Experimental Observation of Spin Delocalisation onto the Aryl-Alkynyl Ligand in the Complexes $[Mo(C{\equiv}CAr)(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)]^+$ (Ar = C_6H_5, C_6H_4-4-F; C_7H_7 = Cycloheptatrienyl): an EPR and ENDOR Investigation.

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SUPPLEMENTARY DATA

Further details of EPR/ENDOR measurements

Details of the X-band cw EPR/ENDOR spectra were given in the main paper. Further pulsed (X-band) and cw (Q-band) measurements were also performed, and the details are given below:

Q-band cw EPR/ENDOR; measurements were performed on a Bruker ESP 300e series spectrometer using a Bruker ER5106QT resonator employing 12 dB RF power from a *3200L* RF amplifier, 250 kHz RF modulation depth and 150 μW power. The ENDOR measurements were performed at 10 K (EPR measurements at 50 K).

X-band Pulsed EPR/ENDOR: All pulse-EPR spectra were recorded on a Bruker E580 Elexsys spectrometer (MW = 9.73 GHz) equipped with a liquid Helium cryostat from Oxford Inc. The spectra were taken at 40 K.

Electron-spin-echo (ESE)-detected EPR: The experiments were carried out with the pulse sequence $\pi/2$- $\pi - \tau$ - *echo*, with pulse lengths $t_{\pi/2}$ = 16 ns and t_{π} = 32 ns, and a τ value of 400ns.

Pulsed ENDOR: Pulsed Mims ^{1}H-ENDOR spectra were recorded (at a field position of 3478 G) on a Bruker E580 spectrometer (microwave frequency 9.73 GHz) equipped with a liquid helium cryostat from Oxford Inc. The experiments were carried out with the pulse sequence $\pi/2$-τ-$\pi/2$-T-$\pi/2$-τ-*echo* with microwave pulse length $t_{\pi/2}$ = 16 ns and an interpulse delay time τ ranging from 128 - 1000 ns. An rf pulse of variable frequency and a length of 10 μs was applied during a time interval T of 12 μs.

cw X-band ENDOR spectra

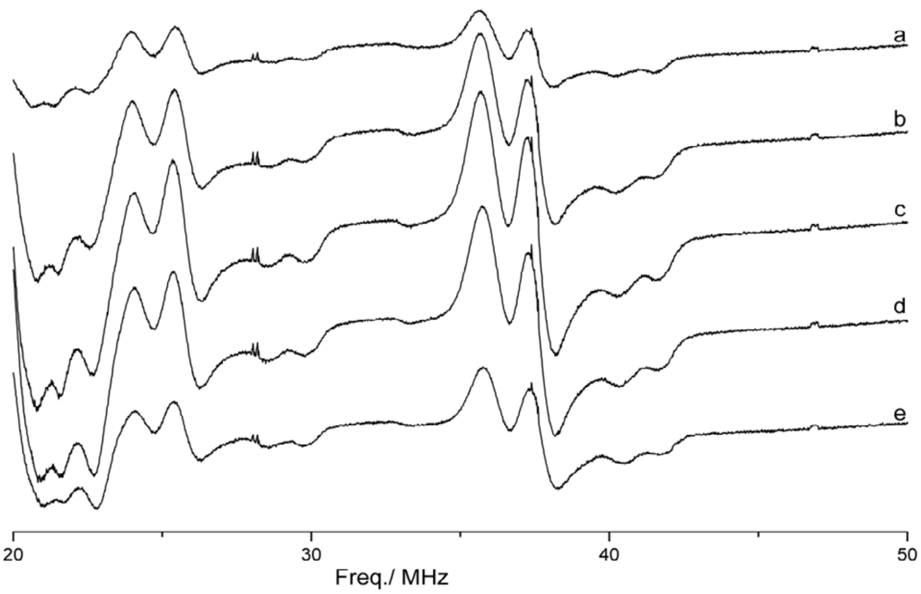

Figure 1: ^{31}P ENDOR spectra [10 K] of [**4**]$^+$ recorded at magnetic field position (a) 3390 G, (b) 3413 G, (c) 3422 G, (d) 3431 G and (e) 3454 G. As expected no orientation selectivity observed, owing to the low ***g*** anisotropy, and dominant s character in the ^{31}P coupling.

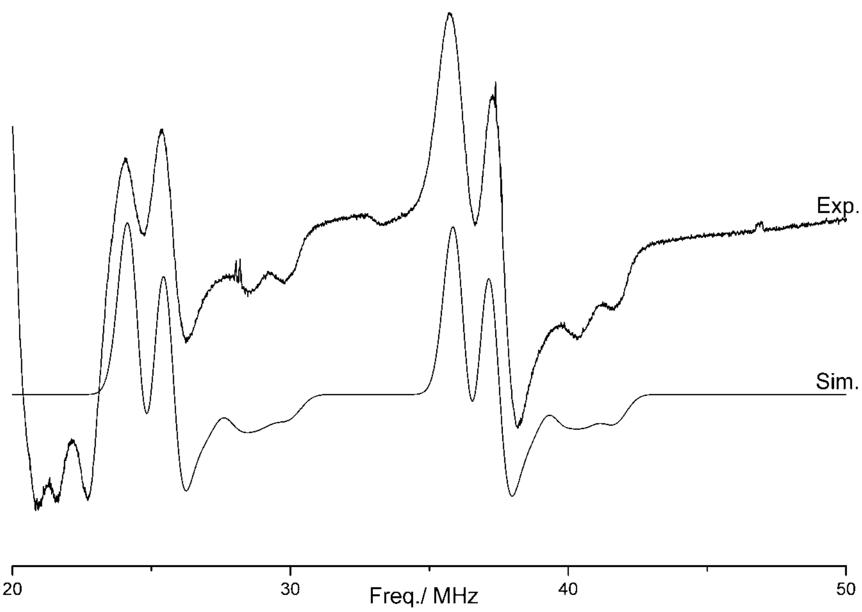

Figure 2; Experimental and simulated X-band ^{31}P ENDOR spectrum of [**4**]$^+$ (recorded at a magnetic field position of 3413 G). The simulation was obtained using the parameters;
$^{31}P_a$; A_1 = 63, A_2 = 63, A_3 = 71.8 MHz;
$^{31}P_b$; A_1 = 60.5, A_2 = 60.5, A_3 = 69.3 MHz;
where $P_{a,b}$ represent the two slightly inequivalent ^{31}P nuclei. θ_H was defined as 90° in both cases.

cw Q-band ENDOR spectra

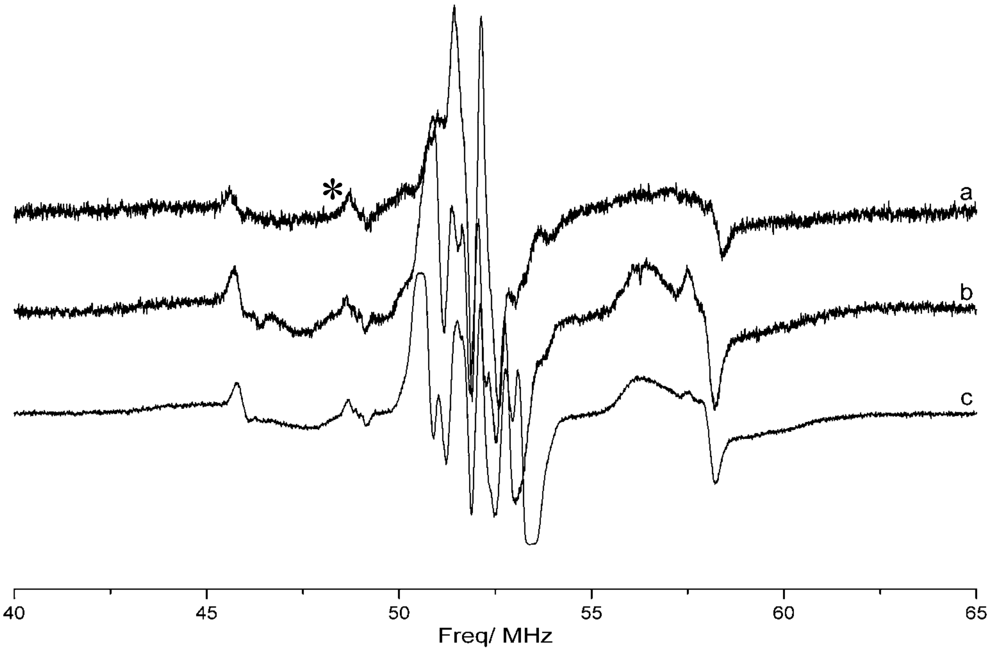

Figure 3: Q-band ^{1}H ENDOR spectra [50 K] of (a) [**4**]$^{+}$, (b) [**1**]$^{+}$ and (c) [**5**]$^{+}$ recorded at 12264.2 G (employing a 250 kHz RF modulation). * = ^{19}F from BF_4. Note the unusual line shape of the cycloheptatrienyl ring protons. These were very broad and poorly resolved at 10 K (see Figure 7 in main paper).

Pulsed X-band EPR/ENDOR

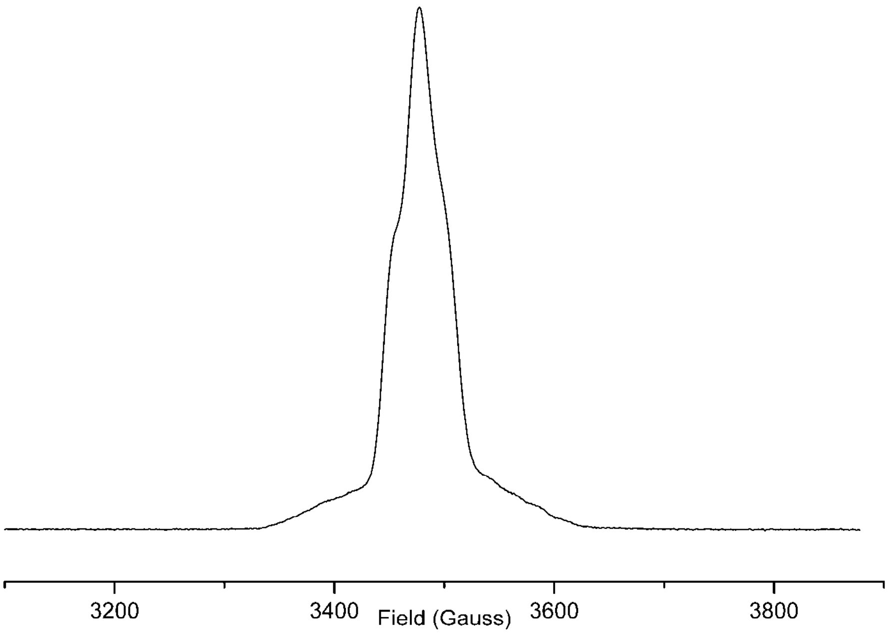

Figure 4: X-band FSE-detected EPR spectrum of [**4**]$^+$ recorded at 40 K. The spectra were obtained with a standard 2-pulse sequence, *π/2- π – τ - echo*, with integration of the echo.

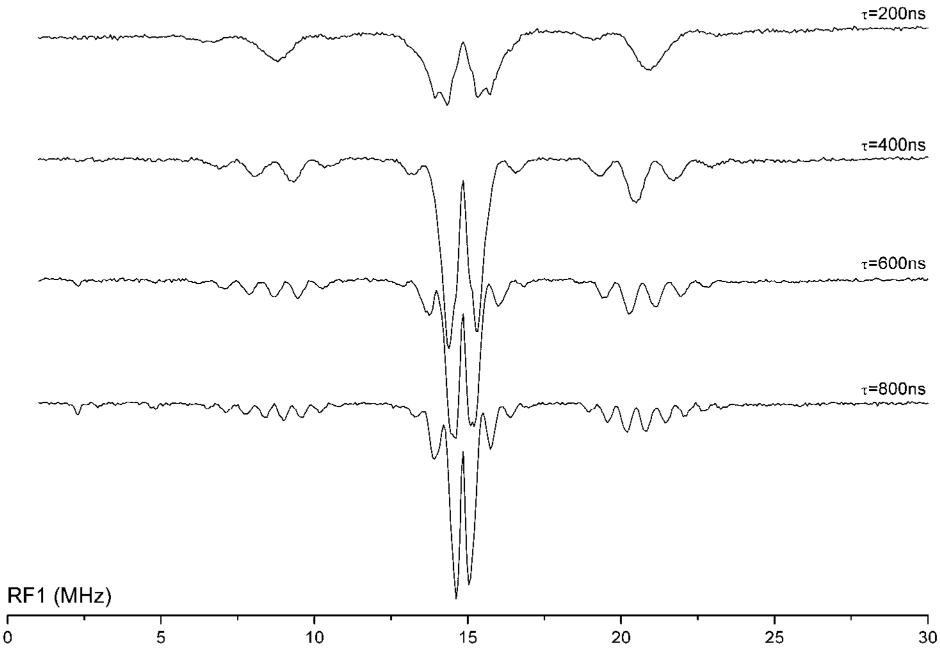

Figure 5: Mims ENDOR spectra (40K) recorded for different values of tau for [**4**]$^+$.