Supplementary Material

Trapping of an Heterometallic Unsaturated Hydride: Structure and Properties of the Ammonia Complex [MoMnCp(μ-H)(μ-PPh$_2$)(CO)$_5$(NH$_3$)]

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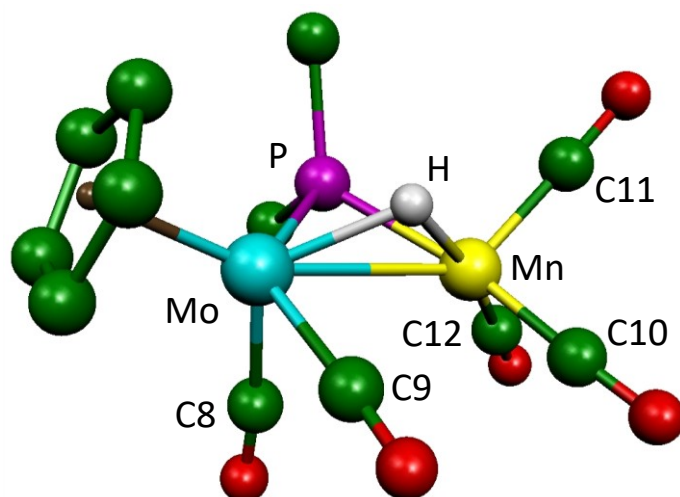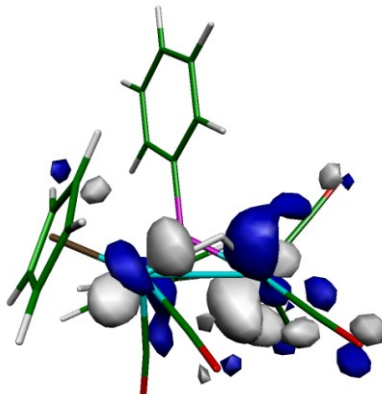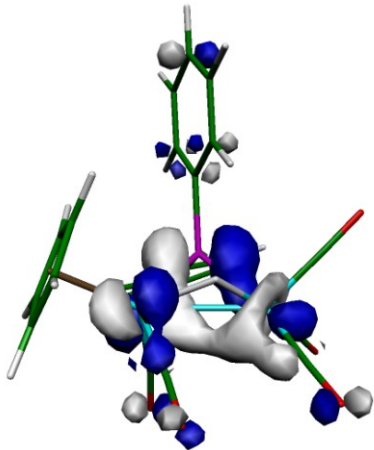*Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain.*
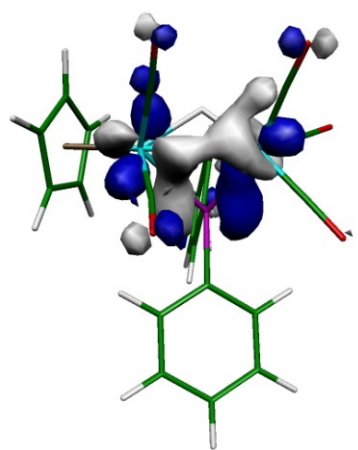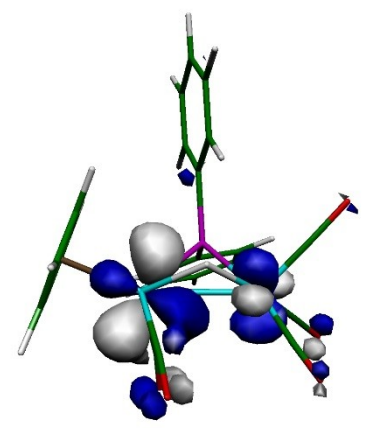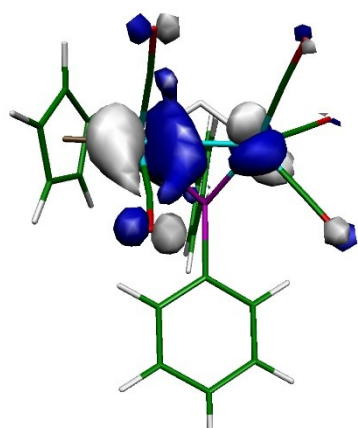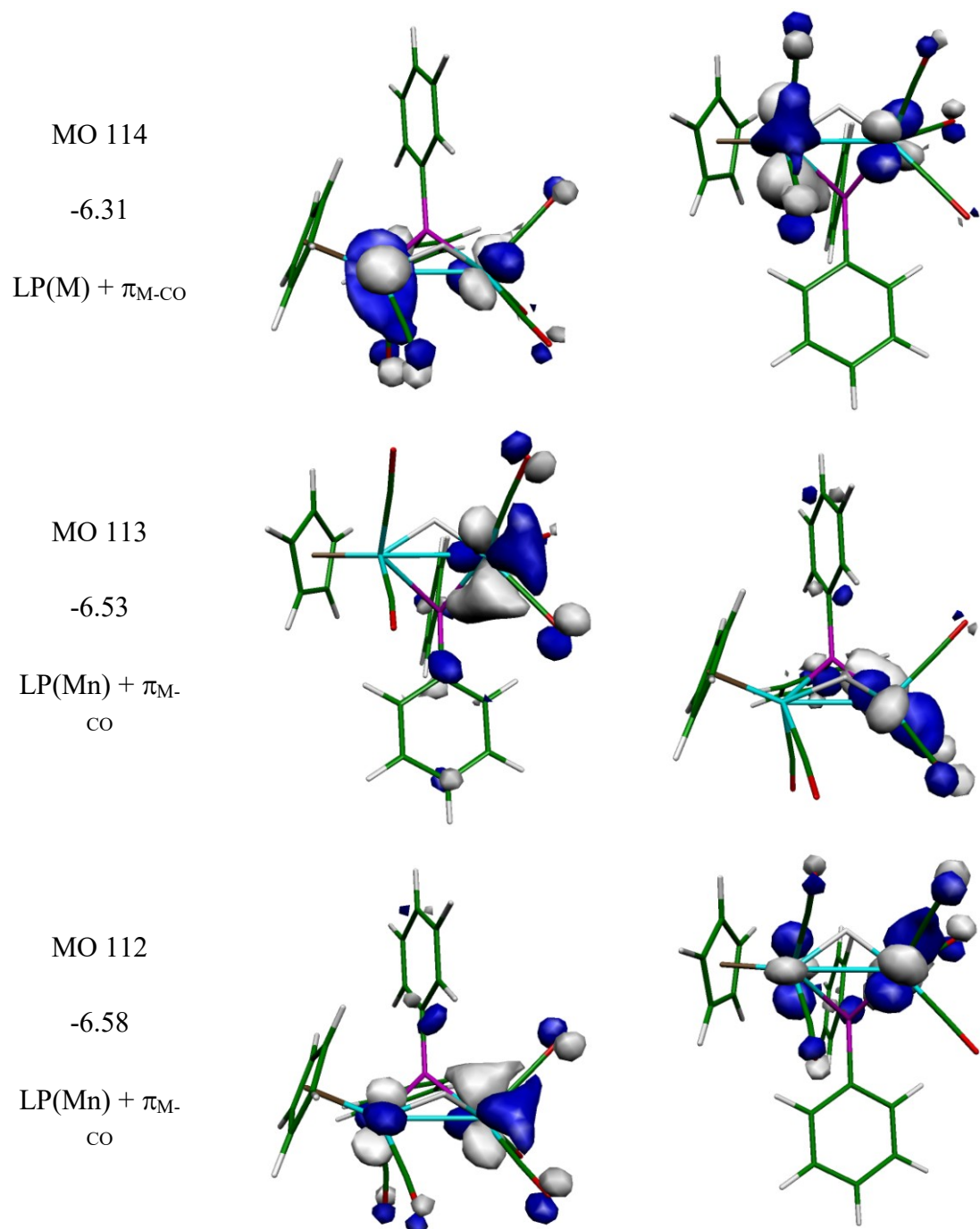
Figure S1. DFT-optimized structure of compound **H**, with most H atoms and Cy rings (except their C[1] atoms) omitted.

Table S1: DFT-Optimized Geometry for **H** (distances in Å, angles in deg.)

Parameter	B3LYP	B3LYP-D	Parameter	B3LYP	B3LYP-D
Mo–Mn	2.796	2.788	Mo–P–Mn	71.6	72.6
Mo–P	2.488	2.452	Mo–H–Mn	99.4	99.0
Mn–P	2.280	2.252	C9–Mo–C8	83.0	83.8
Mo–H	1.860	1.866	C9–Mo–P	130.1	131.0
Mn–H	1.806	1.800	C8–Mo–P	83.7	83.5
Mo–C8	1.985	1.983	C9–Mo–H	72.2	72.3
Mo–C9	2.022	2.024	C8–Mo–H	114.9	115.1
Mn–C10	1.818	1.817	C10–Mn–C11	93.1	94.4
Mn–C11	1.786	1.785	C10–Mn–C12	93.8	95.5
Mn–C12	1.800	1.800	C11–Mn–C12	91.5	92.3
			C10–Mn–P	164.4	162.8
			C11–Mn–P	98.0	98.1
			C12–Mn–P	96.7	95.6
			C10–Mn–H	91.1	90.3
			C11–Mn–H	96.5	94.7
			C12–Mn–H	170.29	170.5
			P–Mo–Mn–H	108.5	109.4

Table S2. Selected molecular orbitals for compound **H** (B3LYP)

OM Energy (eV) Assignment	*view 1 ... ...*	*............. view 2*
LUMO 117 -2.25 π^*(Mo-Mn)		
HOMO 116 -5.80 $\sigma_{M\text{-}P} + \pi_{M\text{-}M}$		
MO 115 -6.07 LP(M) + $\pi_{M\text{-}CO}$		

MO 114

-6.31

LP(M) + π_{M-CO}

MO 113

-6.53

LP(Mn) + π_{M-CO}

MO 112

-6.58

LP(Mn) + π_{M-CO}

MO 111 -6.82 $\sigma_{M\text{-}M} + \pi_{M\text{-}CO}$		

MO 111

-6.82

$\sigma_{M\text{-}M} + \pi_{M\text{-}CO}$

MO 104

-8.74

$\sigma_{M_2H} + \sigma_{M_2P}$

Table S3: Electron density (ρ, eÅ^{-3}) and Mayer Bond Indexes (MBI) at Mo−Mn bonds (B3LYP).

	[MoMnCp(μ-PPh$_2$)(CO)$_6$]$^-$	H	H (B3LYP-D)	1
$\rho*$	0.204	0.284	0.287	0.319
MBI	0.369	0.429	0.432	0.556

*Value computed at the corresponding bond critical point or minimum value at the intermetallic axis
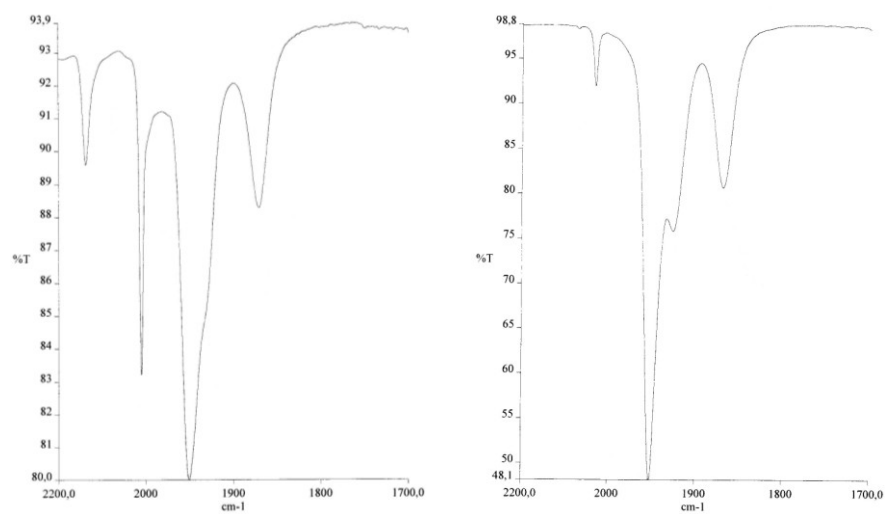
Figure S2. IR spectra of compounds **3a** (left) and **4** (right), recorded in dichloromethane solution.
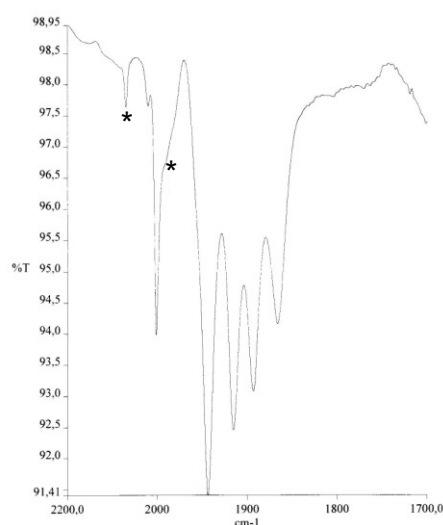
Figure S3. IR spectrum of compound **2** recorded in tetrahydrofuran solution. Peaks marked * correspond to the complex [MoMnCp(μ-H)(μ-PPh$_2$)(CO)$_6$].
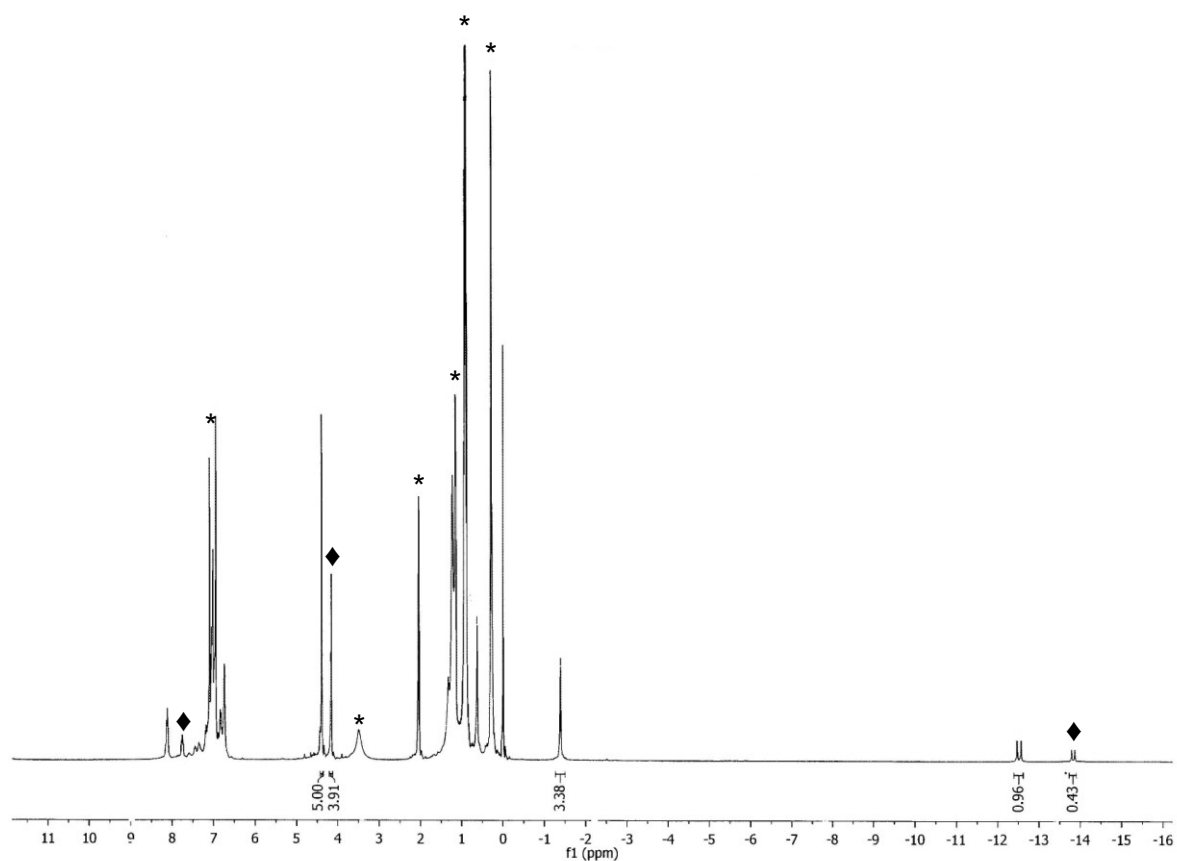

Figure S4. ^{1}H NMR spectrum (400.13 MHz) of crude compound **2**, recorded in toluene-d$_8$ solution at 213 K. Peaks marked * correspond to residual solvents (toluene, tetrahydrofuran, petroleum ether) and grease, and peaks marked ◆ correspond to the complex [MoMnCp(μ-H)(μ-PPh$_2$)(CO)$_6$], formed upon decomposition of **2** during preparation of the sample.