Electronic Supplementary Material (ESI) for Dalton Transactions

A comparative study of the topology of the experimental electron density within 2 and 4e$^-$ donor alkyne complexes

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Supplementary information

Data collection and reduction for complexes $Cp(CO)_2Mn(\eta^2$-PhC≡CPh) (2) and Cl_2(*NNO*)Nb(η^2-MeC≡CMe) (3). A parallelipedic-shaped yellow crystal of **2** of dimensions 0.50 x 0.50 x 0.35 mm^3 was mounted on an Oxford Diffraction Xcalibur 4-circles diffractomer equipped with a Sapphire CCD detector and an Oxford Diffraction Cryojet N_2 gas stream low-temperature device. Graphite-monochromatized Mo K_α radiation was used for collecting diffraction data at a temperature of T = 100(±1) K. The program MOVIE was used to measure the shape of the crystal in view absorption correction.[S1] The frames were reduced using the CRYSALIS software package.[S1] Numerical absorption corrections based on the shape of the crystal were performed; the calculated minimum and maximum transmission coefficients are T_{min} = 0.642 and T_{max} = 0.804.[S2] The resulting 191598 reflections were merged in Laue group *2/m* with the use of the program SORTAV[S3] to give 19241 unique reflections up to a resolution of 1.12 $Å^{-1}$. This data set provided 98.7% of data 3.1° < 2θ < 104.2° ($\sin\theta/\lambda$ = 1.12 $Å^{-1}$). Although the shape of the selected crystal was anisotropic the low internal agreement indice (R_{int} = 0.024. <redundacy> = 9.9 up to 1.12 $Å^{-1}$) supports the good quality and consistency of the merged data set. Other crystallographic and data collection details are given in Table SI1.

For complex **3**, an orange single crystal with dimensions of 0.07 x 0.09 x 0.15 mm^3 was mounted on a Bruker-Nonius Kappa CCD diffractometer equipped with an Apex II detector and a liquid nitrogen Oxford Cryosystem cooling device. Graphite-monochromatized Mo K_α radiation was used for collecting diffraction data at a temperature of T = 100(±1) K. The data were reduced using DENZO as implemented in the HKL2000 package[S4] leading to a total of 455 991 reflections with a maximum resolution of 1.1 $Å^{-1}$. An absorption correction based on Gaussian numerical integration was applied[S5] yielding minimum and maximum transmission factors of 0.891 and 0.950, respectively. The reflections were scaled and averaged with SORTAV[S3] to 22617 unique reflections with an average redundancy of 20.2. The internal agreement factor for the whole data set was R_{int} = 8.02 %. Other crystallographic and data collection details are given in Table SI1.

Structure determination and multipolar refinement. In a first step, the molecular geometry of the complexes **2** and **3** were established following a classical X-ray diffraction structure analysis. The crystal structures were solved by direct methods[S6] then refined by full matrix least-squares on F^2 using the SHELX program.[S7] All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were set idealised positions (H-Csp^3 = 0.98 Å; H-Csp^2 = 0.93 Å; U_{iso} 1.5 (H-Csp^3) or

1.2 (H-Csp^2) time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and refined as "riding" atoms.

In the following refinements, a multipole model was adopted to describe the deformation of ρ(r) from a spherical distribution according to the Hansen and Coppens formalism[S8] as implemented in the MOPRO program.[S9] In this model, the electron density is described as a superposition of non spherical pseudoatoms (eq. 1):

$$\rho(\vec{r}) = \rho_{core}(r) + P_v\kappa^3\rho_{val}(\kappa r) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{+l} P_{lm} y_{lm\pm}(\vartheta,\varphi) \quad (1)$$

$$\text{where } R_l(r) = \frac{\xi_l^{n_l+3}}{(n_l+2)!} r^{n_l} e^{-\xi_l r}$$

The first two terms of eq. (1) correspond, respectively, to spherically averaged Hartree-Fock core and valence electron density, P_v is the electron population of the valence shell. The third term expresses the aspherical part of the atomic electron density projected on real spherical harmonics $y_{lm\pm}$. κ and κ' are contraction/expansion parameters. The core and valence atomic spherical electron densities were constructed using Clementi Hartree-Fock atomic wave functions for ground-state isolated atoms expanded over Slater-type basis functions.[S10] In our models, multipolar expansions were extended up to the hexadecapolar level for Mn. Nb and Cl (l_{max} = 4), octopolar level for O. N. and C (l_{max} = 3); H atoms were described with monopoles and bond directed dipoles. The spherical averaged core and valence electron densities of the free atoms were calculated from relativistic wave functions from Su and Coppens[S11] and Macchi and Coppens[S12], respectively. Slater-type radial functions were chosen with n_l = 4. 4. 4. 4. 4 and ξ_l = 4.0 Bohr^{-1} for manganese, n_l = 4. 4. 4. 6. 8 and ξ_l = 4.25 Bohr^{-1} for chlorine, n_l = 2. 2. 2. 3 for carbon, nitrogen and oxygen with ξ_l = 3.1 Bohr^{-1} for carbon, ξ_l = 3.8 Bohr^{-1} for nitrogen and ξ_l = 4.5 Bohr^{-1} for oxygen. Hydrogen atoms were described with n_l = 1. 1 and ξ_l = 2.0 Bohr^{-1}. Different parameter sets for describing the radial function and valence electron configuration of niobium have been tested. The best description, according to the residual density distribution around Nb derived from difference Fourier maps, was obtained using n_l = 6. 6. 6. 6. 6 and ξ_l = 6.3. 6.3. 6.3. 8.0. 8.0 Bohr^{-1} and a 4d^4 5s^1 hybridization for the valence shell. The anomalous dispersion coefficients were taken from the International Tables.[S13]

For complex **2**, the starting atomic positions were taken from the SHELX refinement and the C-H bond lengths were set to neutrons values [H-Csp^2 = 1.083 Å] by shifting the hydrogen atoms along the C-H directions. The positions and the thermal parameters were first refined using high resolution data only (S > 0.8 A^{-1}). The positions and the isotropic thermal parameters for the hydrogen atoms were allowed to vary in a restrained model as implemented in MOPRO [H-Csp^2 = 1.083 Å; U_{iso} 1.2 time greater than

the U_{eq} of the carbon atom to which the hydrogen atom is attached)]. Then the valence electron density was fitted using low resolution data only ($S < 0.8$ A^{-1}) in successive cycles on P_v, κ, $P_{lm\pm}$ and κ' parameters until convergence was reached. For Mn, the multipoles were allowed to refine assuming $3d^5$ valence configuration, the 4s electrons being set in the core. Attempts to refine separately both 4s and 3d led to physically inconsistent coefficients. Four different sets of κ/κ' for the four type of chemically different C atoms [C_{Cp}. $C_{carbonyl}$. C_{phenyl}. C_{alkyne}] and two different sets of κ/κ' for the two type of chemically different type of H atoms [H_{Cp}. H_{phenyl}] were used and refined. For the hydrogen atoms, the κ' parameter was fixed to 1.20. In the final cycles of refinement, all parameters were allowed to vary [within the limits of the above constraints and restraints] and all data available ($I > 0$) were used. The atomic positions and the temperature factors for all atoms are given in tables SI2 and SI3; selected distances and angles are indicated in table SI4. The Hirshfeld rigid bond test[S14] on atomic displacement parameters deserves some comments. It is respected for most of the interatomic bonds involving light atoms (C, O, H). As expected the Mn-C exhibit rather high discrepancies which is usual for atoms with highly different atomic weight. The carbonyl groups also do not fulfil the rigid bond test (O1-C1: 14 x 10^{-4} $Å^2$. O2-C2: 17 x 10^{-4} $Å^2$).

For complex **3,** the amine-methyl carbon atoms C1, C2 and C14, the methyl carbon atoms bonded to the aromatic ring, C12 and C13, respectively, were constrained to have the same κ and multipole parameters. A similar constraint was applied to all H atoms bonded to sp^3 hybridized carbon atoms (H1-H12 and H15-H29) and the two H atoms H13 and H14 ('aromatic' H atoms). In addition the carbon atoms of the alkyne ligand (C15 and C18; C16 and C17, respectively) were constrained to have the same P_v, κ and P_{lm} parameters at the beginning of the refinement. The starting values of the expansion/contraction parameters (κ and κ') of hydrogen atoms were set to 1.13 and 1.2, respectively,[S15] and the molecule was kept electronically neutral during the whole refinement. Starting from this model and for data with $I > 3\ \sigma(I)$, the valence populations and expansion/contraction of the spherical electron distribution of the non-hydrogen atoms were refined (P_v-κ refinement) using data up to $\sin\theta/\lambda \geq 0.7$ $Å^{-1}$. Subsequently, a new high-order refinement of coordinates and thermal displacement parameters of all non-hydrogen atoms was executed, followed by a refinement of the same parameters for hydrogen atoms up to 0.7 $Å^{-1}$ and a refinement of positions and thermal parameters for all atoms within the whole resolution range (0.0 – 1.1 $Å^{-1}$). This procedure was repeated while successively including the multipoles of the non-hydrogen atoms, κ and the monopoles of the H atoms and their dipoles. In the last refinement cycles, all reflections with $I > 1\ \sigma(I)$ were included and the κ' parameter of all non-hydrogen atoms were refined. The constraints on C-H bond

lengths and on the alkyne carbon atoms were removed. Finally, the resolution limit of the refinement of all parameters was gradually increased to reach global convergence with data up to $\sin\theta/\lambda \leq 1.0$ Å^{-1} yielding agreement factors of R_F = 1.929 % and wR_{2F} = 1.813 % ($\sin\theta/\lambda \leq 1.0$ Å^{-1}; $I/\sigma(I) > 1.0$; 13338 reflections). The atomic positions and the temperature factors for all atoms are given in tables SI5 and SI6, selected distances and angles are indicated in table SI7. Figure SI1 shows the residual densities after the multipole refinements in selected planes. In the plane of the phenyl ring, the residual density is essentially featureless and the residual peaks around the metal center present a disordered distribution (phenyl ring: ρ_{min} = –0.454. ρ_{max} = 0.244. $\Delta\rho$ = 0.698 eÅ^{-3}; Nb-alkyne plane: ρ_{min} = –0.333. ρ_{max} = 0.276. $\Delta\rho$ = 0.609 eÅ^{-3}, the extreme values being observed in the neighbourhood of the metal atom). The good quality of the refinement may also be inferred from the following points: i) the C-H bond lengths maintained their values after removing the bond length restraints during the last refinement cycles, ii) the Hirshfeld rigid bond test[S14] is respected for all of the interatomic bonds involving light atoms (C, O, H). As expected. the Nb-C and Nb-N bonds exhibit rather higher discrepancies which is usual for atoms with highly different atomic weight. The greatest difference between mean-square amplitudes is observed for O1-C7 (1 x 10^{-3} Å^2). The expansion parameters ($\kappa.\kappa'$) are indicated in table SI8, all the multipole populations are given in tables SI9 for complex **2** and in tables SI10 for complex **3**.

The topology and integrated properties derived from the experimental electron density, which were obtained and analyzed using the WinXPro program,[S16] are gathered in Tables SI11 and SI11. The kinetic energy densities G(r) at the *bcp's* given in Tables SI11 and SI12 were estimated using the approximation of Abramov:[S17]

$$G(r) = \frac{3}{10}(3\pi^2)^{2/3}\rho(r)^{5/3} + \frac{1}{6}\nabla^2\rho(r)$$

while the corresponding potential energy densities V(r) at the bcp's were obtained from the local virial theorem:

$$V(r) = \frac{1}{4}\nabla^2\rho(r) - 2G(r)\,.$$

References

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Table SI1. Crystal data and structure refinement for complexes $Cp(CO)_2Mn(\eta^2\text{-PhC}\equiv\text{CPh})$ (**2**) and $Cl_2(NNO)Nb(\eta^2\text{-MeC}\equiv\text{CMe})$ (**3**).

	Crystal data	
Compound	**2**	**3**
empirical formula	$C_{21}H_{15}MnO_2$	$C_{18}H_{29}N_2OCl_2Nb$
T (K), λ (Å)	100(2), 0.71069	100(2), 0.71069
Crystal system, space group (No.)	Monoclinic, P 2_1/c (14)	Monoclinic, P 2_1/c (14)
a (Å)	7.2391(9)	8.491(2)
b (Å)	12.2780(9)	13.154(3)
c (Å)	18.3457(2)	18.406(4)
β (°)	94.000(9)	99.54(3)
V (Å^3), Z	1626.6(2), 4	2027.4(8), 4
μ (mm^{-1}), ρ_{calc} (g cm^{-3})	0.82, 1.447	0.86, 1.485
Crystal size (mm)	0.35 x 0.50 x 0.50	0.07 x 0.09 x 0.15
av. redundancy, completeness (%)	9.9, 99	20.2, 100
R_{int} (%), $(\sin\theta/\lambda)_{max}$ (Å^{-1})	2.4, 1.12	8.02, 1.10
Index range, hkl	-15<h<15; -27<k<27; -34<l<40	-16≤h≤16; -26≤k≤26; -36≤l≤36
Reflections collected	191598	455991
Independent reflections (Rint)	19241	22617
	Multipolar refinement (MoPro)[S9]	
Data ($I/\sigma(I) > 0$), parameters	17418, 758	-
Data ($I/\sigma(I) > 1.0$), parameters	-	13338, 744
gof	1.41	0.398
R_F [$I/\sigma(I)$>0.0]; wR_{2F} [$I/\sigma(I)$>0.0]	0.0312; 0.0137	-
R_F [$I/\sigma(I)$>1.0]; wR_{2F} [$I/\sigma(I)$>1.0]	-	0.0193; 0.0181

Table SI2 Atomic fractional coordinates for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**) after the multipolar refinement.

Atom	x	y	z	U(eq)/U(iso) [Å^2]
Mn1	0.67178(1)	0.98314(1)	0.71790(1)	0.0102(1)
O1	0.38433(9)	1.14759(6)	0.68146(4)	0.0215(1)
O2	0.36178(9)	0.83324(6)	0.73573(5)	0.0239(1)
C1	0.49982(4)	1.08453(2)	0.69666(1)	0.0141(1)
C2	0.48444(4)	0.89129(2)	0.72731(1)	0.0148(1)
C3	0.69128(4)	0.90170(2)	0.61726(1)	0.0129(1)
C4	0.71737(4)	1.00233(2)	0.60680(1)	0.0132(1)
C11	0.75507(4)	1.01314(3)	0.83008(2)	0.0170(1)
C12	0.84234(5)	1.09048(3)	0.78577(2)	0.0179(1)
C13	0.95806(4)	1.03300(3)	0.73946(2)	0.0181(1)
C14	0.94304(4)	0.91997(3)	0.75507(2)	0.0169(1)
C15	0.81832(4)	0.90766(3)	0.81081(2)	0.0162(1)
C21	0.68116(4)	0.79055(2)	0.59204(1)	0.0125(1)
C22	0.71706(4)	0.70259(2)	0.63970(2)	0.0153(1)
C23	0.71759(4)	0.59618(3)	0.61296(2)	0.0180(1)
C24	0.67794(4)	0.57630(3)	0.53863(2)	0.0189(1)
C25	0.63577(4)	0.66336(3)	0.49132(2)	0.0182(1)
C26	0.63874(4)	0.76961(3)	0.51737(2)	0.0152(1)
C31	0.76913(4)	1.09310(2)	0.56260(2)	0.0138(1)
C32	0.80310(4)	1.19697(3)	0.59263(2)	0.0167(1)
C33	0.85929(5)	1.28235(3)	0.54924(2)	0.0205(1)
C34	0.88028(5)	1.26578(4)	0.47510(2)	0.0226(1)
C35	0.84509(5)	1.16300(4)	0.44462(2)	0.0228(1)
C36	0.79047(5)	1.07708(3)	0.48770(2)	0.0185(1)
H11	0.6567(6)	1.0314(5)	0.8702(2)	0.023(2)
H12	0.8213(9)	1.17780(10)	0.7867(4)	0.022(2)
H13	1.0423(7)	1.0678(5)	0.6988(3)	0.026(2)
H14	1.0107(8)	0.8537(3)	0.7285(3)	0.026(2)
H15	0.7772(8)	0.8307(3)	0.8336(3)	0.022(2)
H22	0.7472(8)	0.7183(5)	0.69740(10)	0.024(2)
H23	0.7492(8)	0.5297(3)	0.6506(2)	0.030(2)
H24	0.6763(9)	0.4936(2)	0.5181(3)	0.030(2)
H25	0.5990(8)	0.6478(5)	0.43400(10)	0.026(2)
H26	0.6067(8)	0.8373(3)	0.4808(2)	0.018(2)
H32	0.7839(8)	0.2107(5)	0.64990(10)	0.024(2)
H33	0.8853(9)	1.3612(2)	0.5744(3)	0.027(2)
H34	0.9255(9)	1.3320(3)	0.4416(3)	0.036(2)
H35	0.8620(10)	1.1481(5)	0.38730(10)	0.040(2)
H36	0.7637(9)	0.9971(2)	0.4645(3)	0.029(2)

U(eq) = 1/3 of the trace of the orthogonalized U tensor

Table SI3 Anisotropic or isotropic displacement parameters for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**) after the multipolar refinement. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

Atom	U(1.1)	U(2.2)	U(3.3)	U(2.3)	U(1.3)	U(1.2)
Mn1	0.0097(1)	0.0112(1)	0.0098(1)	-0.0006(1)	0.0008(1)	0.0002(1)
O1	0.0183(2)	0.0198(2)	0.0262(3)	0.0007(2)	-0.0004(2)	0.0089(2)
O2	0.0142(2)	0.0222(2)	0.0355(3)	0.0045(2)	0.0034(2)	-0.0064(2)
C1	0.0132(1)	0.0145(1)	0.0145(1)	-0.0010(1)	0.0008(1)	0.0026(1)
C2	0.0116(1)	0.0153(1)	0.0175(1)	0.0005(1)	0.0018(1)	-0.0010(1)
C3	0.0146(1)	0.0121(1)	0.0121(1)	-0.0013(1)	0.0010(1)	0.0004(1)
C4	0.0153(1)	0.0126(1)	0.0117(1)	0.0005(1)	0.0016(1)	0.0002(1)
C11	0.0193(1)	0.0200(1)	0.0117(1)	-0.0024(1)	0.0005(1)	0.0011(1)
C12	0.0197(1)	0.0144(1)	0.0188(1)	-0.0018(1)	-0.0044(1)	-0.0019(1)
C13	0.0128(1)	0.0236(1)	0.0177(1)	0.0032(1)	-0.0007(1)	-0.0042(1)
C14	0.0129(1)	0.0207(1)	0.0168(1)	-0.0011(1)	-0.0005(1)	0.0039(1)
C15	0.0181(1)	0.0163(1)	0.0140(1)	0.0024(1)	-0.0010(1)	0.0008(1)
C21	0.0130(1)	0.0126(1)	0.0117(1)	-0.0016(1)	0.0006(1)	0.0007(1)
C22	0.0182(1)	0.0137(1)	0.0138(1)	0.0001(1)	0.0000(1)	-0.0003(1)
C23	0.0195(1)	0.0130(1)	0.0210(1)	-0.0004(1)	-0.0015(1)	-0.0004(1)
C24	0.0188(1)	0.0145(1)	0.0228(1)	-0.0052(1)	-0.0017(1)	0.0001(1)
C25	0.0201(1)	0.0180(1)	0.0162(1)	-0.0060(1)	-0.0015(1)	0.0010(1)
C26	0.0171(1)	0.0157(1)	0.0124(1)	-0.0023(1)	-0.0009(1)	0.0018(1)
C31	0.0146(1)	0.0151(1)	0.0118(1)	0.0019(1)	0.0015(1)	0.0005(1)
C32	0.0198(1)	0.0147(1)	0.0155(1)	0.0026(1)	0.0004(1)	-0.0014(1)
C33	0.0203(1)	0.0181(1)	0.0227(1)	0.0071(1)	-0.0009(1)	-0.0030(1)
C34	0.0186(1)	0.0272(2)	0.0221(1)	0.0115(1)	0.0021(1)	-0.0025(1)
C35	0.0225(1)	0.0312(2)	0.0152(1)	0.0071(1)	0.0048(1)	-0.0003(1)
C36	0.0202(1)	0.0231(1)	0.0124(1)	0.0017(1)	0.0036(1)	0.0008(1)

Table SI4. Bond lengths [Å] and angles [°] for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**) after the multipolar refinement.

Bond lengths	
Mn1-C1	1.7842(3)
Mn1-C2	1.7814(4)
Mn1-C3	2.1129(3)
Mn1-C4	2.1006(3)
Mn1-C11	2.1358(5)
Mn1-C12	2.1441(5)
Mn1-C13	2.1706(4)
Mn1-C14	2.1762(4)
Mn1-C15	2.1534(4)
O1-C1	1.1593(8)
O2-C2	1.1574(8)
C3-C4	1.2666(4)
C3-C21	1.4413(4)
C4-C31	1.4430(4)
Bond angles	
C1-Mn1-C2	86.48(2)
C1-Mn1-C3	103.15(1)
C1-Mn1-C4	82.20(1)
C2-Mn1-C3	83.27(1)
C2-Mn1-C4	109.71(1)
C3-Mn1-C4	34.99(1)
C4-C3-C21	151.61(2)
C3-C4-C31	152.37(2)

Table SI5 Atomic fractional coordinates for complex ($Nb(C_{14}H_{23}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**) after the multipolar refinement.

Atom	x	y	z	U(eq)/U(iso) [Å^2]
NB1	0.71671(1)	0.75594(1)	0.32356(1)	0.01074(1)
CL1	0.66852(2)	0.85069(1)	0.209467(1)	0.01862(1)
CL2	1.00456(2)	0.79853(1)	0.332643(1)	0.018993(1)
O1	0.76160(5)	0.65037(3)	0.39480(2)	0.01260(3)
N1	0.47079(6)	0.67860(4)	0.27296(3)	0.01401(3)
N2	0.79150(6)	0.60871(4)	0.24974(3)	0.01319(3)
C1	0.41161(8)	0.61600(5)	0.33026(4)	0.01800(4)
C2	0.33923(8)	0.74901(6)	0.24253(4)	0.01969(4)
C3	0.49837(8)	0.61128(5)	0.21065(4)	0.01674(4)
C4	0.64546(8)	0.54544(4)	0.23095(4)	0.01525(4)
C5	0.92305(7)	0.54663(5)	0.29286(3)	0.01465(3)
C6	0.88161(7)	0.49742(4)	0.36115(3)	0.01261(3)
C7	0.80431(7)	0.55276(4)	0.41007(3)	0.01194(3)
C8	0.76896(7)	0.50932(4)	0.47516(3)	0.01337(3)
C9	0.81397(8)	0.40843(4)	0.49018(3)	0.01529(4)
C10	0.89134(8)	0.35067(4)	0.44263(3)	0.01505(4)
C11	0.92341(7)	0.39642(4)	0.37787(3)	0.01422(3)
C12	0.68669(9)	0.57170(5)	0.52616(4)	0.01714(4)
C13	0.9388(1)	0.24222(5)	0.46082(4)	0.02207(5)
C14	0.84901(9)	0.63933(5)	0.18127(4)	0.01925(5)
C15	0.44460(10)	0.84877(6)	0.43136(5)	0.02314(5)
C16	0.58210(7)	0.83878(4)	0.39088(3)	0.01519(4)
C17	0.71957(8)	0.88399(4)	0.39078(4)	0.01576(4)
C18	0.8190(1)	0.96877(6)	0.42561(5)	0.02532(5)
H1	0.387(1)	0.6629(8)	0.3709(6)	0.035(3)
H2	0.494(1)	0.5647(8)	0.3511(6)	0.029(3)
H3	0.310(1)	0.5784(8)	0.3070(6)	0.037(3)
H4	0.240(1)	0.7057(9)	0.2224(6)	0.038(3)
H5	0.368(1)	0.7896(9)	0.2010(6)	0.035(3)
H6	0.315(1)	0.7937(9)	0.2832(6)	0.040(3)
H7	0.509(1)	0.6576(8)	0.1662(6)	0.035(3)
H8	0.400(1)	0.5650(8)	0.1963(6)	0.033(3)
H9	0.635(1)	0.5028(7)	0.2748(5)	0.023(3)
H10	0.656(1)	0.4978(8)	0.1879(6)	0.032(3)
H11	1.016(1)	0.5974(8)	0.3065(6)	0.035(3)
H12	0.956(1)	0.4908(8)	0.2602(6)	0.030(3)
H13	0.788(1)	0.3745(9)	0.5411(6)	0.028(3)
H14	0.985(1)	0.3566(9)	0.3415(6)	0.024(3)
H15	0.687(1)	0.5339(10)	0.5732(7)	0.052(4)
H16	0.575(1)	0.5851(9)	0.5015(6)	0.043(3)
H17	0.742(1)	0.6358(9)	0.5372(6)	0.044(3)
H18	0.894(2)	0.199(1)	0.4217(8)	0.074(5)
H19	0.907(2)	0.222(1)	0.5033(8)	0.072(5)

H20	1.054(2)	0.238(1)	0.4656(10)	0.094(6)
H21	0.879(1)	0.5762(9)	0.1563(6)	0.036(3)
H22	0.944(1)	0.6858(8)	0.1944(6)	0.034(3)
H23	0.763(1)	0.6772(9)	0.1475(6)	0.037(3)
H24	0.459(1)	0.791(1)	0.4705(7)	0.053(4)
H25	0.340(1)	0.8416(9)	0.3980(6)	0.040(3)
H26	0.445(1)	0.920(1)	0.4562(7)	0.058(4)
H27	0.756(2)	1.0147(10)	0.4499(7)	0.058(4)
H28	0.851(2)	1.0088(10)	0.3841(7)	0.059(4)
H29	0.916(2)	0.942(1)	0.4539(7)	0.061(4)

U(eq) = 1/3 of the trace of the orthogonalized U tensor

Table SI6 Anisotropic or isotropic displacement parameters for complex $(Nb(C_{14}H_{23}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**) after the multipolar refinement. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

Atom	U(1.1)	U(2.2)	U(3.3)	U(2.3)	U(1.3)	U(1.2)
NB1	0.01077(1)	0.00985(1)	0.01194(1)	0.00051(1)	0.00286(1)	-0.00089(1)
CL1	0.02331(6)	0.01661(5)	0.01635(6)	0.00555(4)	0.00450(5)	0.00108(5)
CL2	0.01303(5)	0.02197(6)	0.02270(6)	-0.00066(5)	0.00506(4)	-0.00412(4)
O1	0.0150(2)	0.0106(1)	0.0127(1)	0.0014(1)	0.0038(1)	0.0006(1)
N1	0.0123(2)	0.0137(2)	0.0158(2)	-0.0011(1)	0.0018(1)	-0.0008(1)
N2	0.0152(2)	0.0133(2)	0.0118(2)	0.0011(1)	0.0043(1)	0.0009(1)
C1	0.0166(2)	0.0174(2)	0.0210(3)	-0.0003(2)	0.0059(2)	-0.0042(2)
C2	0.0143(2)	0.0198(2)	0.0240(3)	-0.0004(2)	0.0003(2)	0.0030(2)
C3	0.0162(2)	0.0172(2)	0.0158(2)	-0.0026(2)	-0.0003(2)	0.0007(2)
C4	0.0167(2)	0.0137(2)	0.0151(2)	-0.0020(2)	0.0020(2)	0.0001(2)
C5	0.0147(2)	0.0160(2)	0.0144(2)	0.0018(2)	0.0056(2)	0.0028(2)
C6	0.0144(2)	0.0120(2)	0.0120(2)	0.0004(1)	0.0037(1)	0.0012(1)
C7	0.0136(2)	0.0114(2)	0.0113(2)	0.0007(1)	0.0034(1)	0.0002(1)
C8	0.0161(2)	0.0125(2)	0.0121(2)	0.0005(1)	0.0040(1)	-0.0005(1)
C9	0.0205(2)	0.0128(2)	0.0129(2)	0.0018(1)	0.0038(2)	-0.0006(2)
C10	0.0197(2)	0.0114(2)	0.0140(2)	0.0010(1)	0.0023(2)	0.0014(2)
C11	0.0166(2)	0.0124(2)	0.0138(2)	0.0003(1)	0.0030(2)	0.0020(1)
C12	0.0208(2)	0.0168(2)	0.0155(2)	-0.0014(2)	0.0079(2)	-0.0005(2)
C13	0.0327(3)	0.0128(2)	0.0209(2)	0.0028(2)	0.0050(2)	0.0035(2)
C14	0.0240(3)	0.0207(2)	0.0152(2)	0.0032(2)	0.0093(2)	0.0027(2)
C15	0.0223(3)	0.0246(3)	0.0252(3)	-0.0052(2)	0.0116(2)	-0.0005(2)
C16	0.0158(2)	0.0135(2)	0.0171(2)	-0.0022(2)	0.0049(2)	-0.0002(2)
C17	0.0165(2)	0.0116(2)	0.0190(2)	-0.0022(2)	0.0021(2)	-0.0016(2)
C18	0.0239(3)	0.0161(2)	0.0341(4)	-0.0071(2)	-0.0005(3)	-0.0039(2)

Table SI7. Bond lengths [Å] and angles [°] for complex $Nb(C_{14}H_{23}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**, D denotes midpoint of the alkyne bond C16-C17) after the multipolar refinement.

Bond lengths	
Nb1–Cl1	2.4179(2)
Nb1–Cl2	2.4860(2)
Nb1–O1	1.9043(4)
Nb1–N1	2.3702(5)
Nb1–N2	2.507(1)
Nb1–C16	2.1207(6)
Nb1–C17	2.0874(6)
C15-C16	1.4914(9)
C16-C17	1.3098(9)
C17-C18	1.4797(9)
Bond angles	
Cl1-Nb1-Cl2	88.006(6)
Cl1-Nb1-N1	82.45(1)
Cl2-Nb1-O1	92.05(1)
O1-Nb1-N1	91.16(2)
N2-Nb1-N1	75.00(2)
N2-Nb1-O1	76.70(2)
D-Nb1-N1	102.47(2)
D-Nb1-Cl1	98.95(2)
D-Nb1-Cl2	100.45(1)
D-Nb1-O1	97.13(2)
C15-C16-C17	137.06(6)
C16-C17-C18	141.82(6)
N2-Nb1-Cl1	87.08(1)
N2-Nb1-Cl2	82.88(1)

Table SI8. Kappa parameters for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**) and for complex (Nb($C_{14}H_{23}N_2O$)($H_3CC{\equiv}CCH_3$)Cl_2 (**3**).

Atom (complex 2)	κ	κ'
Mn1	1.07594	1.00561
O1	1.01073	1.32384
O2	1.01073	1.32384
C1, C2	1.02477	0.81915
C3, C4	1.01992	0.9415
C11 to C15	1.0276	0.92457
Other C atoms	1.03022	0.95341
H11, H14, H15	1.07936	1.2
Other H atoms	1.08997	1.2

Atom (complex 3)	κ	κ'
Nb1	1.10(2)	0.99(2)
Cl1	0.969(3)	0.89(3)
Cl2	0.972(3)	1.16(6)
O1	0.971(4)	0.80(4)
N1	0.972(6)	0.89(3)
N2	0.979(6)	0.96(3)
C1, C2, C14	1.040(9)	0.94(2)
C3	1.01(1)	0.95(3)
C4	1.03(1)	1.02(3)
C5	1.03(1)	0.90(3)
C6	0.99(1)	1.02(3)
C7	1.01(1)	0.99(2)
C8	1.00(1)	1.01(3)
C9	1.00(1)	1.04(3)
C10	1.02(1)	1.02(3)
C11	1.00(1)	0.91(3)
C12, C13	0.984(9)	0.82(1)
C15	1.01(1)	0.86(3)
C16	0.95(1)	0.90(2)
C17	0.95(1)	0.90(2)
C18	1.00(1)	0.84(2)
H(-C(sp^3))	1.13(2)	1.20
H13, H14	1.08(7)	1.20

Table SI9. Multipolar refinement parameters for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**) after the multipolar refinement

	P_{val}	P_{11+}	P_{11-}	P_{10}	P_{20}	P_{21+}	P_{21-}	P_{22+}	P_{22-}
Mn1	4.99	-0.008	0.034	-0.008	0.02	0.011	0.074	0.035	-0.008
O1	6.065	0.028	-0.016	0.007	0.135	0.015	0.014	-0.017	-0.014
O2	6.087	-0.009	0.005	0.011	0.145	-0.002	0.004	-0.032	-0.008
C1	4.171	-0.029	-0.023	-0.059	0.498	0.017	-0.007	0.004	0.02
C2	4.164	0.005	0.006	-0.072	0.488	-0.015	0.012	-0.003	-0.026
C3	4.137	0	0.057	-0.004	-0.156	0	-0.01	-0.086	0.137
C4	4.22	0.015	0.102	0.019	-0.181	-0.02	-0.014	-0.116	0.153
C11	3.996	0.032	0.048	0	-0.189	0.02	-0.01	0.018	0.013
C12	3.917	0.018	0.026	0.018	-0.201	0.016	-0.012	0.045	0.018
C13	4.004	0.035	0.003	0.011	-0.199	0.011	0.015	0.05	0.013
C14	3.993	0.059	-0.013	-0.007	-0.173	0.023	0.007	0.031	0.026
C15	4.01	0.056	0.016	0.004	-0.203	0.006	0.01	0.023	0.015
C21	3.987	0.051	-0.002	-0.012	-0.183	0.008	0.001	-0.033	0.007
C22	4.026	0.019	-0.017	-0.006	-0.174	-0.016	-0.003	-0.008	-0.004
C23	4.027	0.068	-0.01	0.012	-0.174	0.006	-0.005	-0.041	-0.026
C24	3.97	0.065	-0.023	0.021	-0.193	0	0.004	-0.026	-0.002
C25	3.963	0.042	-0.003	-0.008	-0.199	-0.005	0.014	-0.035	0.014
C26	3.965	0.015	-0.004	0.009	-0.196	-0.014	0.008	0.009	-0.005
C31	3.968	0.037	0.007	-0.016	-0.181	0.009	-0.003	-0.019	0.015
C32	4.025	0.038	-0.006	0.002	-0.187	-0.001	0	-0.009	0.009
C33	3.993	0.091	0.04	0.006	-0.214	-0.015	0.007	-0.035	-0.012
C34	3.942	0.053	0.067	0.007	-0.216	-0.006	0.014	-0.056	0.021
C35	3.884	0.043	0.049	0.001	-0.189	-0.009	-0.002	-0.021	0.024
C36	4.022	0.022	0.013	-0.016	-0.183	-0.005	-0.012	-0.013	0.007
H11	0.917	0.137							
H14	0.952	0.147							

H15	0.946	0.146
H22	0.977	0.136
H23	1.043	0.166
H24	1.016	0.161
H25	0.974	0.143
H26	0.901	0.129
H32	0.966	0.142
H33	0.977	0.160
H34	1.021	0.165
H35	1.028	0.165
H36	0.984	0.133

	P_{30}	P_{31+}	P_{31-}	P_{32+}	P_{32-}	P_{33+}	P_{33-}
Mn1	0.020	0.009	0.010	0.000	-0.009	-0.008	0.001
O1	0.006	-0.017	0.017	0.000	-0.011	-0.027	0.022
O2	0.015	-0.006	0.007	0.001	-0.018	0.014	-0.019
C1	0.139	-0.005	-0.031	-0.022	-0.028	0.001	0.007
C2	0.131	-0.007	-0.024	0.023	-0.009	0.004	-0.002
C3	0.009	0.008	0.036	-0.017	-0.007	0.063	-0.143
C4	-0.006	-0.004	0.006	0.002	0.027	0.036	-0.139
C11	0.041	0.032	-0.023	0.018	0.003	-0.272	0.007
C12	0.011	0.061	-0.005	-0.011	0.017	-0.257	-0.022
C13	0.035	0.057	0.026	0.039	0.005	-0.275	0.010
C14	0.057	0.040	0.027	0.015	0.011	-0.262	0.003
C15	0.036	0.026	0.010	-0.010	-0.006	-0.268	0.018
C21	0.016	0.010	0.018	-0.003	-0.008	-0.252	0.003
C22	-0.013	0.014	0.008	0.013	-0.003	-0.263	0.009
C23	-0.020	0.005	0.004	0.007	0.010	-0.227	0.004
C24	-0.014	0.014	-0.010	-0.015	0.005	-0.255	0.006

C25	-0.002	0.022	-0.014	0.027	0.021	-0.276	-0.005
C26	-0.011	0.033	0.007	-0.001	0.009	-0.273	-0.009
C31	-0.002	0.024	0.007	0.006	-0.004	-0.240	0.007
C32	0.003	0.015	0.008	-0.001	-0.003	-0.280	0.019
C33	0.007	-0.001	-0.017	0.008	-0.035	-0.240	0.058
C34	-0.007	0.027	-0.031	0.034	-0.026	-0.276	-0.012
C35	0.002	0.021	-0.026	0.021	0.006	-0.230	-0.025
C36	-0.001	0.022	-0.001	0.004	0.004	-0.277	-0.020

	P_{40}	P_{41+}	P_{41-}	P_{42+}	P_{42-}	P_{43+}	P_{43-}	P_{44+}	P_{44-}
Mn1	-0.245	0.008	0.054	-0.132	0.006	0.015	0.043	0.172	0.017

Table SI10 Multipolar refinement parameters for complex ($Nb(C_{14}H_{23}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**) after the multipolar refinement

atom	P_{val}	P_{11+}	P_{11-}	P_{10}	P_{20}	P_{21+}	P_{21-}	P_{22+}	P_{22-}
Nb1	2.71(8)	0.02(1)	-0.01(1)	0.06(1)	0.07(1)	0.16(1)	-0.08(1)	0.04(1)	-0.04(1)
Cl1	7.56(5)	-0.03(2)	-0.08(2)	0.12(2)	0.11(2)	0.03(2)	0.05(2)	-0.03(2)	0.02(2)
Cl2	7.54(5)	0.02(1)	0.04(1)	0.05(1)	-0.03(2)	0.03(2)	0.00(2)	0.04(2)	0.05(2)
O1	6.46(5)	0.10(2)	0.00(2)	0.02(2)	-0.08(2)	-0.02(2)	0.01(2)	0.07(2)	0.06(2)
N1	5.33(7)	0.01(2)	-0.02(2)	0.07(2)	0.08(2)	0.01(2)	0.01(2)	-0.01(2)	0.01(2)
N2	5.30(7)	-0.01(2)	-0.05(2)	-0.01(2)	-0.01(2)	-0.01(2)	0.06(2)	-0.02(2)	0.06(2)
C1,C2,C14	3.6(1)	0.02(1)	0.01(1)	-0.05(2)	-0.05(2)	0.01(2)	-0.02(1)	0.01(2)	-0.02(2)
C3	3.8(1)	0.03(3)	0.01(2)	-0.06(3)	-0.05(3)	-0.02(3)	-0.03(2)	0.05(3)	0.01(2)
C4	3.7(1)	0.02(3)	-0.02(2)	-0.02(2)	-0.05(3)	-0.03(2)	0.03(2)	0.01(2)	0.01(2)
C5	3.7(1)	0.01(3)	0.02(2)	-0.06(2)	-0.05(3)	0.00(2)	-0.04(2)	0.01(3)	0.05(2)
C6	4.1(1)	-0.01(3)	0.03(3)	0.02(2)	-0.16(3)	0.00(2)	-0.03(2)	-0.02(3)	0.01(3)
C7	3.8(1)	0.05(3)	0.13(3)	-0.02(2)	-0.17(3)	0.00(2)	-0.03(2)	0.02(3)	-0.10(3)
C8	3.9(1)	0.05(3)	0.04(3)	-0.03(2)	-0.18(2)	0.01(2)	-0.04(2)	0.01(3)	0.00(3)
C9	4.1(1)	-0.03(3)	0.01(3)	-0.01(2)	-0.15(3)	0.00(2)	0.03(2)	0.00(2)	0.00(2)
C10	3.7(1)	0.02(3)	0.07(2)	-0.04(2)	-0.18(2)	-0.02(2)	0.03(2)	0.00(2)	-0.05(2)
C11	4.1(1)	0.02(3)	0.06(3)	0.02(2)	-0.19(3)	0.01(2)	0.03(2)	-0.01(3)	-0.06(3)
C12, C13	3.8(1)	0.03(2)	-0.03(2)	0.00(2)	0.07(3)	0.01(2)	-0.01(2)	0.03(3)	0.02(3)
C15	3.8(1)	-0.10(3)	-0.01(3)	-0.06(4)	0.07(4)	0.04(3)	0.08(3)	0.05(3)	-0.05(3)
C16	4.4(1)	0.10(5)	-0.16(3)	0.07(3)	-0.25(3)	0.02(3)	-0.01(2)	0.02(3)	-0.02(3)
C17	4.5(2)	0.07(5)	-0.13(3)	-0.02(3)	-0.29(3)	0.03(3)	-0.02(2)	0.00(4)	-0.08(3)
C18	3.6(1)	-0.08(3)	0.01(3)	-0.11(4)	0.02(4)	0.04(4)	0.00(4)	0.08(4)	0.06(4)
H(-C(sp^3))	1.09(3)			0.07(2)					
H13, H14	1.02(7)			0.11(4)					

atom	P_{30}	P_{31+}	P_{31-}	P_{32+}	P_{32-}	P_{33+}	P_{33-}
Nb1	0.03(1)	-0.00(1)	-0.01(1)	-0.02(1)	0.01(1)	-0.01(1)	-0.02(1)
Cl1	0.08(3)	0.00(2)	-0.05(2)	-0.02(2)	-0.02(2)	-0.03(2)	0.1(2)
Cl2	0.08(2)	0.01(2)	-0.01(2)	0.01(2)	0.02(2)	0.01(2)	-0.02(2)
O1	0.04(2)	0.04(2)	-0.01(2)	-0.01(2)	-0.02(2)	-0.01(2)	-0.06(2)
N1	0.19(2)	0.03(2)	0.03(2)	0.00(2)	0.01(2)	0.18(2)	-0.02(2)
N2	0.18(2)	-0.01(2)	-0.04(2)	-0.02(2)	-0.01(2)	0.14(2)	0.00(2)
C1, C2, C14	0.21(2)	-0.03(2)	-0.01(2)	0.01(2)	-0.03(2)	0.10(2)	-0.02(2)
C3	0.21(3)	0.02(3)	-0.05(3)	-0.06(3)	0.01(3)	0.17(3)	0.01(3)
C4	0.22(3)	-0.03(3)	0.04(3)	-0.01(3)	0.00(3)	0.14(3)	-0.04(3)
C5	0.21(3)	0.00(3)	0.03(3)	-0.05(3)	0.02(3)	0.16(3)	-0.05(3)
C6	-0.01(2)	0.05(2)	0.01(2)	0.03(3)	0.00(3)	0.25(3)	-0.05(3)
C7	-0.00(3)	0.04(2)	0.05(2)	0.03(3)	0.01(3)	0.28(3)	-0.07(3)
C8	0.02(3)	-0.01(2)	0.03(2)	0.02(3)	-0.2(3)	0.25(3)	0.03(3)
C9	0.05(2)	0.01(2)	0.01(2)	0.02(2)	-0.02(3)	0.24(3)	-0.01(3)
C10	0.01(2)	0.00(2)	0.02(2)	0.01(2)	0.01(2)	0.20(3)	0.03(3)
C11	0.02(3)	-0.02(3)	0.04(3)	0.01(3)	-0.04(3)	0.26(4)	0.03(4)
C12, C13	0.46(3)	-0.02(3)	0.06(3)	-0.02(3)	0.00(3)	-0.14(3)	-0.01(3)
C15	0.32(4)	0.04(4)	-0.02(4)	-0.02(4)	0.03(4)	-0.04(4)	-0.01(4)
C16	-0.02(3)	0.01(3)	0.00(2)	-0.01(3)	0.01(3)	0.15(3)	-0.21(3)
C17	-0.01(3)	0.02(3)	-0.04(3)	0.05(3)	-0.01(3)	0.14(4)	-0.20(3)
C18	0.37(4)	0.07(4)	0.02(4)	-0.04(5)	-0.07(4)	-0.20(4)	0.01(5)

atom	P_{40}	P_{41+}	P_{41-}	P_{42+}	P_{42-}	P_{43+}	P_{43-}	P_{44+}	P_{44-}
Nb1	-0.08(2)	0.12(1)	0.00(1)	-0.11(2)	0.00(1)	-0.04(1)	-0.09(1)	-0.01(1)	-0.02(1)
Cl1	-0.01(3)	-0.01(2)	0.01(2)	-0.02(3)	0.02(3)	0.03(3)	-0.05(3)	-0.02(3)	-0.02(3)
Cl2	0.04(3)	-0.01(2)	-0.02(2)	0.02(2)	0.03(2)	0.01(2)	0.04(2)	-0.01(2)	0.06(2)

Table SI11. Topological properties of the experimental electron density at selected bond critical points for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**).[a]

	d_{ij} /Å	$\rho(r)$	$\nabla^2\rho(r)$	λ_1	λ_2	λ_3	ε	G	V	H
Mn1-C1	1.7842(3)	0.99	+13.52	–4.57	–4.39	+22.48	0.04	1.42	–1.90	–0.48
Mn1-C2	1.7814(4)	1.01	+13.4	–4.88	–4.60	+22.88	0.06	1.44	–1.94	–0.50
Mn1-C3	2.1129(3)	0.48	+6.77	–1.64	–0.42	+8.83	2.89	0.55	–0.63	–0.08
Mn1-C4	2.1006(3)	0.48	+6.85	–1.63	–0.42	+8.91	2.88	0.56	–0.63	–0.07
C1-O1	1.1593(8)	3.18	–3.68	–30.41	–29.88	+56.61	0.02	5.37	–10.99	–5.62
C2-O2	1.1574(8)	3.17	–0.1	–30.74	–29.84	+60.48	0.03	5.51	–11.02	–5.51
Mn1-C11	2.1358(5)	0.44	+6.38	–1.56	–0.18	+8.13	7.69	0.50	–0.56	–0.06
Mn1-C12	2.1441(5)	0.44	+6.3	–1.53	-0.21	+8.04	6.23	0.50	–0.56	–0.06
Mn1-C13	2.1706(4)	0.43	+5.93	–1.42	–0.23	+7.59	5.20	0.47	–0.53	–0.06
Mn1-C14	2.1762(4)	0.42	+5.9	–1.35	–0.14	+7.39	8.71	0.47	–0.52	–0.05
C3-C4	1.2666(4)	2.66	–23.98	–18.28	–17.06	+11.36	0.07	2.99	–7.66	–4.67
C3-C21	1.4413(4)	1.91	–12.76	–13.88	–12.42	+13.54	0.12	1.77	–4.43	–2.66
C4-C31	1.4430(4)	1.90	–12.06	–13.58	–12.36	+13.88	0.10	1.78	–4.41	–2.62
rcp's										
Cp rcp		*0.33*	*+7.22*	*–0.53*	*+3.84*	*+3.91*				
Ph1 rcp		*0.14*	*+3.41*	*–0.28*	*+1.80*	*+1.88*				
Ph2 rcp		*0.14*	*+3.40*	*–0.28*	*+1.80*	*+1.88*				
Mn1-C3-C4 rcp		*0.48*	*+7.01*	*–1.58*	*+0.25*	*+8.34*				

[a] d_{ij} /Å is the interatomic distance; $\rho(r)$ /e.Å^{-3}, $\nabla^2\rho(r)$ /e.Å^{-5}, λ /e.Å^{-5} and ε are the ED, the Laplacian of the ED, the curvature of the ED and the ellipticity of the bond, respectively, while G /hartree.Å^{-3}, V /hartree.Å^{-3} and H /hartree.Å^{-3} are the kinetic, the potential and the total energy densities at the *bcp*.

Table SI12. Topological properties of the experimental electron density at selected bond critical points for complex $Nb(C_{14}H_{23}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**).[a]

	d_{ij} /Å	$\rho(r)$	$\nabla^2\rho(r)$	λ_1	λ_2	λ_3	ε	G	V	H
Nb1–Cl1	2.42	0.48	6.04	–1.88	–1.77	9.69	0.06	0.52	-0.61	-0.10
Nb1–Cl2	2.49	0.38	4.80	–1.43	–1.26	7.49	0.13	0.38	-0.43	-0.05
Nb1–O1	1.90	0.93	16.65	–5.27	–5.17	27.09	0.02	1.49	-1.81	-0.32
Nb1–N1	2.37	0.37	5.11	–1.64	–1.58	8.34	0.04	0.39	-0.43	-0.03
Nb1-N2	2.51	0.27	3.89	–1.04	–1.03	5.96	0.01	0.27	-0.27	0.00
Nb1–C16	2.12	0.69	7.94	–3.00	–1.58	12.52	0.90	0.80	-1.05	-0.25
Nb1–C17	2.09	0.75	7.92	–3.30	–2.31	13.53	0.43	0.87	-1.18	-0.31
C16–C17	1.31	2.40	–24.00	–14.75	–14.60	5.36	0.01	2.34	-6.36	-4.02
C15–C16	1.49	1.69	–12.11	–11.22	–10.54	9.65	0.06	1.36	-3.57	-2.21
C17–C18	1.48	1.73	–13.38	–11.63	–10.98	9.23	0.06	1.38	-3.70	-2.32
rcp's										
Nb1-C16-C17		*0.67*	*9.01*	*–2.70*	*1.46*	*10.26*		*0.83*	*-1.04*	*-0.20*
Ph1		*0.16*	*3.19*					*0.19*	*-0.15*	*0.04*

[a] d_{ij} /Å is the interatomic distance; ρ(r) /e.Å^{-3}, $\nabla^2\rho$(r) /e.Å^{-5}, λ /e.Å^{-5} and ε are the ED, the Laplacian of the ED, the curvature of the ED and the ellipticity of the bond, respectively, while G /hartree.Å^{-3}, V /hartree.Å^{-3} and H /hartree.Å^{-3} are the kinetic, the potential and the total energy densities at the *bcp*.

Figure SI1. Residual electron density maps for complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CPh)$ (**2**) after the multipolar refinement within the planes Mn1/O1/O2, Mn1/C3/C4 and C11/C12/C14 (0.1 e.Å $^{-3}$ isocontours; positive: full lines; negative: dashed lines) for I > 0 and S < 0.8 Å^{-1} (left) and I > 0 and S < 1.12 Å^{-1} (right).

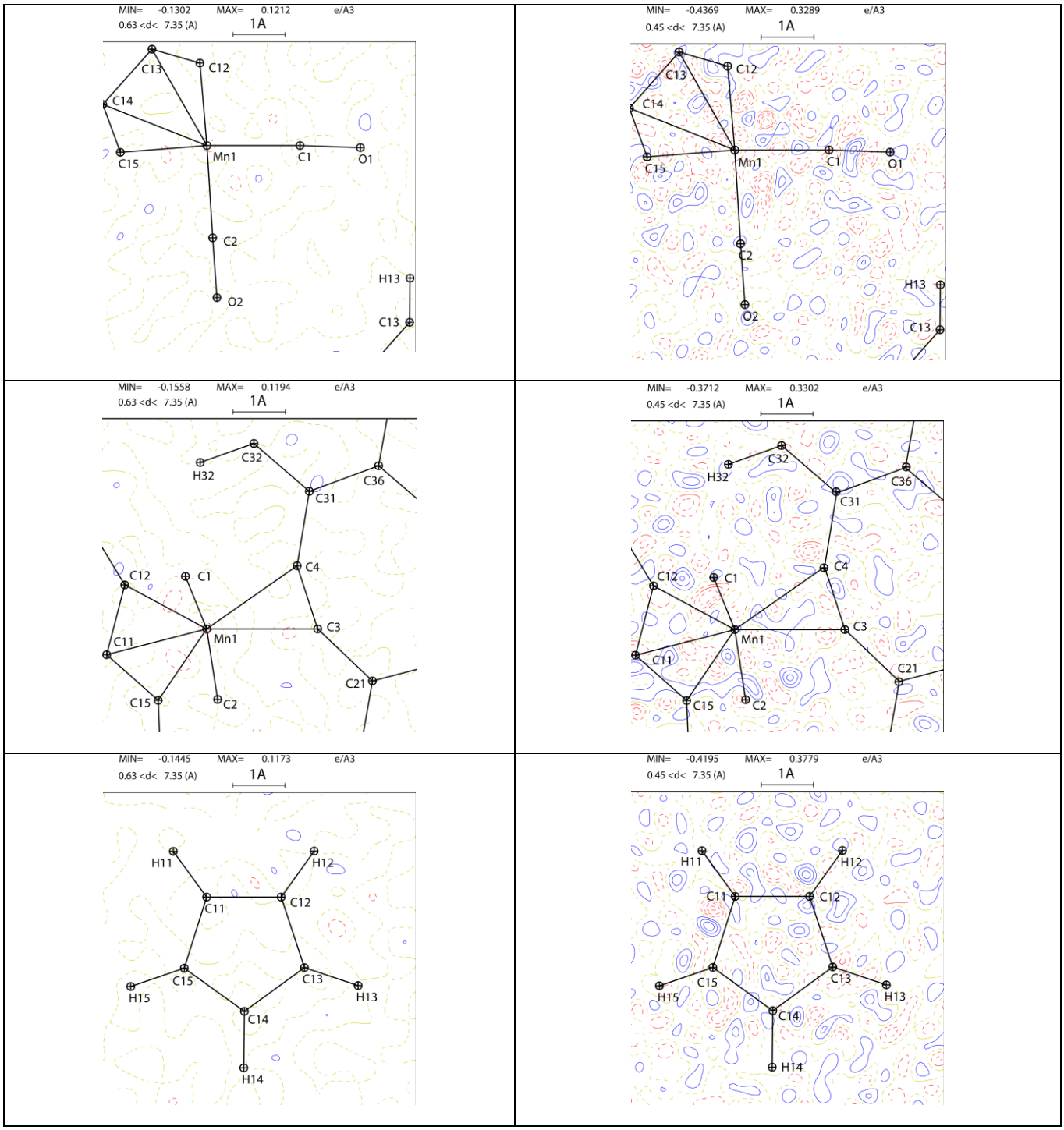


Figure SI2. Experimental $-\nabla^2\rho(r)$ function. *na*'s (black dots), *bp*'s (black lines) and *bcp*'s (red circles) for complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}PhC{\equiv}CPh)$ (**2**) within the plane Mn1/O1/O2. Contours are drawn at 0.000, ±2.0 x 10^n, ±4.0 x 10^n, ±8.0 x 10^n e.Å^{-5} levels where n = 0, -3, ±2, ±1; positive: solid (red) lines, negative: dashed (blue) lines.

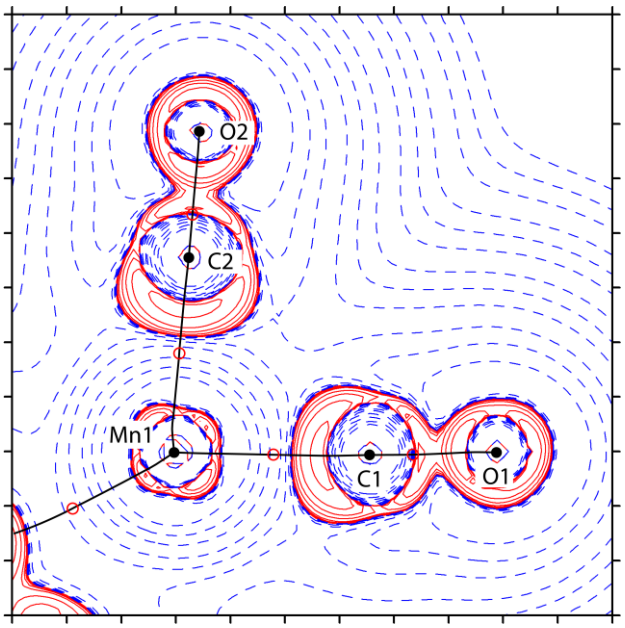


Figure SI3. Residual electron density maps for complex $Nb(C_{14}H_{23}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**) after the multipolar refinement within the planes C6/C7/C8 (left) and Nb1/C16/C17 (right) (0.05 e.Å^{-3} isocontours; positive: solid (blue) lines; negative: dashed (red) lines) for $I/\sigma(I) > 1.0$ and $S < 1.0$ Å^{-1}.

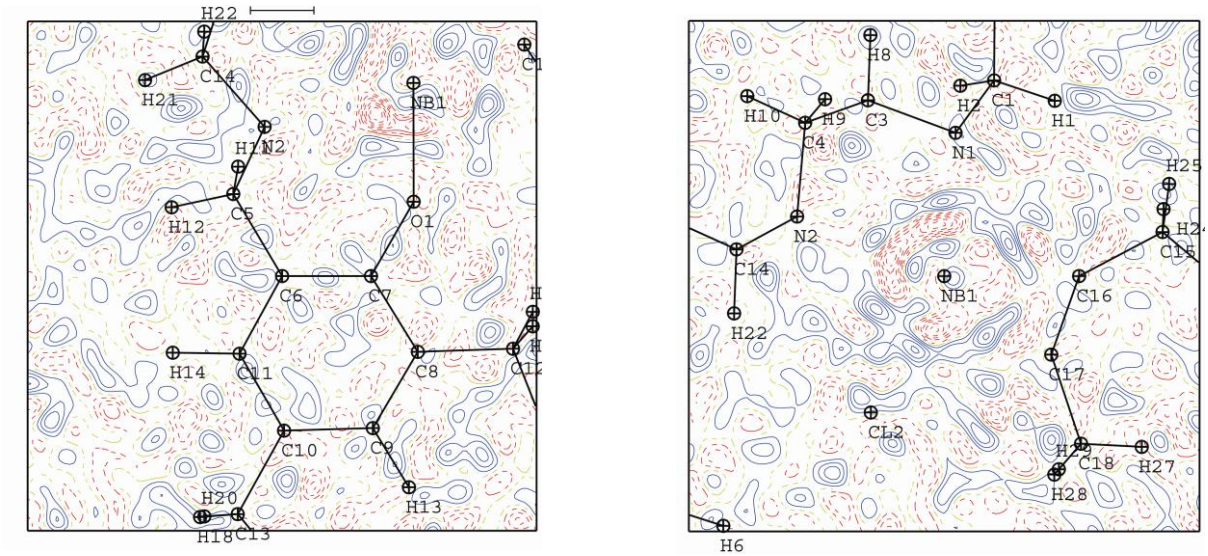


Figure SI4. Molecular graph for complex (η^5-C_5H_5)$(CO)_2$Mn(η^2-PhC≡CPh) (**2**) showing *bp*'s (black lines), *bcp*'s (small red dots), *rcp*'s (small yellow cubes) and *ccp* (small purple triangle).

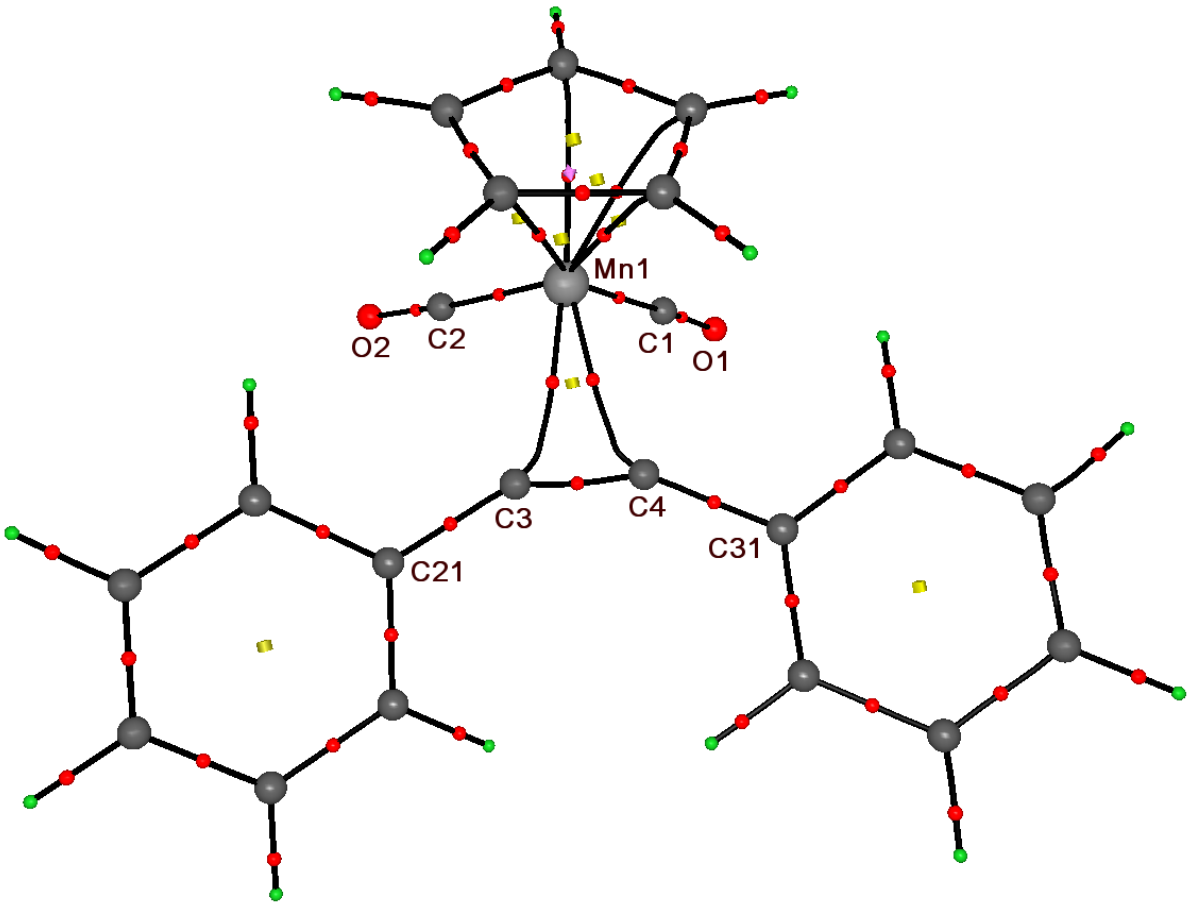
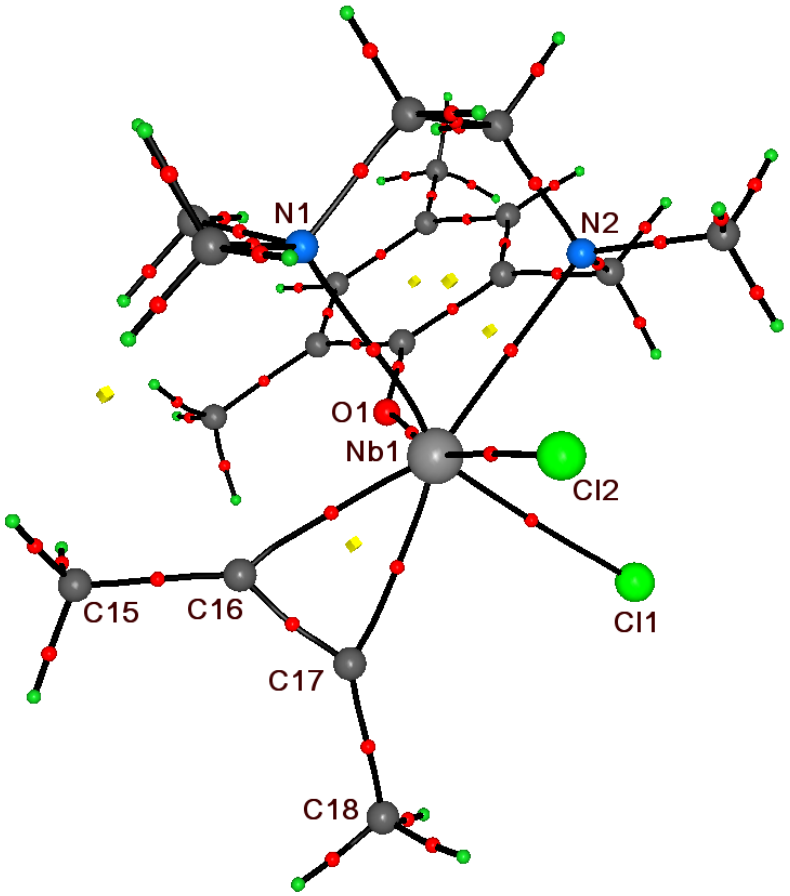


Figure SI5. Molecular graph for complex $Nb(C_{18}H_{29}N_2O)(H_3CC{\equiv}CCH_3)Cl_2$ (**3**) showing *bp*'s (black lines), *bcp*'s (small red dots) and *rcp*'s (small yellow cubes).



checkCIF/PLATON (full publication check) for complex 2

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found.
Please wait while processing ....

CIF dictionary
Interpreting this report

Datablock: I

Bond precision: C-C = 0.0005 A Wavelength=0.71069
Cell: a=7.2391(9) b=12.2780(9) c=18.3457(2)
alpha=90 beta=94.000(9) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1626.6(2)	1626.6(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H15 Mn O2	C21 H15 Mn O2
Sum formula	C21 H15 Mn O2	C21 H15 Mn O2
Mr	354.27	354.27
Dx,g cm-3	1.447	1.447
Z	4	4
Mu (mm-1)	0.820	0.820
F000	728.0	728.0
F000'	729.61	
h,k,lmax	16,27,40	15,27,40
Nref	18661	18739
Tmin,Tmax	0.670,0.751	0.642,0.804
Tmin'	0.657	

Correction method= ANALYTICAL
Data completeness= 1.004 Theta(max)= 52.120
R(reflections)= 0.0207(17418) wR2(reflections)= wR= 0.0138(17418)
S = 1.411 Npar= 715

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Mn1 -- C11 .. 16.4 su
PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Mn1 -- C15 .. 15.9 su
PLAT366_ALERT_2_B Short? C(sp?)-C(sp?) Bond C3 - C4 ... 1.27 Ang.

Alert level C

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low 0.978
PLAT230_ALERT_2_C Hirshfeld Test Diff for O2 -- C2 .. 5.7 su

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 15
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 -- C1 .. 11.9 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 -- C2 .. 13.1 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 -- C3 .. 12.8 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mn1 -- C4 .. 14.5 su

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PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Mn1    --  C12     ..       14.8 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Mn1    --  C13     ..       13.9 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Mn1    --  C14     ..       13.0 su
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found          !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......         60

   0 ALERT level A = Most likely a serious problem - resolve or explain
   3 ALERT level B = A potentially serious problem. consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  11 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error. inconsistent or missing data
  11 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement. methodology. query or suggestion
   2 ALERT type 5 Informative message. check
```

checkCIF publication errors

Alert level A

```
PUBL006_ALERT_1_A  _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
           Abstract of paper in English.
PUBL024_ALERT_1_A The number of authors is greater than 5.
             Please specify the role of each of the co-authors
             for your paper.
```

Alert level G

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PUBL013_ALERT_1_G The _publ_section_comment (discussion of study) is
           missing. This is required for a full paper submission (but is
           optional for an electronic paper).
PUBL017_ALERT_1_G The _publ_section_references section is missing or
           empty.

   5 ALERT level A = Data missing that is essential or data in wrong format
   2 ALERT level G = General alerts. Data that may be required is missing
```

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights. errors and omissions in your CIF or refinement strategy. so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However. the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters. but every test has its limitations and alerts that are not important in a particular case may appear. Conversely. the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and. if necessary. seek expert advice.

If level A alerts remain. which you believe to be justified deviations. and you intend to submit this CIF for publication in Acta Crystallographica Section C or Section E. you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. Your explanation will be considered as part of the review process.

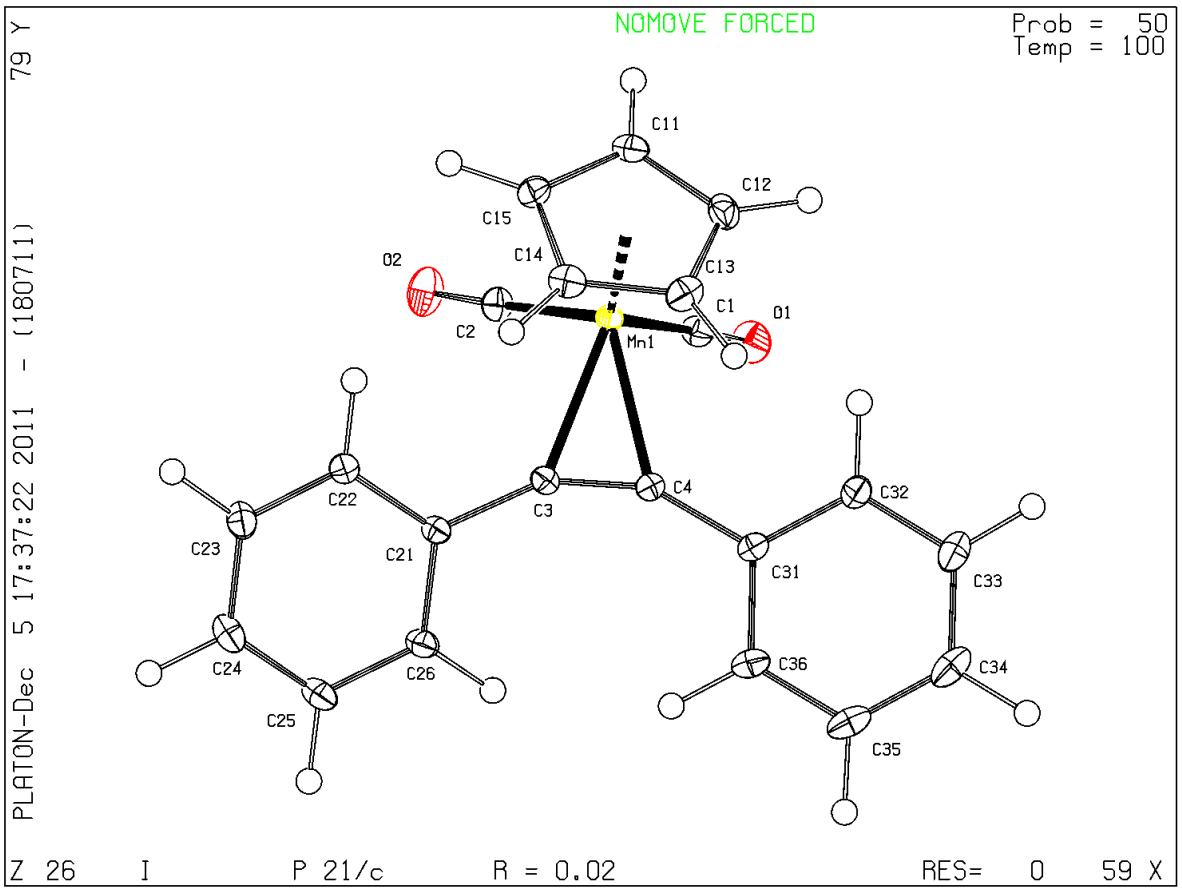
If you intend to submit to another section of Acta Crystallographica or Journal of Applied Crystallography or Journal of Synchrotron Radiation. you should make sure that at least a basic structural check is run on the final version of your CIF prior to submission.

```
# start Validation Reply Form
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
_vrf_PUBL024_GLOBAL
;
PROBLEM: The number of authors is greater than 5.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E. you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal. you will be asked. either during electronic submission or by the Co-editor handling your paper. to upload your CIF via our web site.

PLATON version of 18/07/2011; check.def file version of 04/07/2011

Datablock I - ellipsoid plot



[Download CIF editor (publCIF) from the IUCr]
[Download CIF editor (enCIFer) from the CCDC]
[Test a new CIF entry]

checkCIF/PLATON (standard) for complex 3

You have not supplied any structure factors. As a result the full set of tests cannot be run.
No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: I

Bond precision: C-C = 0.0009 A Wavelength=0.71073

Cell: a=8.491(2) b=13.154(3) c=18.406(4)
alpha=90 beta=99.54(3) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2027.4(8)	2027.4(8)
Space group	P 21/c	P 2(1)/c
Hall group	-P 2ybc	P 2(1)/c
Moiety formula	C18 H29 Cl2 N2 Nb O	C18 H29 Cl2 N2 Nb O
Sum formula	C18 H29 Cl2 N2 Nb O	C18 H29 Cl2 N2 Nb O
Mr	453.24	453.23
Dx,g cm-3	1.485	1.485
Z	4	4
Mu (mm-1)	0.865	0.865
F000	936.0	936.0
F000'	928.97	
h,k,lmax	16,26,36	16,26,36
Nref	16970	13338
Tmin,Tmax	0.911,0.941	0.887,0.957
Tmin'	0.878	

Correction method= NUMERICAL

Data completeness= 0.786 Theta(max)= 45.290

R(reflections)= 0.0158(11573) wR2(reflections)= wR= 0.0181(13338)

S = 0.391 Npar= 333

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

GOODF01_ALERT_2_A The least squares goodness of fit parameter lies outside the range 0.40 <> 6.00
Goodness of fit given = 0.391

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low 0.892

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as numerical

PLAT030_ALERT_1_C _diffrn_reflns_number .LE. _reflns_number_total ?
PLAT126_ALERT_1_C Error in or Uninterpretable Hall Symbol ..... P 2(1)/C
PLAT127_ALERT_1_C Implicit Hall Symbol Inconsistent with Explicit P 2(1)/c
PLAT162_ALERT_4_C Missing or Zero su (esd) on y-coordinate for ... NB1
PLAT163_ALERT_4_C Missing or Zero su (esd) on z-coordinate for ... NB1

PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.4 Ratio
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C16 - C17 ... 1.31 Ang.
PLAT391_ALERT_3_C Deviating Methyl C18 H-C-H Bond Angle ..... 118 Deg.
PLAT731_ALERT_1_C Bond Calc 2.4179(6), Rep 2.4179(2) ..... 3 su-Ra
NB1 -CL1 1.555 1.555 # 1
PLAT731_ALERT_1_C Bond Calc 2.4860(6), Rep 2.4860(2) ..... 3 su-Ra
NB1 -CL2 1.555 1.555 # 2
PLAT732_ALERT_1_C Angle Calc 82.45(3), Rep 82.46(1) ..... 3.00 su-Ra
CL1 -NB1 -N1 1.555 1.555 1.555 # 11
PLAT732_ALERT_1_C Angle Calc 92.05(3), Rep 92.05(1) ..... 3.00 su-Ra
CL2 -NB1 -O1 1.555 1.555 1.555 # 14
PLAT732_ALERT_1_C Angle Calc 156.27(3), Rep 156.27(1) ..... 3.00 su-Ra
CL2 -NB1 -N1 1.555 1.555 1.555 # 15
PLAT738_ALERT_1_C D-H..A Calc 129.4(7), Rep 129.4(3) ..... 2.33 su-Ra
C5 -H11 -CL2 1.555 1.555 1.555 # 109

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 29
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max datum .... ?
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min datum .... ?
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Nb1 -- Cl2 .. 18.3 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Nb1 -- N1 .. 6.5 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Nb1 -- N2 .. 8.0 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Nb1 -- C16 .. 6.5 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Nb1 -- C17 .. 7.0 su
PLAT793_ALERT_4_G The Model has Chirality at N2 (Verify) .... S
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found !
PLAT982_ALERT_1_G The Nb-f'= -2.061 Deviates from the IT-value -2.073
PLAT983_ALERT_1_G The Nb-f"= 0.634 Deviates from the IT-Value 0.622

2 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
15 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
14 **ALERT level G** = General information/check it is not something unexpected

15 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
7 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full

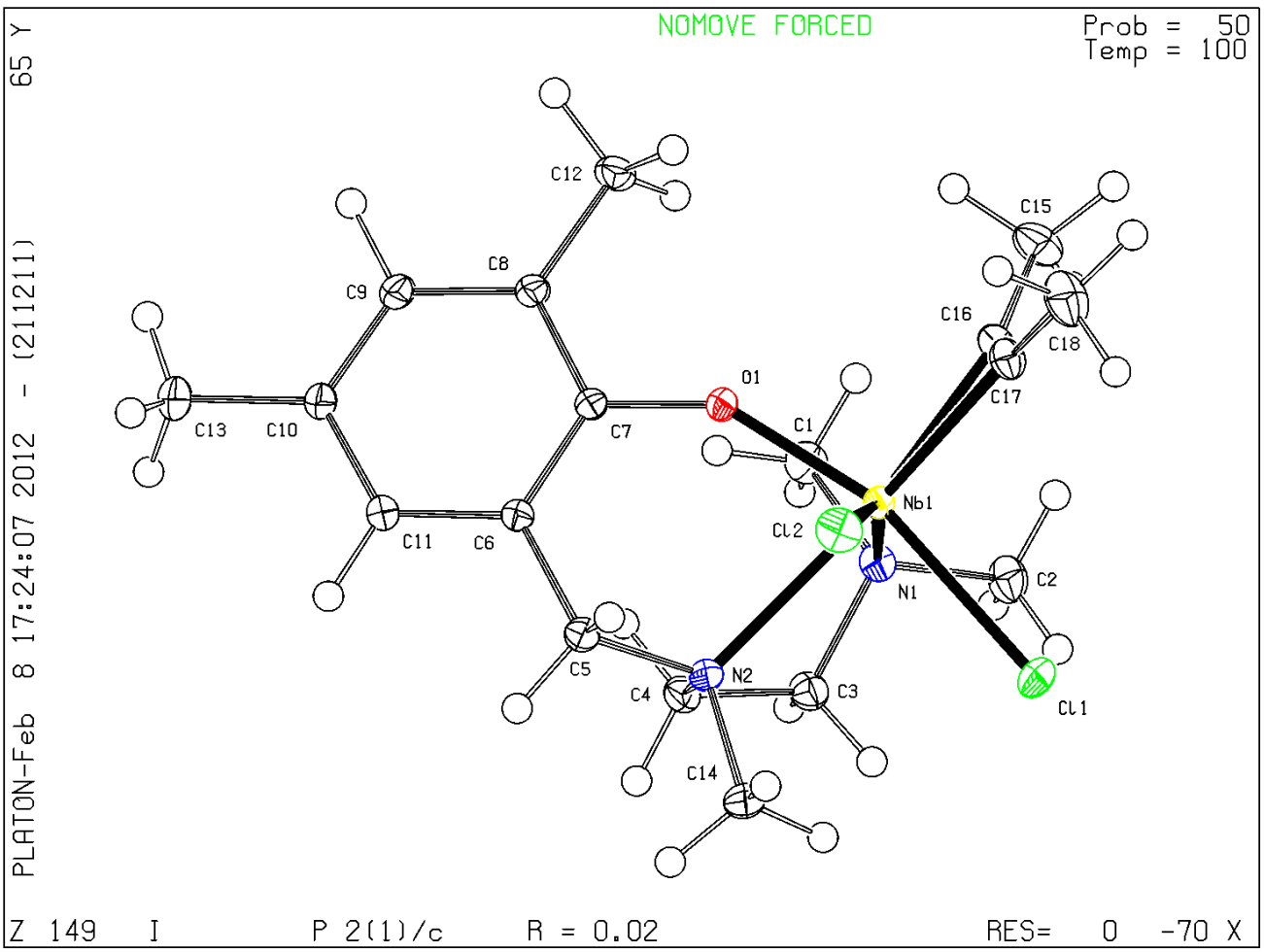
publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 21/12/2011; check.def file version of 16/12/2011

Datablock I - ellipsoid plot



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