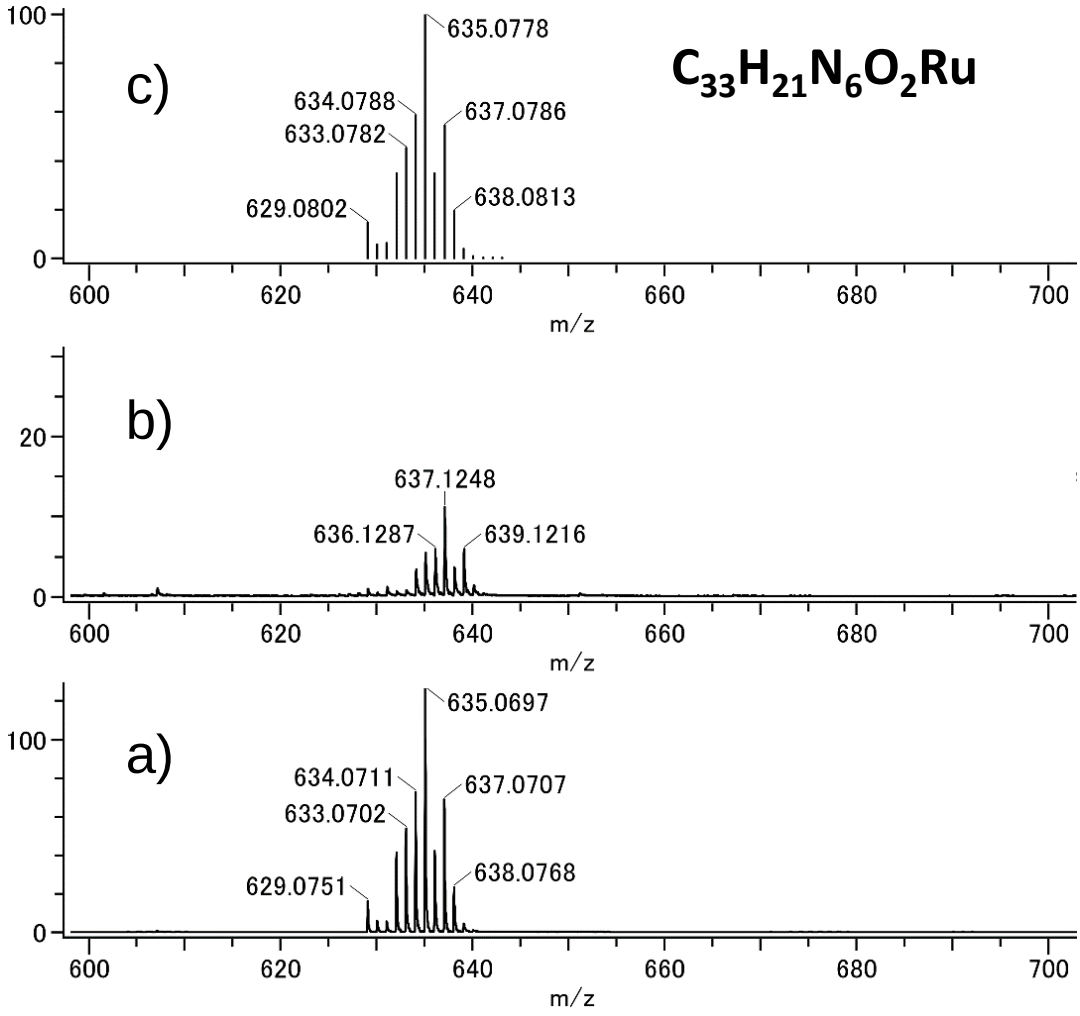


Figure S11. a) Observed ESI-MS spectrum of the Ru-OCO-bridge complex **3** obtained by the reaction of metallacycle **2** with 10 equiv. of NH_4PF_6 in H_2O/CH_3CN (1:1 v/v) under air; b) ESI-MS spectrum obtained by the reaction of metallacycle **2** with 10 equiv. of NH_4PF_6 in H_2O^{18}/CH_3CN (1:1 v/v) in presence of molecular oxygen; c) calculated one.

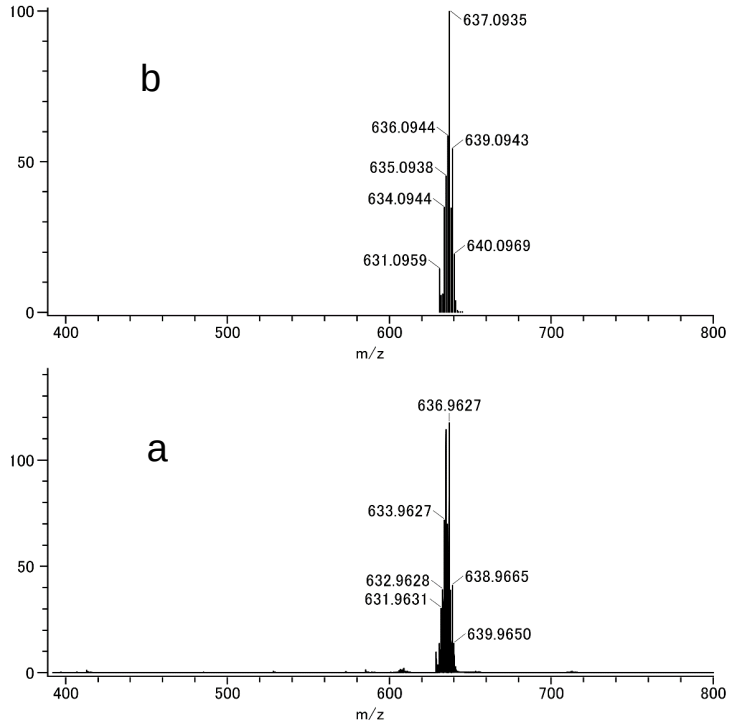


Figure S12. a) Observed ESI-MS spectrum of the Ru-O^{18}CO-bridge complex **3** obtained by the reaction of metallacycle **2** with 10 equiv. of NH_4PF_6 in H_2O^{18}/CH_3CN (1:1 v/v) in presence of DDQ; c) calculated one.

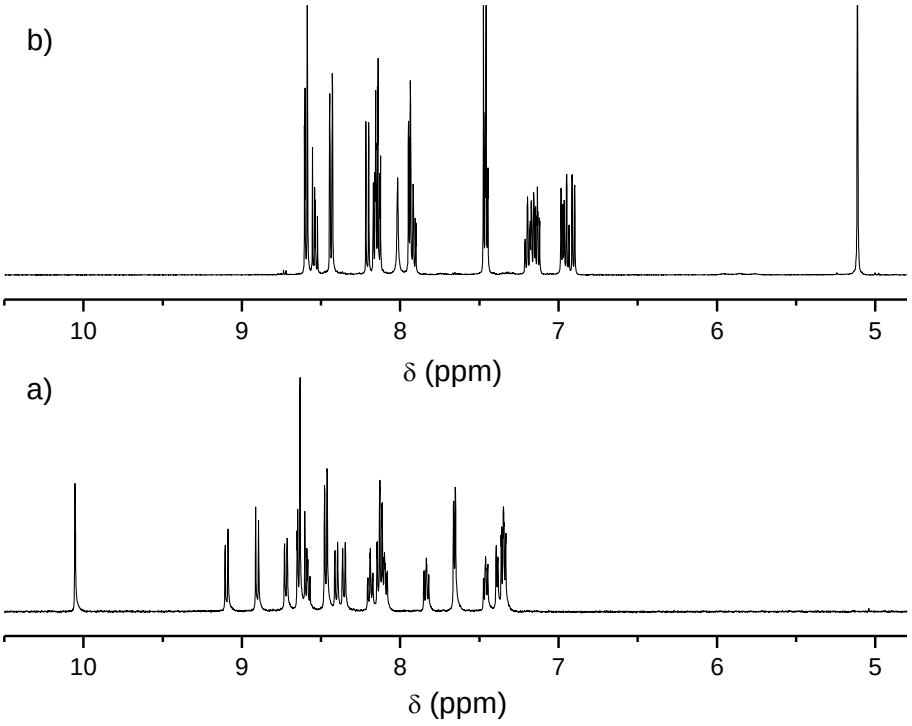


Figure S13. ^{1}H NMR spectra of (a) $[Ru(tpy)(pbn)(CO)]^{2+}$ and (b) $[Ru(tpy)(pbnHH)(CO)]^{2+}$ in CD_3CN.

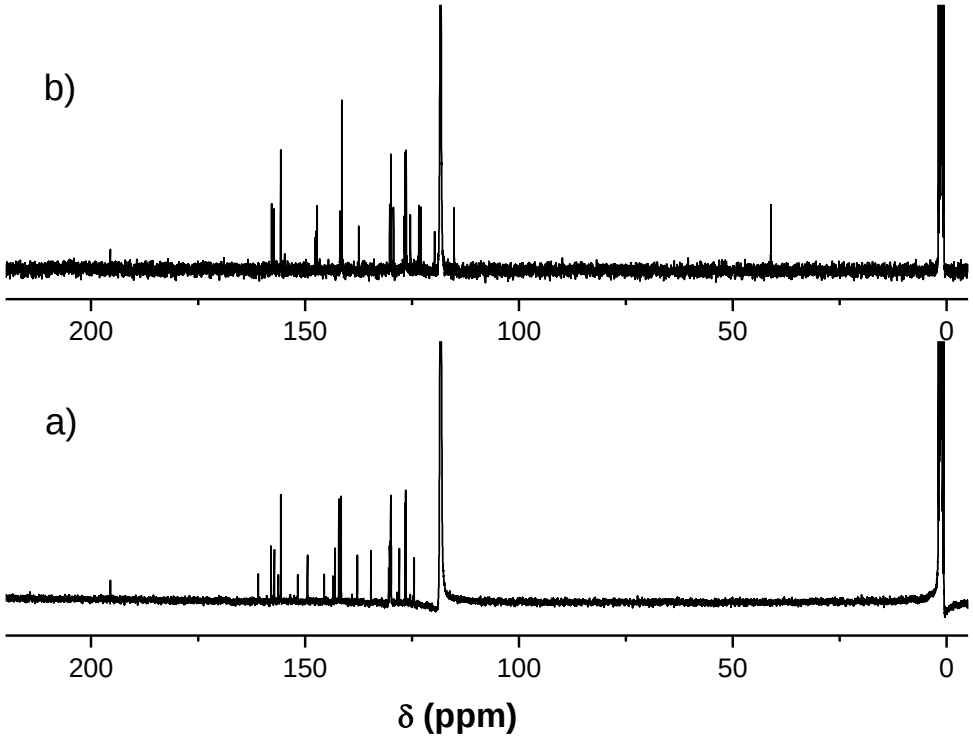


Figure S14. ^{13}C NMR spectra of (a) $[Ru(tpy)(pbn)(CO)]^{2+}$ and (b) $[Ru(tpy)(pbnHH)(CO)]^{2+}$ in CD_3CN.

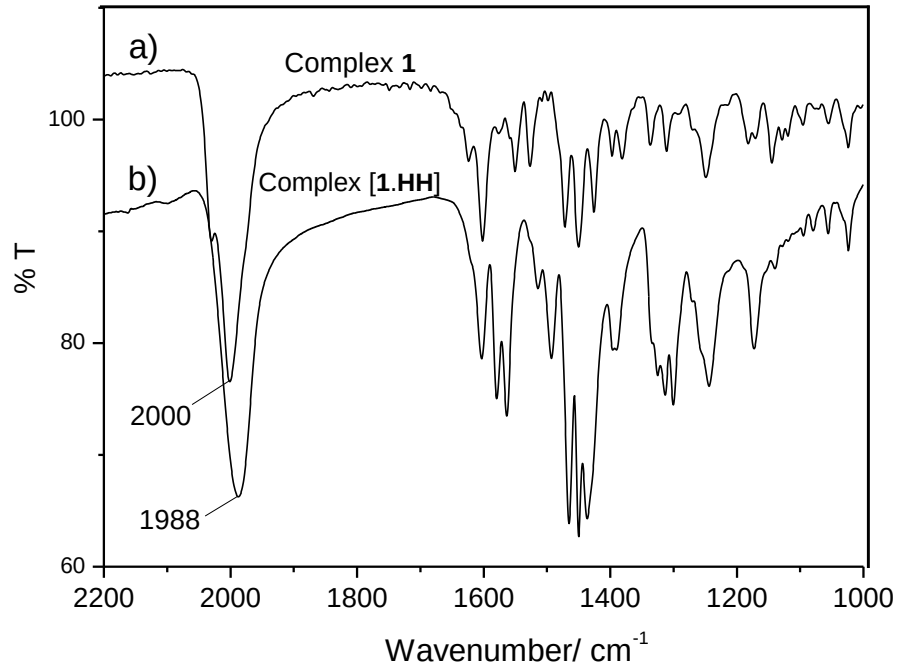


Figure S15. FT-IR spectra of (a) $[Ru(tpy)(pbn)(CO)](PF_6)_2$ (**1**) and (b) $[Ru(tpy)(pbnHH)(CO)](PF_6)_2$ [**1**.**HH**].

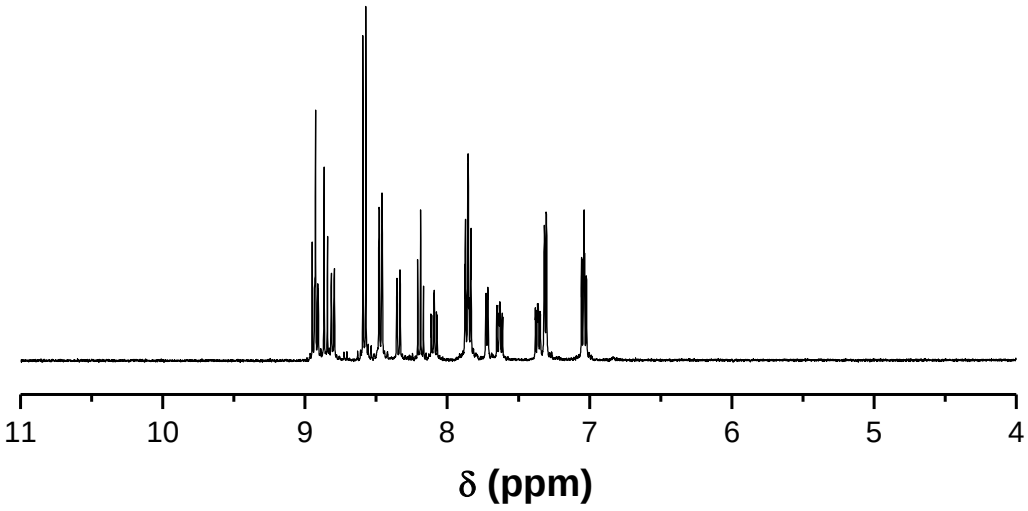


Figure S16. ^{1}H NMR spectrum of Ru-CO-bridge metallacycle **2** in CD_3CN.

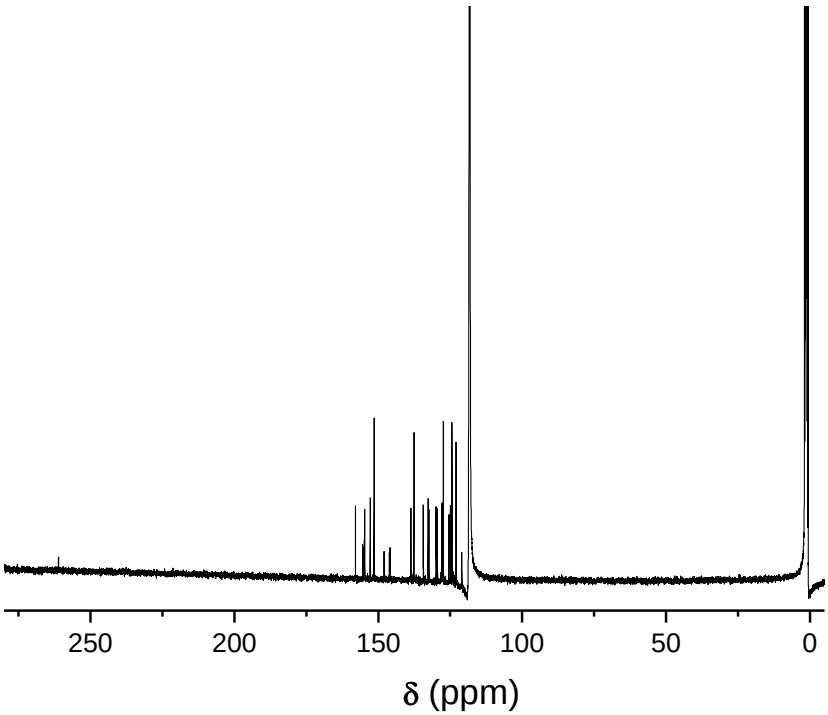


Figure S17. ^{13}C NMR spectrum of Ru-CO-bridge metallacycle **2** in CD_3CN.

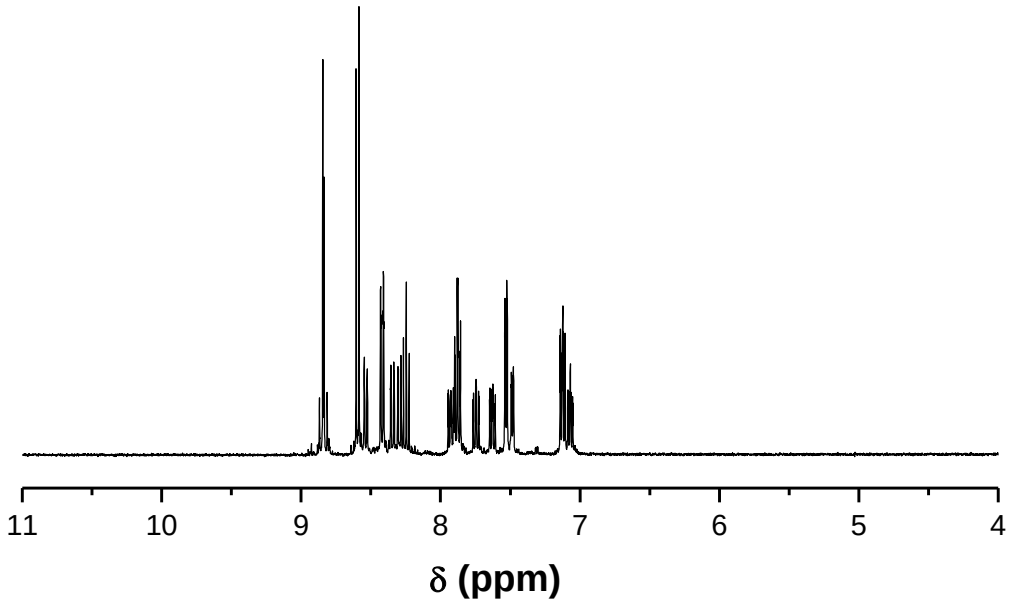


Figure S18. ^{1}H NMR spectrum of Ru-OCO-bridge complex **3** in CD_3CN.

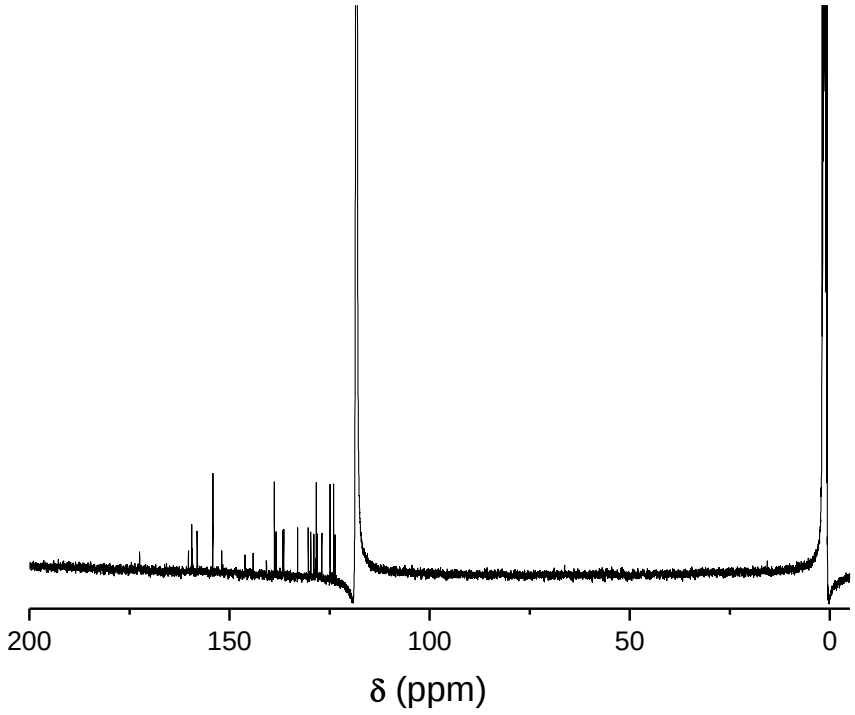


Figure S19. ^{1}H NMR spectrum of Ru-OCO-bridge complex **3** in CD_3CN.

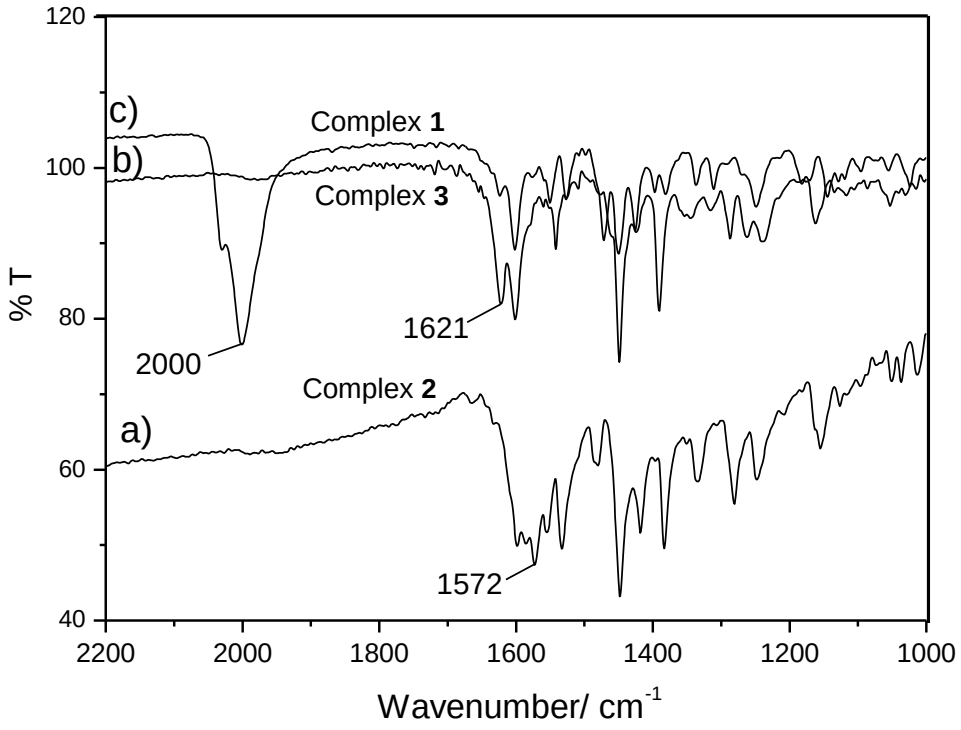


Figure S20. FT-IR spectra of (a) metallacycle complex **2**; (b) complex **3** and (c) complex **1**.

References

1. D. E. Polyansky, D. Cabelli, J. T. Muckerman, T. Fukushima, K. Tanaka, and E. Fujita, *Inorg. Chem*., 2008, **47**, 3958.
2. T. Fukushima, T. Wada, H. Ohtsu and K. Tanaka, *Dalton Trans*., 2010, **39**, 11526.
3. H. Nagao, T. Mizukawa and K. Tanaka, *Inorg. Chem*., 1994, **33**, 3415.