Supporting Information

From μ_3- to μ- Agostic Methyl Coordination:
NMR and Solid State Study of Donor Ligands Uptake by the
Triangular Cluster Anion [Re$_3$(μ-H)$_3$(μ_3-CH$_3$)(CO)$_9$]$^-$.

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Dedicated to Professor Renato Ugo for his fundamental contribution in coordination chemistry and organometallic compounds.

Table S1. Bandwidth (Hz) of the signals of the different isotopomers of the methyl group in the anion **2**, at different temperatures.

	$\Delta_{1/2}$ (T = 283 K)	$\Delta_{1/2}$ (T = 193 K)
CH_3	4.62	8.91
CH_2D	6.3	9.25
CHD_2	7.3	9.25

Table S2. Chemical shifts and $\Delta\delta$ (ppm) for the different isotopomers of the partially deuterated methyl group of the anion **2** at different temperatures.

T (K)	δ (CH_3)	δ (CH_2D)	$\Delta\delta$	δ (CHD_2)	$\Delta\delta$
193	-3.219	-3.442	0.223	-3.704	0.262
213	-3.204	-3.406	0.202	-3.639	0.233
233	-3.185	-3.370	0.185	-3.581	0.211
253	-3.170	-3.341	0.172	-3.533	0.193
283	-3.147	-3.301	0.154	-3.472	0.171

Table S3. Calculated values of the chemical shift for the agostic (δ_b) and the terminal (δ_t) hydrogens of the methyl group in the anion **2**, and of the A and ΔE parameters.

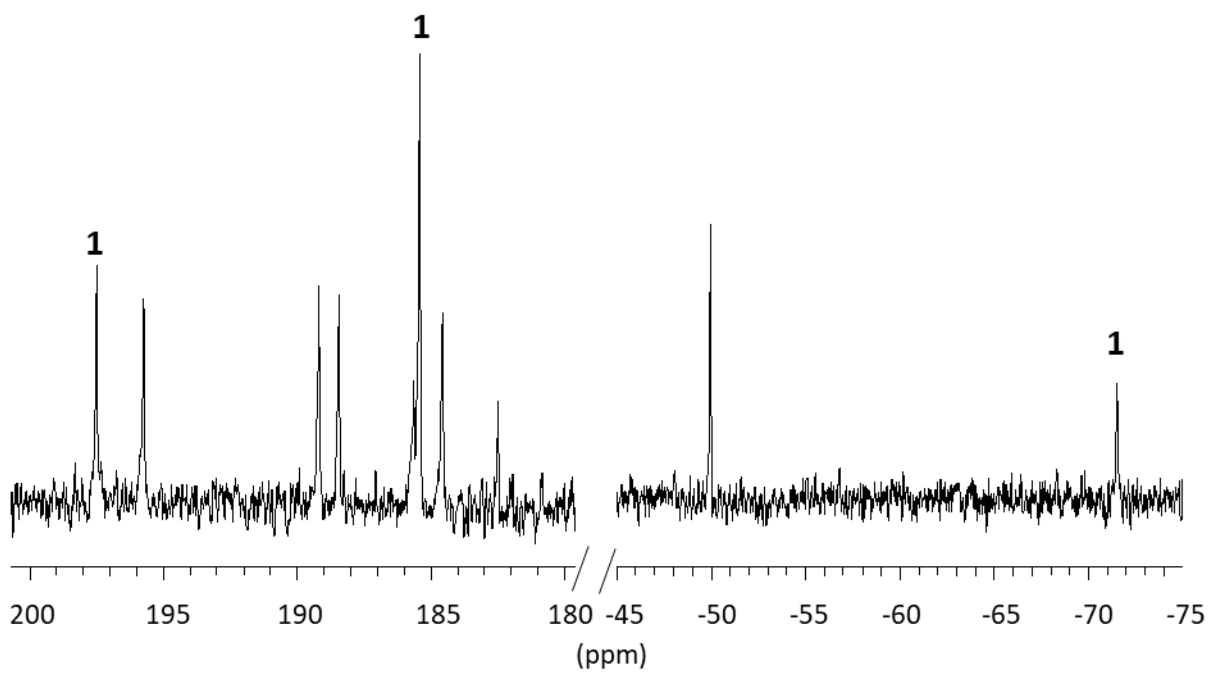| T (K)	δ_t ppm	δ_b ppm	A	ΔE (J .mol^{-1})
193	-0.442	-8.773	0.777	96.77
213	-0.376	-8.860	0.800	94.45
233	-0.370	-8.815	0.815	94.72
253	-0.175	-9.156	0.837	89.45
283	-0.200	-9.040	0.851	90.73

Fig. S1. ^{13}C NMR spectrum of a sample of **2** containing a residual amount of **1** (CD$_2$Cl$_2$, 203 K, 7.5 T).
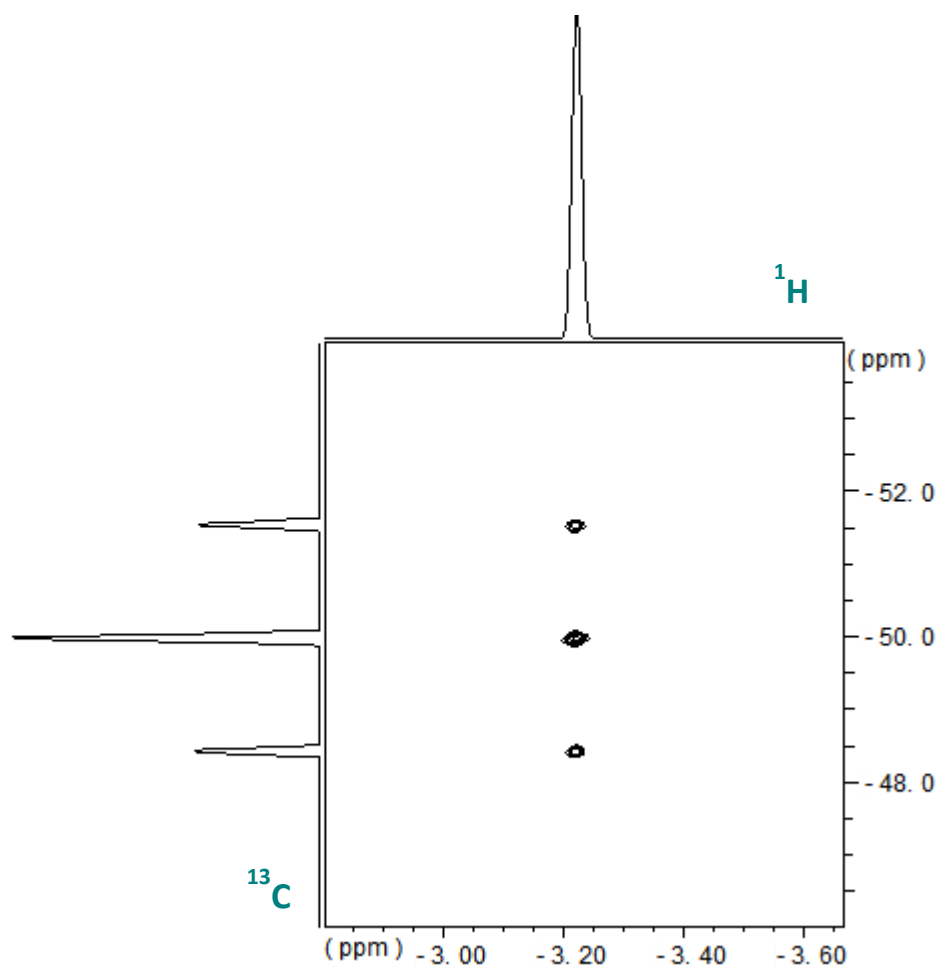
Fig. S2. 2D ^{1}H-^{13}C modified HMQC correlation experiment (CD$_2$Cl$_2$, 203 K, 7.05 T) that confirmed the presence of three hydrogens bound to the carbon at −49.97 ppm and enabled to measure the scalar coupling constant ($^1J_{CH}$ 116 Hz).

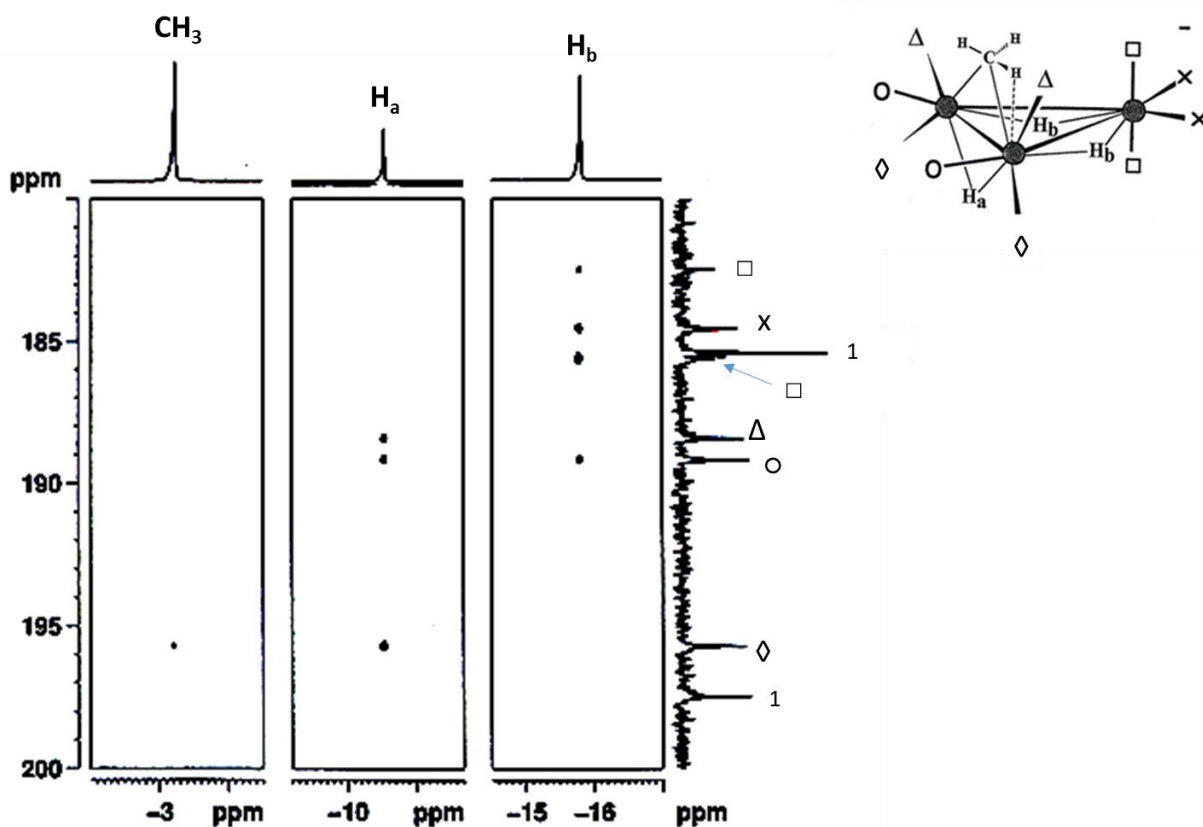**Fig. S3**. Selected regions of a 2D ^{1}H-^{13}C HMQC correlation experiment (CD$_2$Cl$_2$, 203 K, 7.05 T), that revealed the following correlations: the hydrides H$_b$ at −15.81 (s, 2H) ppm correlate with the vertex CO signals that lye at higher fields [182.47 (1C, □), 184.56 (2C, ×), 185.62 (1C, □)], as well as with the CO at lower fields centred at 189.18 (2C, o) ppm, which is attributable to the two CO in *trans* position on the basal fragment, being the *J trans* much higher than the *cis* one. The H$_a$ hydride at −10.54 (s, 1H) ppm correlates with the three basal CO signals centred at 188.43 (2C, Δ), 189.18 (2C, o) and 195.72 (2C, ◊). The last CO signal correlates also with the ^{1}H methyl signal at −3.22 ppm (*trans* relationship)
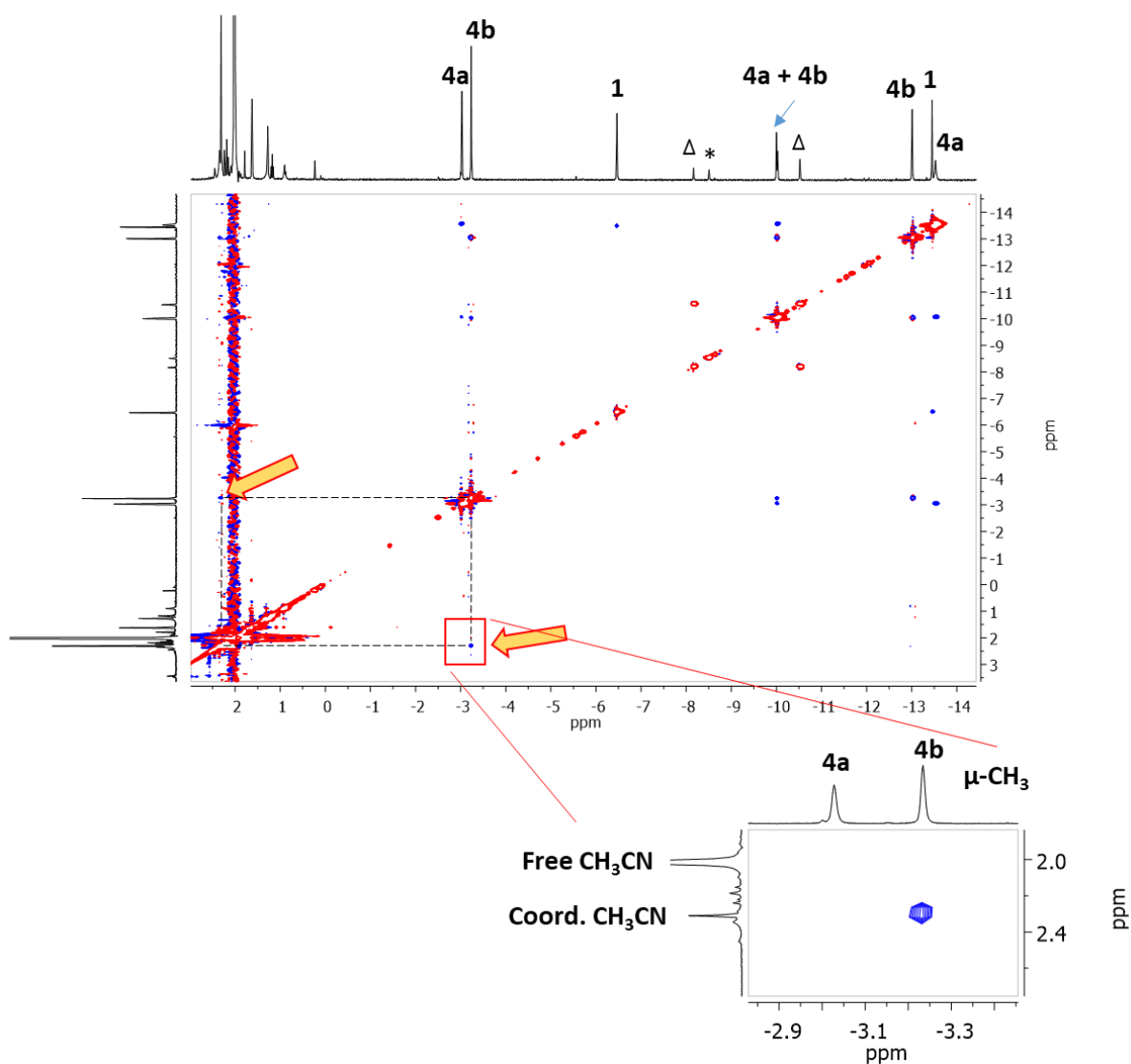
Fig. S4. Selected region of a 2D ^{1}H NOESY experiment on a sample of compound **4** (CD$_2$Cl$_2$, 203 K, 7.1 T) showing the nOe cross peak between the μ-CH$_3$ signal of isomer **4b** and the acetonitrile CH$_3$ signal. Signals indicated with Δ are tentatively attributed to [Re$_3$(μ-H)$_3$(μ-OH)(CO)$_9$(NCMe)].
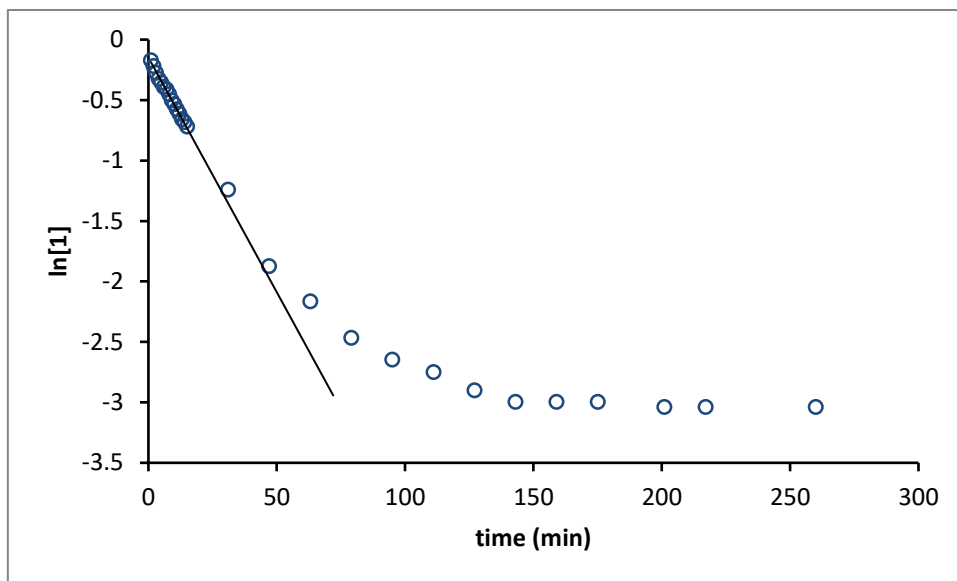
Fig. S5. First order plots of the decrease of ln[**1**] in the presence of 20 equivalents of MeCN at 263 K.
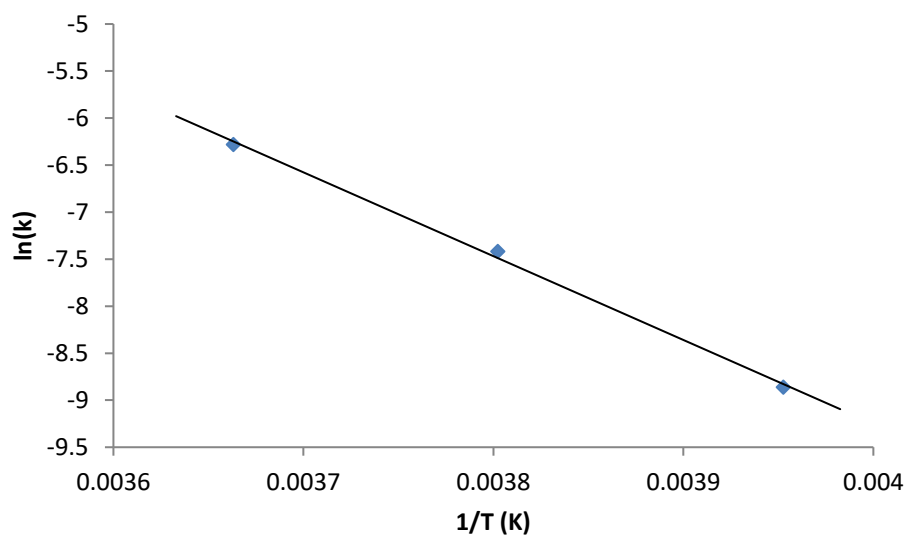
Fig. S6. Arrhenius plot for the kinetic constants for the reaction of **1** with 10 equivalents of MeCN, estimated from the initial rates of the reaction.
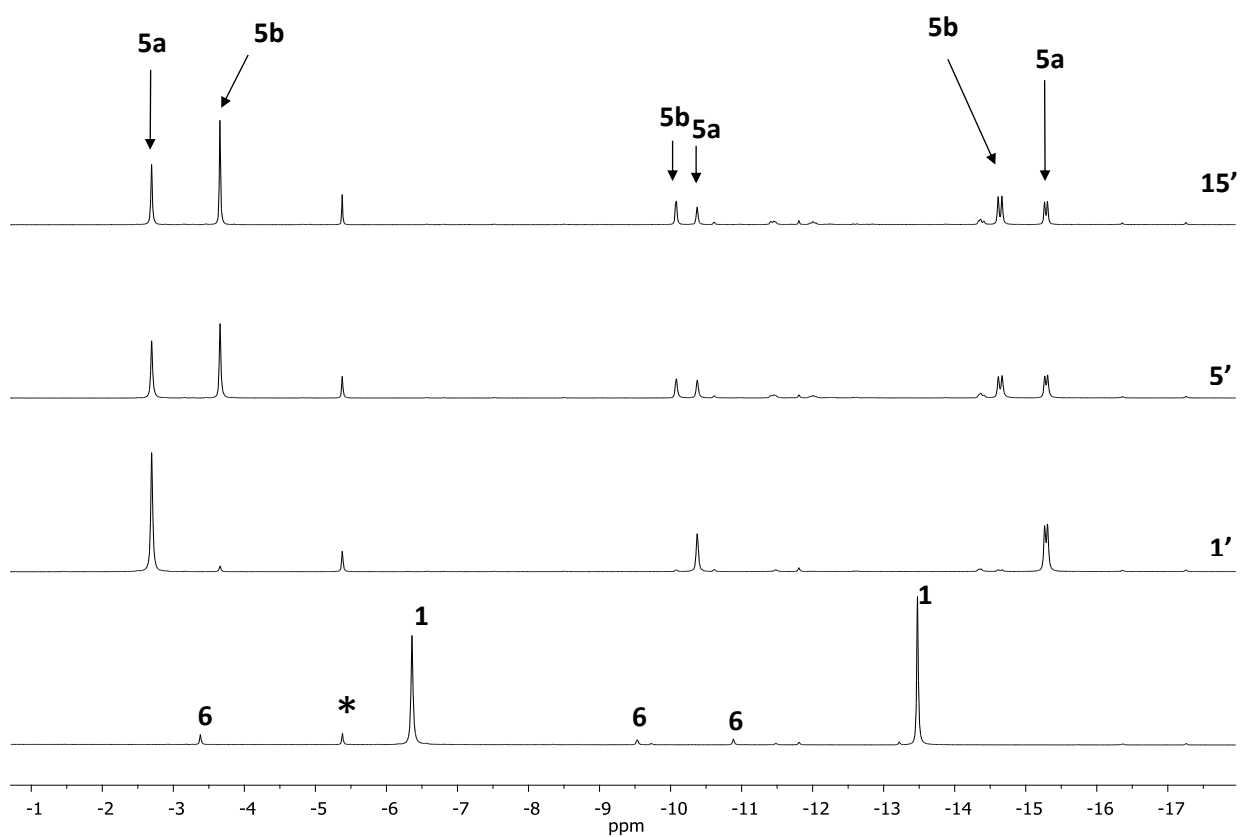
Fig. S7. ^{1}H NMR monitoring of the transformation of **1** into the equilibrium mixture **5a/5b**, in THF-d$_8$, at 193K in the presence of 1 equivalent of PMePh$_2$ at different times after ligand addition at room temperature. The bottom trace shows also minority signals due to species **6**, and a signal, marked with an asterisk, tentatively attributable to [Re$_2$(μ-H)$_2$(CO)$_6$(THF)$_2$] (see Results and Discussion of the main text)