Supporting information for:

Intermolecular π-hole / *n*→π* interactions with carbon monoxide ligands in crystal structures

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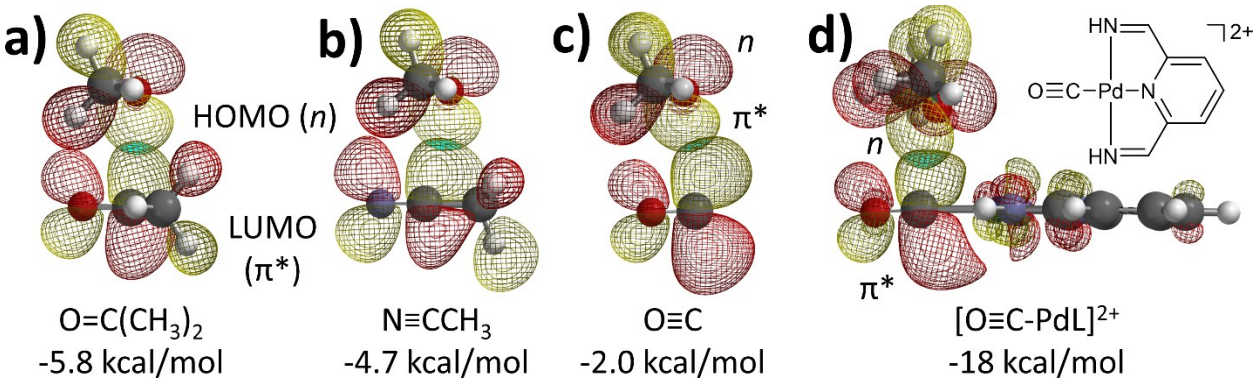


Figure S1. Ball and stick representations with selected (*n* / π*) orbitals of complexes with dimethyl ether (dme, always on top) and acetone (a), acetonitrile (b), carbon monoxide (c) and a carbon monoxide ligand in a Palladium-pyridine-2,6-diyldimethanimine complex. The areas highlighted in green indicate orbital overlap. In the Palladium complex (d) the *n* and π* orbitals are delocalized over both molecular fragments. Geometry optimizations and energy computations were performed at the DFT/B3LYP-D3/def2-TZVP level of theory.[‡] See for Cartesian coordinated Table S1 and see Figure 1 for an 'atoms in molecules analysis'. A fragment analysis with ADF at the B3LYP-D3/TZ2P level of theory (no frozen cores and scalar relativity) was also performed, revealing a pauli repulsion of: 6.87 (a), 4.95 (b), 2.43 (c) and 15.5 (d) kcal/mol; an electrostatic attraction of: -5.43 (a), -4.56 (b), -1.45 (c) and -17.1 (d) kcal/mol; orbital interactions of: -2.21 (a), -1.51 (b), -0.84 (c) and -11.0 (d) kcal/mol; and dispersion energies of: -4.94 (a), -3.40 (b), -1.90 (c) and -5.17 (d) kcal/mol.

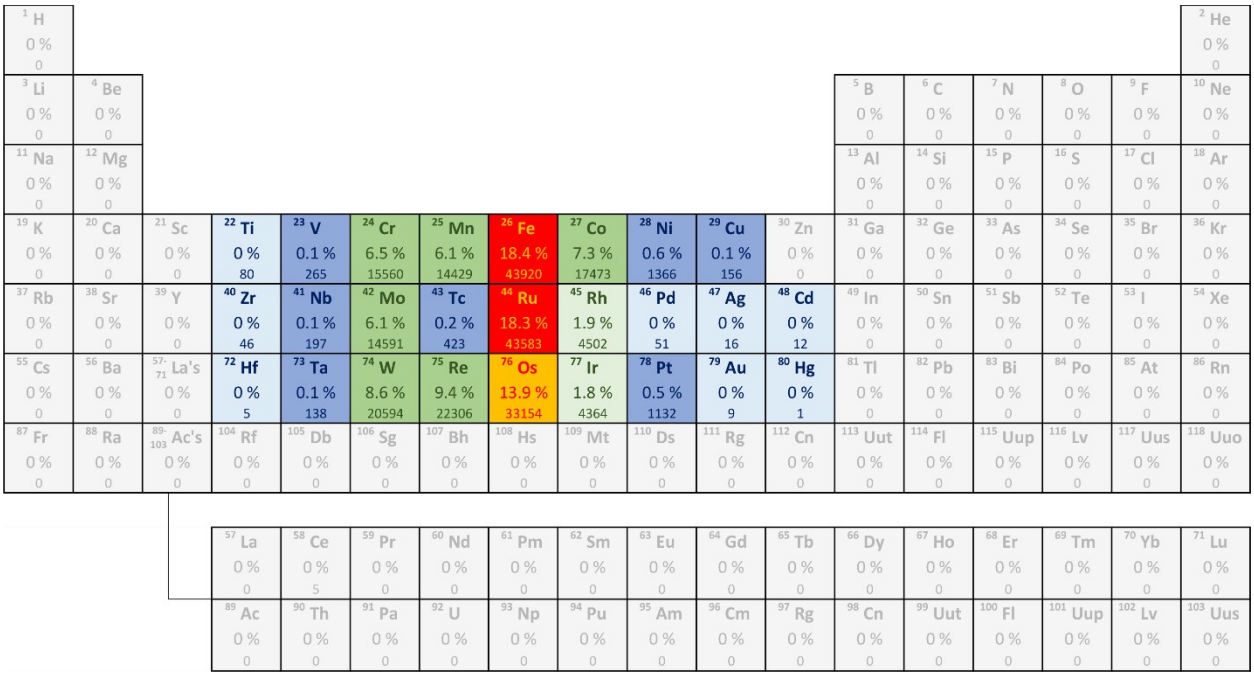


Figure S2. Schematic representation of the distribution of metals coordinated by a carbon monoxide ligand. The data represents 251,262 M---C≡O structures found within 48,019 CIFs (see also entry 1 in Table S1). The color code is meant as a guide to the eye, where red is the highest percentage of data, then green and light blue the lowest.

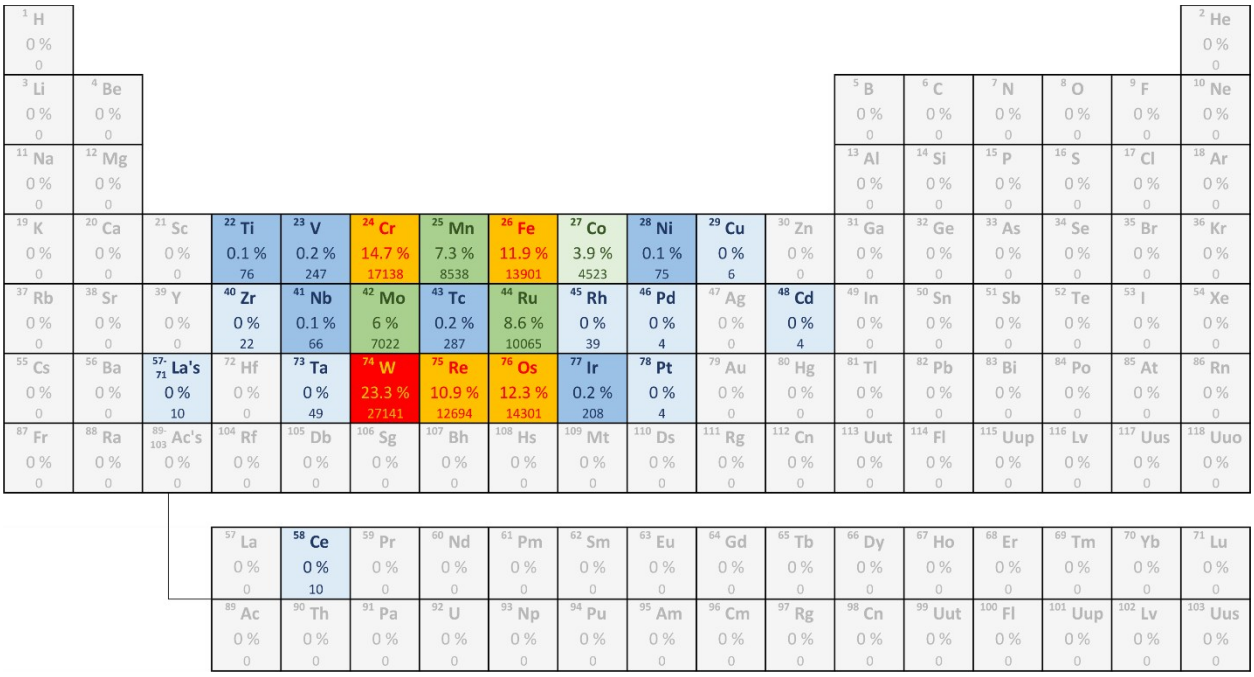
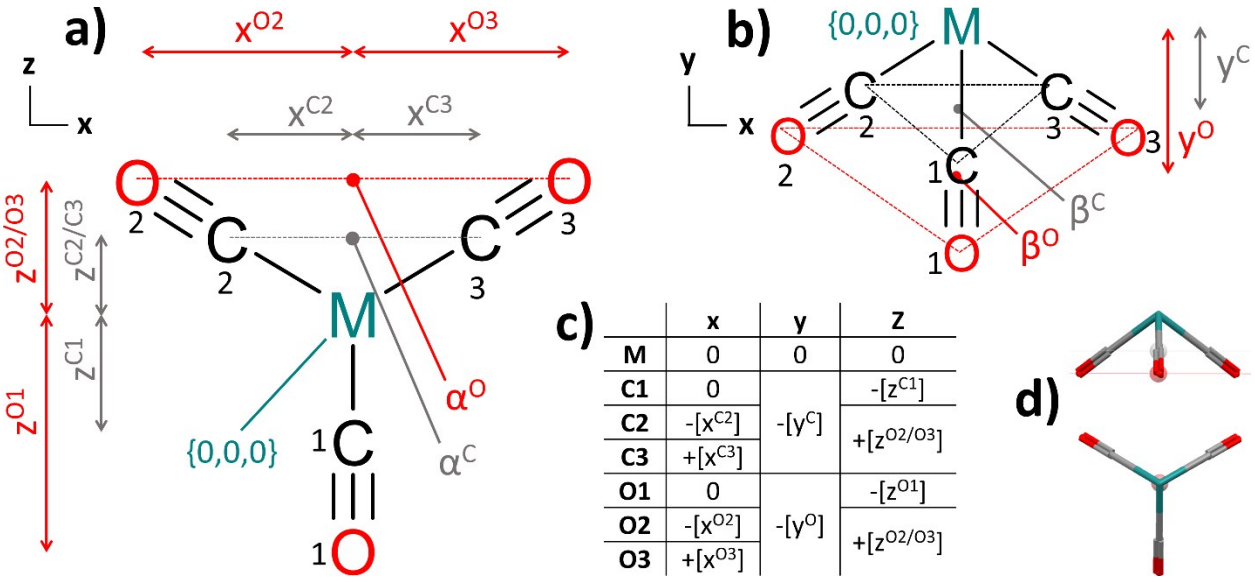


Figure S3. Schematic representation of the distribution of metals coordinated by a carbon monoxide ligand in $M(CO)_3$ structures (see also Figure Sx). The data represents 113,065 $M(C{\equiv}O)_3$ structures (45% of all M---C≡O structures) found within 28,597 CIFs (60% of all M---C≡O containing CIFs, see also entry 7 in Table S1). The color code is meant as a guide to the eye, where red is the highest percentage of data, then green and light blue the lowest.



	x	y	z
M	0	0	0
C1	0	-[y^C]	-[z^{C1}]
C2	-[x^{C2}]		+[$z^{O2/O3}$]
C3	+[x^{C3}]		
O1	0	-[y^O]	-[z^{O1}]
O2	-[x^{O2}]		+[$z^{O2/O3}$]
O3	+[x^{O3}]		

Figure S4. Schematic representation of the query used to construct the model of $M(CO)_3$ structures as viewed along the y-axis (a) and the z-axis (b). Using the measurement defined in (a) and (b), the cartesian coordinates of the model are represented in the table in (c) with the measured vales being as follows: $x^{C2} = x^{C3} = 1.374 \pm 0.074$ Å; $x^{O2} = x^{O3} = 2.194 \pm 0.120$ Å; $y^C = 1.021 \pm 0.172$ Å; $y^O = 1.651 \pm 0.266$ Å; $z^{C1} = 1.585 \pm 0.088$ Å; $z^{C2/C3} = 0.793 \pm 0.044$ Å; $z^{O2/O3} = 1.266 \pm 0.071$ Å; $z^{O1} = 2.532 \pm 0.143$ Å. The reconstructed model is shown in (d) along the z-axis (top) and y-axis (bottom). In the query, all C-M-C angles were constrained to ≤ 140° to exclude trans-coordinated CO ligands and M could be any metal (see also Figure 2). The measurements for the model were taken from 76,959 structures found within 27,305 CIFs.

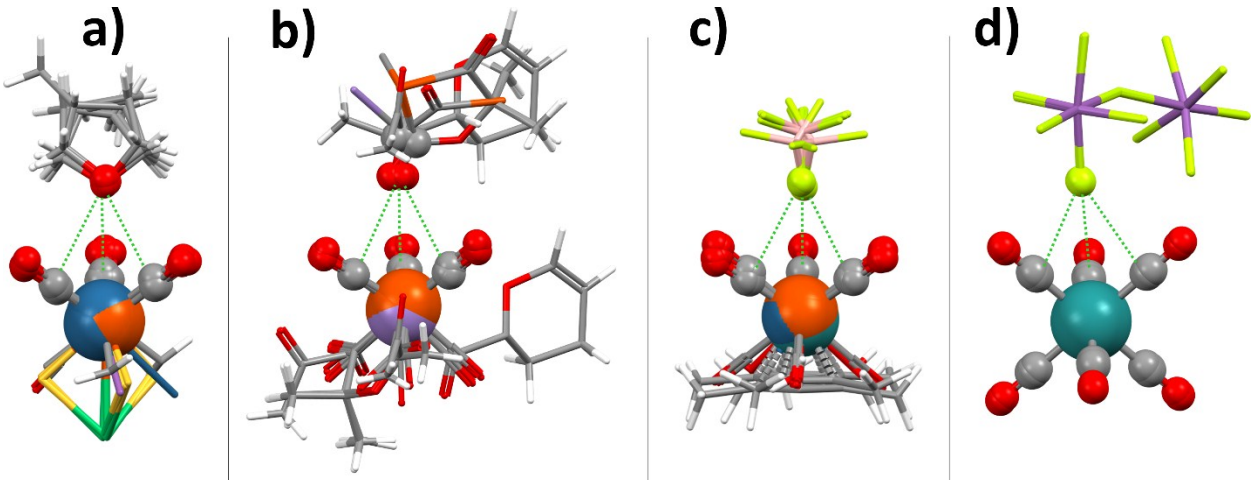


Figure S5. Perspective views with associated average distances of aligned structured involving $M(CO)_3$ fragments in close contact with sp^3 hybridized O-atoms (a), sp^2 hybridized O-atoms (b), BF_4^- anions (c) and $Sb_2F_{11}^-$ anions (d). Alignments were conducted in PyMOL using the pair fitting wizard. The structures used in (a) were MOPZUO, NOFRUW (3 distinct fragments) and VEWKED; in (b) were ACUZII, ACUZII01, HIDSIW, PYRMNC and QENCOC; in (c) were CEHHIH, CEHHON, CUWYOW, CUWYOW01 (two distinct fragments), DUSYIZ, GOZYOJ and VOTJAP; and in (d) were HOLMOK, LARPIE and LARPOK. The average van der Waals overlap in each cases is 0.085 Å (a); 0.162 Å (b); 0.199 Å (c); 0.285 Å (d). See Table S4 for single point energy computations.

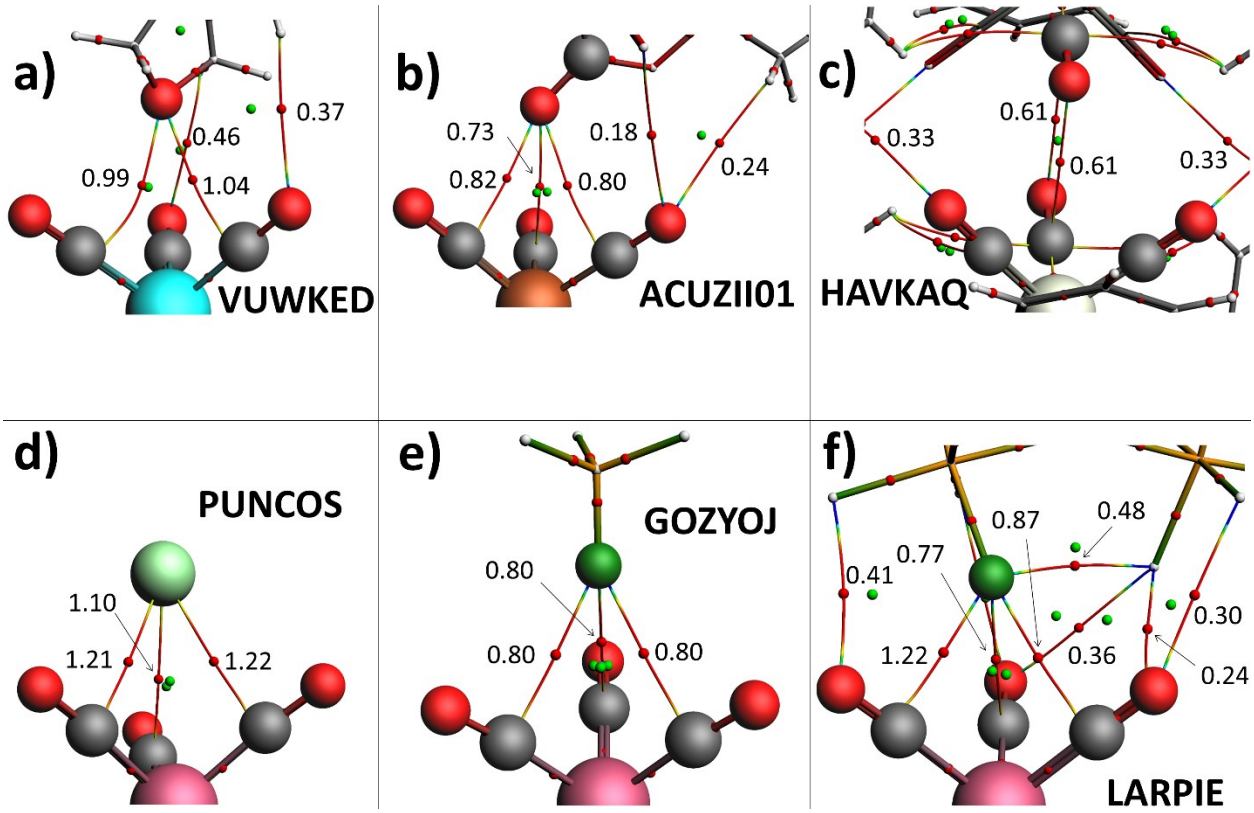


Figure S5. Perspective views of ball and stick representations with selected bond critical points (ρ in 10^{-2} x a.u., small red dots), ring critical points (small green dots) and bond paths (thin lines) of the complexes highlighted in Figure 4. Calculations were conducted with ADF at the B3LYP-D3/TZ2P level of theory (no frozen cores and scalar relativity), except for HAVKAQ (c), which was computed at the GGA:BP-D3(BK)/DZ level of theory due to the large cluster involved. **NB:** Note that in all cases the most dense bond critical points involve a C-atom of a CO ligand and the interacting electron rich atom (O, Cl, or F).

Table S1. Cartesian coordinates of the geometry optimized structures shown in Figure 1. Computations were done with the density functional theorem at the B3LYP-D3/def2-TZVP level of theory. For references purposes, a methane dimer was computed with ΔE = – 0.570 kcal/mol (not shown).

$[O{=}C(CH_3)_2\cdots O(CH_3)_2]$ (Figure 1a)
ΔE = –5.830 kcal/mol

	X	Y	Z
C	-0.2448	-1.1768	-1.7583
C	-0.2463	1.1735	-1.7587
C	0.4042	-1.2810	1.6416
C	-0.3670	0.0023	1.4326
C	0.4064	1.2837	1.6457
H	0.7970	-1.3242	2.6608
H	-0.4346	-1.2189	-2.8389
H	-1.2004	-1.2368	-1.2239
H	0.3769	-2.0263	-1.4772
H	0.3736	2.0238	-1.4763
H	-1.2027	1.2317	-1.2257
H	-0.4345	1.2159	-2.8396
H	-0.2382	-2.1393	1.4584
H	1.2575	-1.3009	0.9609
H	-0.2369	2.1440	1.4751
H	1.2536	1.3083	0.9576
H	0.8084	1.3183	2.6616
O	-1.5348	0.0038	1.1128
O	0.4625	-0.0011	-1.4088

$[N{\equiv}CCH_3\cdots O(CH_3)_2]$ (Figure 1b)
ΔE = –4.701 kcal/mol

	X	Y	Z
C	-1.0680	0.0026	2.0131
C	0.3473	-1.1767	-1.3083
C	0.3843	0.0002	1.9457
C	0.3442	1.1742	-1.3057
H	0.5973	1.2349	-2.3725
H	1.2683	1.2200	-0.7175
H	-0.2830	-2.0279	-1.0505
H	1.2713	-1.2214	-0.7199
H	0.6008	-1.2345	-2.3752
H	-1.4624	-0.8748	1.5022
H	-1.4596	0.8858	1.5102
H	-1.3969	-0.0012	3.0528
H	-0.2882	2.0231	-1.0459
N	1.5327	-0.0018	1.8898
O	-0.3881	-0.0025	-1.0182

$[LPd{-}C(O)\cdots O(CH_3)_2]^{2+}$
ΔE = –17.69 kcal/mol

C	1.7217	-1.0592	2.8471
C	1.3213	1.2223	3.3824
C	-1.5191	-0.1063	2.3447
C	-0.5269	1.1594	-2.1158
C	-0.7390	2.2727	-1.1771
C	-0.5187	-1.2010	-2.1537
C	-0.7242	-2.3451	-1.2531
C	-0.2395	1.2123	-3.4764
C	-0.2315	-1.2124	-3.5148
C	-0.0936	0.0110	-4.1718
H	1.4188	-1.4030	3.8408
H	2.8034	-0.9028	2.8368
H	1.4667	-1.8156	2.1052
H	1.0127	0.9786	4.4032
H	0.7664	2.0933	3.0353
H	2.3894	1.4535	3.3751
H	-1.1642	2.7414	0.6815
H	-1.1463	-2.8789	0.5893
H	-0.6661	3.3055	-1.5091
H	-0.6515	-3.3661	-1.6203
H	-0.1344	2.1632	-3.9820
H	-0.1213	-2.1476	-4.0485
H	0.1265	0.0279	-5.2316
N	-1.0160	1.9673	0.0381
N	-0.9973	-2.0826	-0.0265
N	-0.6543	-0.0311	-1.5138
O	-1.8470	-0.1333	3.4148
O	1.0354	0.1429	2.4856
Pd	-1.0714	-0.0662	0.4144

$[O{\equiv}C\cdots O(CH_3)_2]$ (Figure 1c)
ΔE = –2.042 kcal/mol

	X	Y	Z
C	-2.6772	0.0606	-0.8452
C	0.6423	-1.1356	0.0101
C	0.5229	1.2126	0.0506
H	-0.0676	-1.2503	0.8400
H	1.6613	-1.1414	0.4197
H	0.5291	-1.9772	-0.6723
H	-0.1666	1.2087	0.9057
H	0.2864	2.0593	-0.5926
H	1.5468	1.3262	0.4313
O	-2.6656	-0.4047	0.1802
O	0.3882	0.0418	-0.7274

$[O{\equiv}C\cdots O(CH_3)_2]$ in THF (implicit)
ΔE = –1.610 kcal/mol

C	-0.3543	-0.0013	-2.7689
C	-0.0863	-1.1785	0.5812
C	-0.0861	1.1774	0.5790
H	0.1257	-1.2311	1.6565
H	0.8644	-1.2252	0.0355
H	-0.7043	-2.0290	0.2954
H	0.1268	1.2314	1.6540
H	-0.7043	2.0275	0.2924
H	0.8642	1.2232	0.0324
O	0.7606	0.0063	-2.6151
O	-0.8066	-0.0008	0.2577

Table S2. Numerical breakdown of a topological analysis of the metal bound carbon monoxide ligands present in the CSD. As is evident from entries 1-5, virtually all carbon monoxide ligands in the CSD are η^1-coordinated. Moreover, the majority of data involved metals with multiple CO ligands (entries 6-11). In about 60 % of all CIFs, three or more CO ligands are present (i.e. 28,597, see entry 7). Relatively few structures contain CO as the sole ligand, as is indicated in entries 12-16. As is detailed in entries 17-31, there is a large variety in the amount of atoms that are bound to metal in M-CO structures with t=2 up to t=14. These large t-values are a result of ligands that bind in a polytypic fashion such as η^2-acetylene (Ac), η^2-ethylene (Et), η^5-cyclopentadienyl (Cp) and η^6-benzene (Bn). A specification of structures and geometries that contain only monotopic (η^1) ligands is listed in entries 32-39. Octahedral structures are by far the most abundant (15,312 CIFs, entry 39) far the most abundant geometry, followed by trigonal bipyramidal (1,822 CIFs, entry 38) and square planar complexes (1,689 CIFs, entry 35). The geometries with the multitopic ligands Ac, Et, Cp, and Bn were analyzed separately, considering structures of the type ML_4 (entries 40-43), ML_5 (entries 44-47) and ML_6 (entries 48-51). Finally, the geometries of $L_nM\cdots(C\equiv O)_3$ complexes was analyzed (entries 52-62), revealing that octahedral (11,264 CIFs, entry 58) and pianostool-like complexes (2,913 CIFs, entries 61 and 62) constitute most of the data.

Entry	Query[a]	CIFs
	Hapticity of CO ligands:	
1	M···C≡O (η^1)	48,019
2	M_2···C≡O (η^2)	9
3	M_3···C≡O (η^3)	3
4	M_4···C≡O (η^4)	0
5	M_5···C≡O (η^5)	0
	Number of CO ligands bound to the same metal:	
6	$L_nM\cdots(C\equiv O)_2$	39,389 (10,792)[b]
7	$L_nM\cdots(C\equiv O)_3$	28,597 (18,979)[b]
8	$L_nM\cdots(C\equiv O)_4$	9,618 (5,709)[b]
9	$L_nM\cdots(C\equiv O)_5$	3,909 (3,861)[b]
10	$L_nM\cdots(C\equiv O)_6$	48 (48)[b]
11	$L_nM\cdots(C\equiv O)_7$	0
	Structures where CO is the only ligand	
12	M···$(C\equiv O)_2$	2
13	M···$(C\equiv O)_3$	0
14	M···$(C\equiv O)_4$	100
15	M···$(C\equiv O)_5$	37
16	M···$(C\equiv O)_6$	42
	Number of atoms bonded to M in M···C≡O (t)	
17	t = 1	0
18	t = 2	8
19	t = 3	36
20	t = 4	2,355
21	t = 5	2,570
22	t = 6	25,145
23	t = 7	10,296
24	t = 8	10,014
25	t = 9	6,426
26	t = 10	2,023
27	t = 11	440
28	t = 12	141
29	t = 13	22
30	t = 14	3
31	t = 15	0

Entry	Query[a]	CIFs
	Geometry of $L_nM\cdots C\equiv O$ complexes	
32	n = 2[c]	8
33	n = 3[c]	36
34	n = 4[tetrahedral, d]	344
35	n = 4[square planar, e]	1,689
36	n = 5[planar pentagonal, f]	175
37	n = 5[square pyramidal, g]	541
38	n = 5[trigonal bipyramidal, h]	1,822
39	n = 6[octahedral, i]	15,312
	Geometry of $PL_nM\cdots C\equiv O$ complexes (P = π-donor ligand)[j]	
40	n = 2, P = Ac (ML_4)	24
41	n = 2, P = Et "	24
42	n = 2, P = Cp[k] "	4,351
43	n = 2, P = Bn[k] "	1,532
44	n = 3, P = Ac[l] (ML_5)	764
45	n = 3, P = Et[l] "	280
46	n = 3, P = Cp[k] "	3,193
47	n = 3, P = Bn[k] "	68
48	n = 4, P = Ac[m] (ML_6)	473
49	n = 4, P = Et[m] "	1,682
50	n = 4, P = Cp[k,n] "	1,513
51	n = 4, P = Bn[k,n] "	11
	Geometry of $L_nM\cdots(C\equiv O)_3$ complexes[o]	
52	$L_nM\cdots(C\equiv O)_3$ (= entry 7)	28,597
53	$LM\cdots(C\equiv O)_3$[tetrahedral, d]	183
54	$LM\cdots(C\equiv O)_3$[squarse planar, e]	4
55	$L_2M\cdots(C\equiv O)_3$[planar pentagonal, f]	0
56	$L_2M\cdots(C\equiv O)_3$[square pyramidal, g]	21
57	$L_2M\cdots(C\equiv O)_3$[trigonal bipyramidal, h]	938
58	$L_3M\cdots(C\equiv O)_3$[octahedral]	11,264
59	$AcM\cdots(C\equiv O)_3$	949
60	$EtM\cdots(C\equiv O)_3$	1,735
61	$CpM\cdots(C\equiv O)_3$	1,549
62	$BnM\cdots(C\equiv O)_3$	1,364

[a] O is always bound to only one atom, the CO ligand is η^1 coordinated unless otherwise specified and L stands for any other monoatomic ligand; [b] Amount of CIFs found with the structure indicated in the entry, minus the amount of CIFs of structure with one additional CO ligand (two rows down); [c] exact geometry not specified; [d] all L–M–L angles were constrained to 109,5 ± 9°; [e] two trans L–M–L angles were constrained to 160-180°; [f] All L–$[ML_5]^{plane}$ distances were confined to 0 ± 1 Å; [g] the trans L–M–L angles of equatorial ligands were constrained to 160-180° and one L–M–L angle with the axial ligand was confined to 20 - 160°. A CO ligands is axial in 71 CIFs and equatorial in 470 CIFs; [h] the trans L–M–L angle of axial ligands was constrained to 160-180° and the three L–M–L angles with the equatorial ligands was confined to 120 ± 10°. A CO ligands is axial in 771 CIFs and equatorial in 1051 CIFs; [i] the three trans L–M–L angles were constrained to 160-180°; [j] the number of atoms bonded to M was set under the assumption that all atoms of π-ligand were bound. The π-ligand considered where (substituted) acetylene (Ac, 1,697 CIFs), ethylene (Et, 3,394 CIFs), cyclopentadienyl (Cp, 9,507 CIFs) and benzene (Bn, 1,639 CIFs) (allyl = 1522 cifs). There were 159 CIFs where n = 0 or 1; [k] piano-stool complexes; [l] tetrahedral and square planar complexes (nearly all cis); [m] octahedral complexes, polymetallic clusters and complexes with an allyl ligand; [n] mostly polymetallic clusters and complexes with an allyl ligand; [o] There are also 415 CIFs with an allyl ligand, making a total of 18,422 CIFs found with the indicated geometry. The remaining 10,175 CIFs likely involve clusters;

Table S3. Numerical overview of the nature of the possibly interacting electron rich atom (ElR) found in the database for the analysis with M-CO and $M(CO)_3$ structures (see also Figure 3).

	M–C(O)···ElR		M–$(CO)_3$ ···ElR	
ElR	***N***	**%**	***N***	**%**
N	35,737	4.9	7,962	2.8
O	599,381	83	252,753	88
F	37,752	5.2	12,574	4.4
P	5,217	0.7	903	0.3
S	14,697	2.0	3,770	1.3
Cl	24,713	3.4	6,874	2.4
As	480	0.1	131	0.1
Se	1,670	0.2	309	0.1
Br	3,250	0.5	968	0.3
Te	916	0.1	154	0.1
I	1,974	0.3	423	0.2
At	0	0	0	0.0
Total	725,787	100	286,821	100

Table S4. Energies in kcal/mol of the complexes highlighted in Figure 4 and Figure S5 computed with DFT at the B3LYP-D3/def2-TZVP level of theory (ΔE^1). At this level of theory the methane and water dimers have an energy of respectively – 0.57 and –6.32 kcal/mol (coordinates not given). For the structures highlighted in Figure 4 an additional fragment analysis was conducted with ADF giving ΔE^2.

CSD entry	With	$\Delta E^{1,a}$	$\Delta E^{2,b}$	PR[c]	EA[c]	OI[c]	DS[c]
HAVKAQ	sp O-atom	-20.76[d]	-38.96[e]	10.23	-20.6	-8.92	-19.67
ACUZII	sp^2 O-atom	-8.80					
ACUZII01	sp^2 O-atom	-8.49	-8.39	7.47	-7.45	-2.56	-5.85
HIDSIW	sp^2 O-atom	-8.23					
PYRMNC	sp^2 O-atom	-7.92					
QENCOC	sp^2 O-atom	-7.41					
MOPZUO	sp^3 O-atom	-11.17[d]					
NOFRUW	sp^3 O-atom	-10.42[d]					
VUWKED	sp^3 O-atom	-9.05	-8.18	10.84	-8.12	-2.63	-8.27
PUNCOS	Cl^-	-88.20	-84.35	21.42	-81.55	-20.24	-3.98
CEHHIH	BF_4^-	-154.98					
CEHHON	BF_4^-	-155.67					
CUWYOI01	BF_4^-	-55.91[f]					
CUWYOI01	BF_4^-	-56.10[g]					
DUSYIZ	BF_4^-	-63.39					
GOZYOJ	BF_4^-	-139.70	-138.54	6.02	-131.4	-10.08	-3.08
VOTJAP	BF_4^-	-64.10					
HOLMOK	SbF_6^-	-135.07					
LARPIE	SbF_6^-	-134.71	-133.16	9.63	-121.74	-13.99	-7.06
LARPOK	SbF_6^-	-134.48					

[a] ΔE^1 was computed by single point energy computation of the geometries lifted from the CSD of the complex minus those of the complex without anion and the anion. [b] ΔE^2 was obtained by a similar single point calculation with ADF at the B3LYP-D3/TZ2P level of theory (no frozen cores and scalar relativity); [c] Results of an ADF fragment analysis with the total bonding energy (ΔE^2) split up into the Pauli repultion (PR), electrostatic attraction (EA), orbital interactions (OI) and dispersion (DS). [d] Energy computed at B3LYP-D3/6-31G* level of theory due to the large cluster involved. [e] Energies computed at GGA:BP-D3(BK)/DZ level of theory due to the large cluster involved. [f] In the complex concerned the three CO ligands are staggered with respect to the CP*'s methyl groups. [g] In the complex concerned the three CO ligands are eclipsed with respect to the CP*'s methyl groups.