Supplementary Material (ESI) for Chemical Communications
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Supporting Information for:

Structurally Insights into Transition Metal Carbonyl Bonding

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1. Search Criteria and Data Retrieval

All reported unique TM-carbonyl bonds from crystal structures with R-factors <7.5% were catalogued according to metal and the TM-C and C≡O bond-lengths placed in arrays using CSD software.[1] Where sufficient data existed, subsets with different coordination numbers, oxidation states, and *trans*-ligands were analysed.

To identify the trends, data sets were divided into subsets with different TM-C bond lengths using increments of ~0.01 Å. For each of these increments the C≡O bond lengths were averaged and the confidence interval (CI) on the mean calculated using the formula $CI = \alpha\sigma N^{-1/2}$, for a 95% confidence interval $\alpha = 1.96$, σ represents the standard deviation, and N is the number of observations.[2,3] As a dataset gets larger you are more certain of its mean, as the standard deviation or dataset variation is larger you are less certain of the mean. This formula represents this quantitatively with respect to the assumption of a normal distribution and is detailed in many statistical text-books.[3,4]

a. Separation of Oxidation States

Oxidation states were separated manually on the basis of authors reports.

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b. Separation of *trans*-ligands

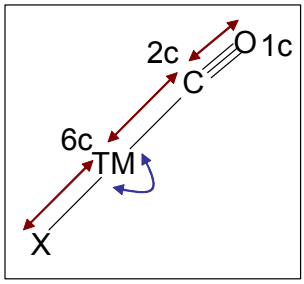

Figure S.1. Search criteria used to identify *trans*-ligands.

All observations containing a carbonyl group and the *trans*-ligand of interest were recorded, as was the angle between the two groups. The structures were designated "trans" or "cis" when this angle was 150-180° or 90-100° respectively those structures with angles in the range 100-150° were excluded, due to the ambiguity of the classification.

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2. Scatter plots for Osmium

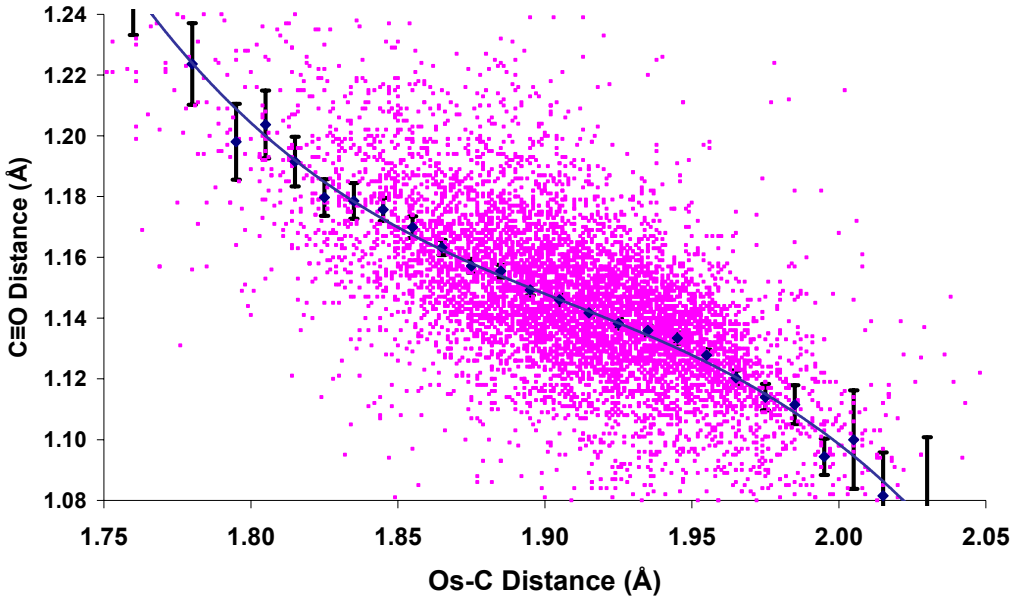

Figure S.2. Plot of C≡O bond-length vs. Os-C bond-length (Å). Error bars represent 95% confidence interval on the mean over the range the data-point is given for.

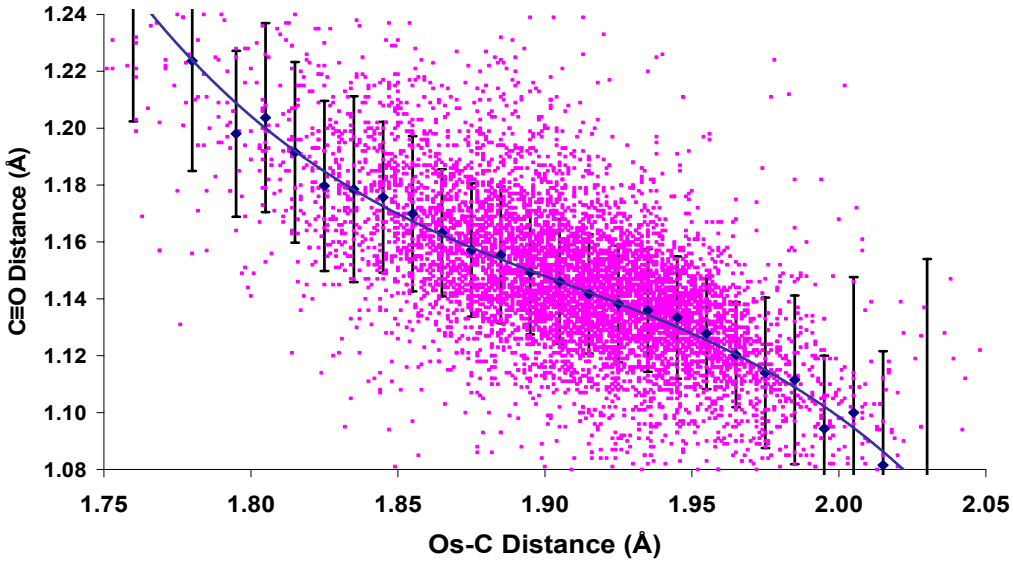

Figure S.3. Plot of C≡O bond-length vs. Os-C bond-length (Å), error bars represent 1 standard deviation.

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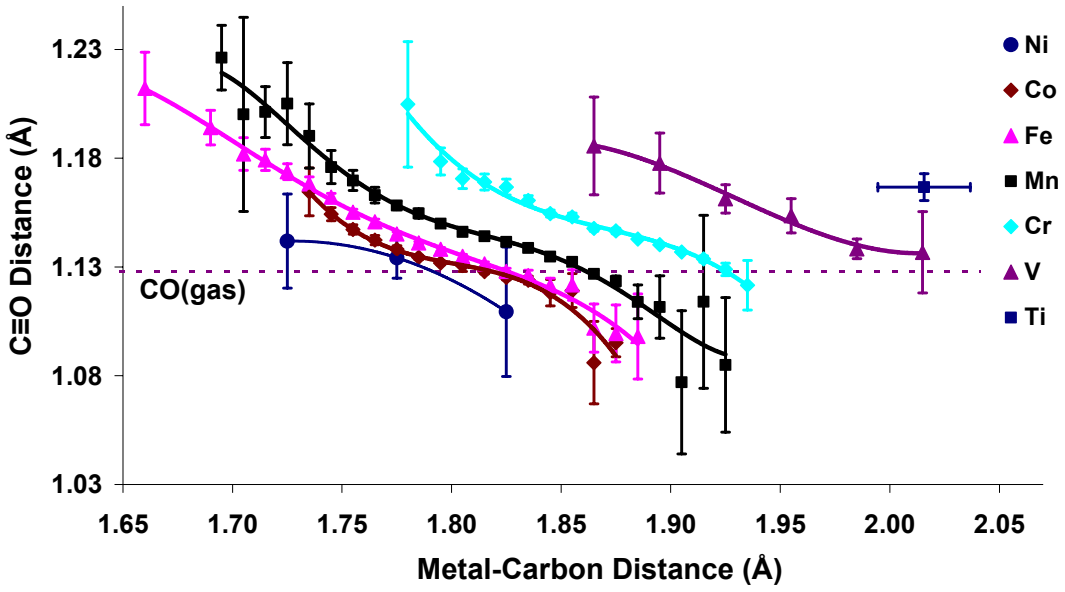
3. **Plot of M-C Distance vs C≡O Distance not included in paper and colour figures.**



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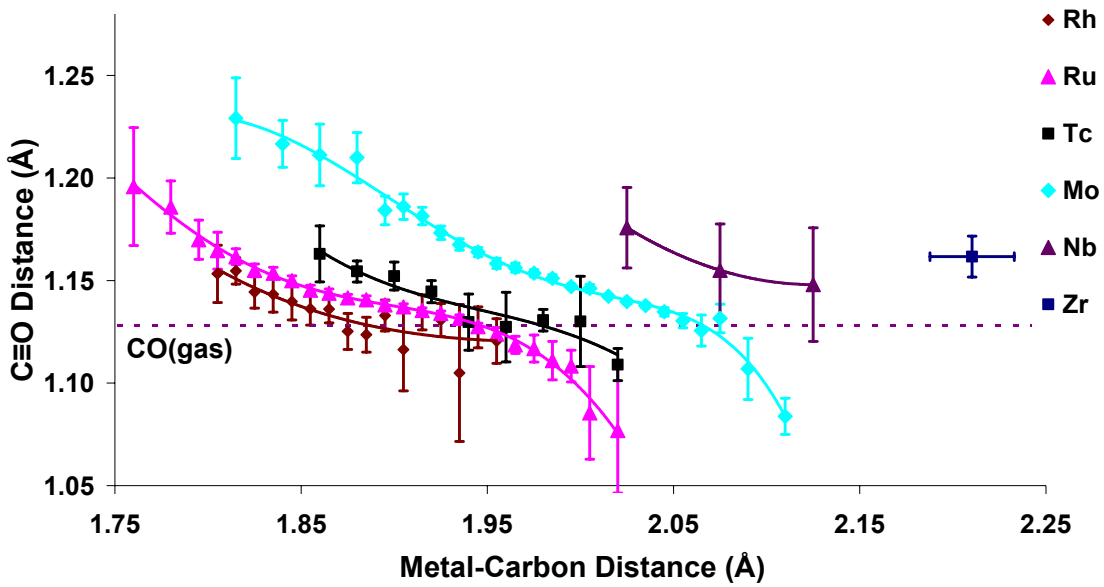

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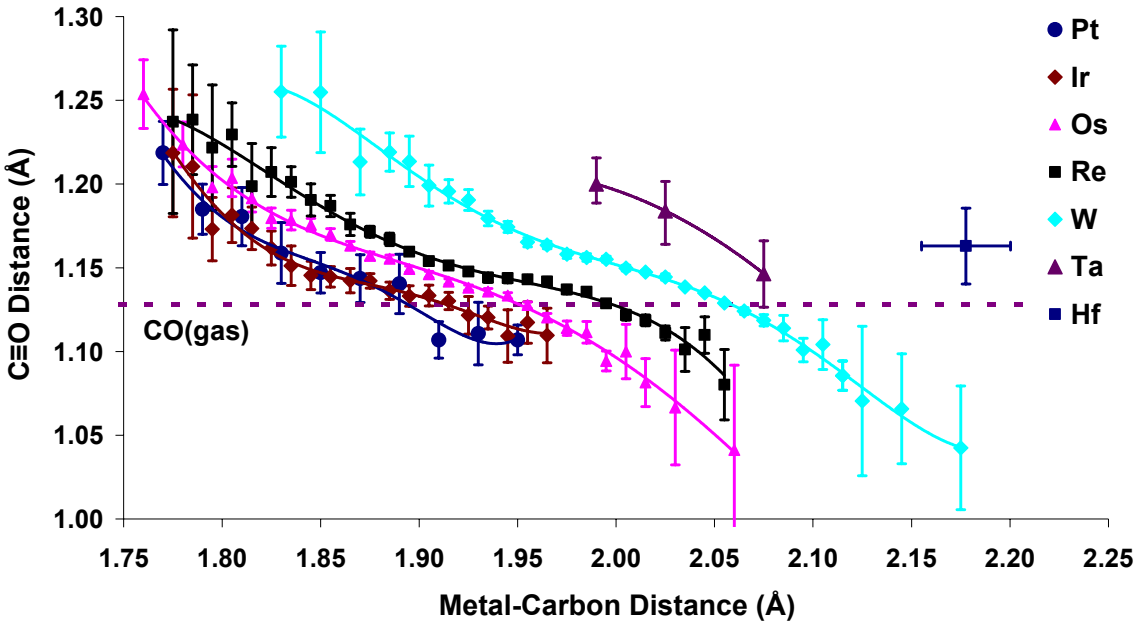

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8.1.1.1. The periodic trends down the groups for groups 6, 7, 8 and 9.

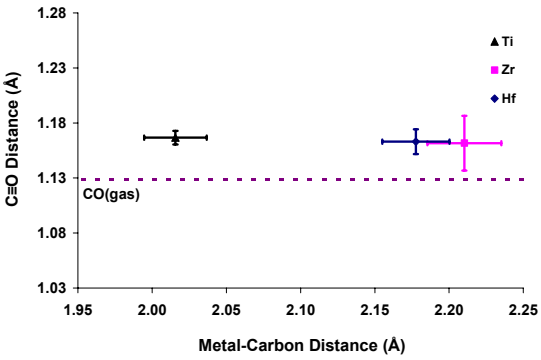

Figure S.7. Group 4 Triad

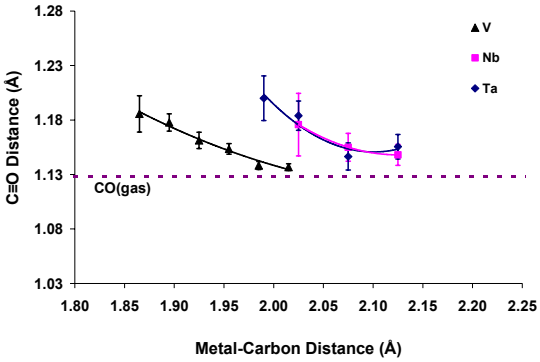

Figure S.8. Group 5 Triad

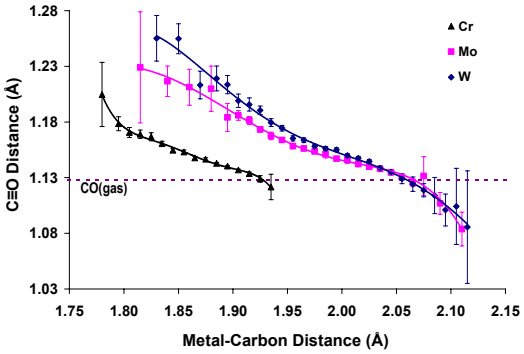

Figure S.9. Group 6 Triad

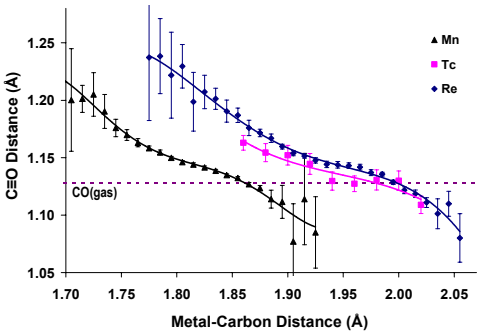

Figure S.10. Group 7 Triad

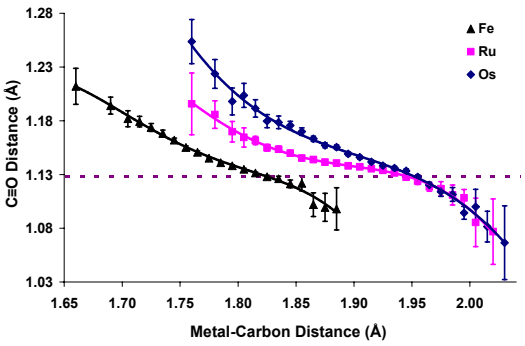

Figure S.11. Row 8 Triad

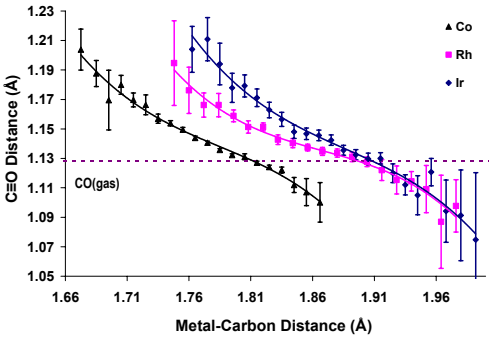

Figure S.12. Row 9 Triad

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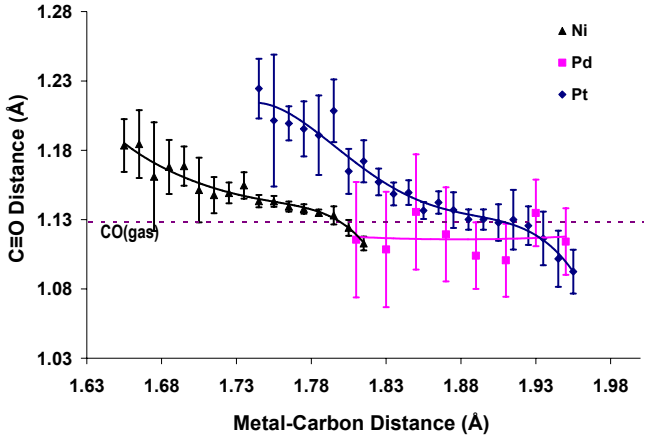

Figure S.13. Row 9 Triad

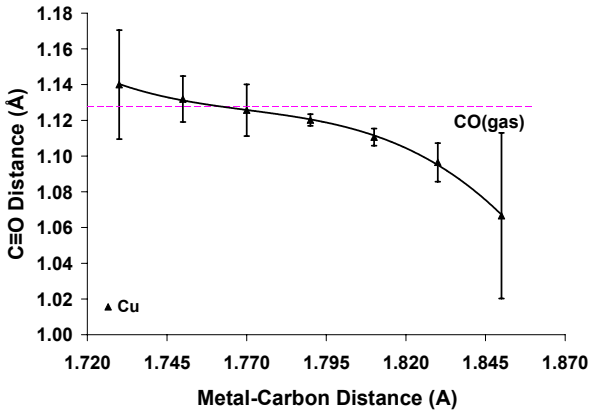

Figure S.14. Row 10,
Copper there is no data for Au or Ag

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Table S.1. Quantification of the gradient in Regions 1, 2 and 3, for different TM Centres, the gradient of the plot is solved for the given bond length.

Element	**Region I** (Very Short TM-C distances, max)		**Region II** (Typical TM-C distances, min)		**Region III** (Very Long TM-C distances, max)	
	Bond Length	**Gradient**	**Bond Length**	**Gradient**	**Bond Length**	**Gradient**
Ti	*Insufficient data*					
V	**1.900**	**-0.411**	**2.00**	**-0.136**	*N/A*	*N/A*
Cr	**1.801**	**-1.728**	**1.824**	**-1.319**	**1.920**	**-1.644**
Mn	**1.700**	**-1.074**	**1.826**	**-0.3619**	**1.900**	**-0.668**
Fe	**1.691**	**-0.5375**	**1.810**	**-0.221**	**1.872**	**-0.527**
Co	**1.730**	**-1.178**	**1.800**	**-0.0019**	**1.860**	**-0.719**
Ni	*Insufficient data*					
Zr	*Insufficient data*					
Nb	*Insufficient data*					
Mo	**1.860**	**-0.4167**	**2.00**	**-0.080**	**2.08**	**-0.628**
Tc	*N/A*	*N/A*	**1.950**	**-0.216**	*N/A*	*N/A*
Ru	**2.00**	**-0.932**	**1.90**	**-0.1615**	**1.80**	**-0.5795**
Rh	**1.790**	**-1.16082**	**1.92**	**-0.09982**	*N/A*	*N/A*
Hf	*Insufficient data*					
Ta	*Insufficient data*					
W	**1.870**	**-0.889**	**2.00**	**-0.377**	**2.10**	**-0.808**
Re	**1.850**	**-0.670**	**1.956**	**-0.220**	**2.04**	**-0.884**
Os	**1.821**	**-0.678**	**1.891**	**-0.365**	**2.00**	**-0.779**
Ir	**1.823**	**-0.797**	**1.874**	**-0.345**	*N/A*	*N/A*
Pt	*N/A*	*N/A*	**1.850**	**-0.546**	*N/A*	*N/A*

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4. Dataset Statistics and Examples

Table S.2 Table Detailing Data-Set Composition

Metal	**Total No. of 6c Structures R<7.5%**	**No of crystallographically independent M-C bonds.**	**No. of M-M bonds and (%)**	**No of complexes in oxidation state other than 0 or 1.**
Ti	*4*	*5*	*0(0.0%)*	*(-2) 2* *(-1) 1*
Zr	*1*	*3*	*0(0.0%)*	*(-2) 1*
Hf	*1*	*3*	*0(0.0%)*	*(-2) 1*
V	*22*	*60*	*0(0.0%)*	*(-1) 2*
Nb	*7*	*9*	*0(0.0%)*	*(-1) 1*
Ta	*12*	*13*	*0(0.0%)*	*(-1) 2*
Cr	*848*	*2,798*	*93(10.9%)*	*Mostly 0 and 1*
Mo	*755*	*3,240*	*29(3.8%)*	*Mostly 0 and 1*
W	*1206*	*6,206*	*75(6.2%)*	*Mostly 0 and 1*
Mn	*723*	*3,426*	*185(25.5%)*	*Mostly 0 and 1*
Tc	*31*	*118*	*1(3.2%)*	*Mostly 0 and 1*
Re	*993*	*4,838*	*164(16.5%)*	*Mostly 0 and 1*
Fe	*1956*	*9,231*	*1566(80.0%)*	*[+2/+3] 189 (2.0%)* *Mostly 0 and 1*
Ru	*1643*	*6,196*	*1112(67.7%)*	*[+2/+3] 358 (5.8%)* *Mostly 0 and 1*
Os	*1412*	*6,552*	*1223(86.6%)*	*[+2/+3] 118(1.8 %)* *Mostly 0 and 1*
Co	1011	3,329	979 (96.8%)	*Mostly 0 and 1*
Rh	145	244	116 (80.0%)	*Mostly 0 and 1*
Ir	373	857	196 (52.5%)	*Mostly 0 and 1*
Ni	23	175	21 (91.3%)	0
Pd	2	Not derived	2(100%)	0
Pt	60	73	60 (100%)	0

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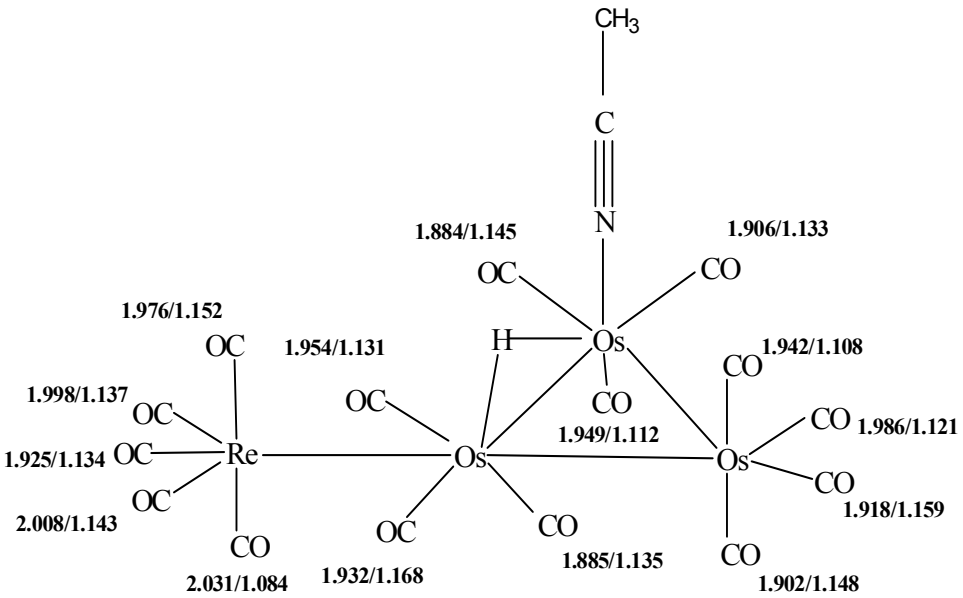

Figure S.15. The Structure ACREOS10, the carbonyl bond lengths are numbered {M-L/C≡O}[5] This structure is very typical of all the members of the datasets and illustrates the variation observed in M-C bond-lengths in a single complex,

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5. The Effect of Oxidation State of the Metal on Trends

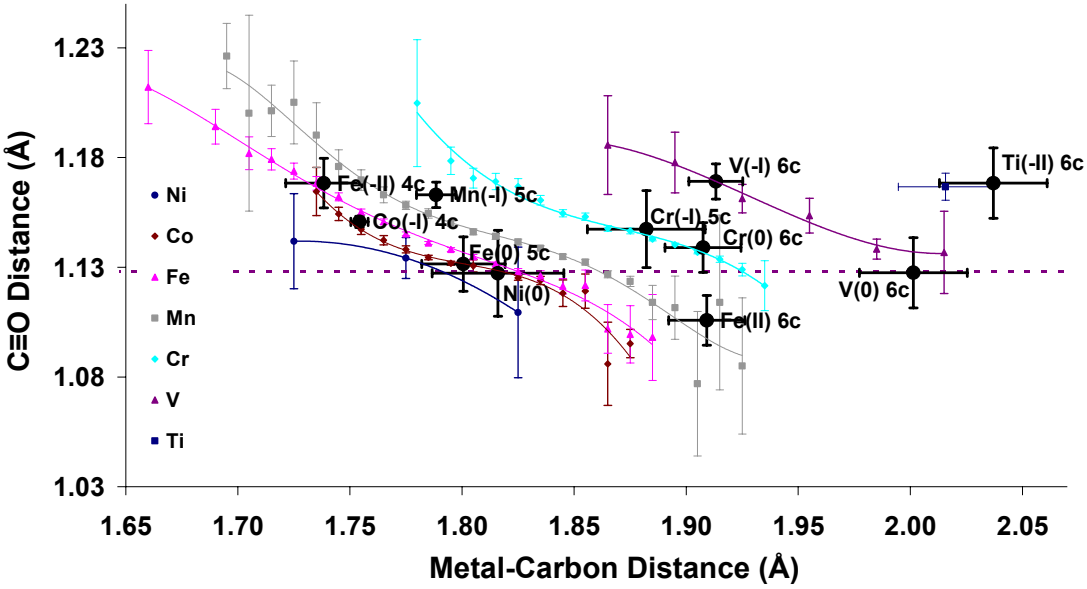

Figure S.16. Homoleptic Metal-Carbonyl Complexes superposed on the first row transition metals. Large ranges in oxidation states are observed, due to the propensity of the complexes to be 18 electron species

6. Homoleptic Metal-Carbonyl Species

To understand mutual ligand effects, it is advantageous/preferable to first examine coordination spheres that are not effected by them. The best way to do this is through the small subset of compounds containing only carbonyl ligands. This small subset of the larger datasets comprising <0.4% of the data is important for two reasons: Firstly, in a homoleptic species there can on average be no net polarization of d-orbitals toward or away from other ligands. Secondly, the oxidation state of the metal is more obvious that in mixed ligand systems which may involve multiple metal-metal bonds. It is also important to consider this

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in terms of the proportions of the dataset, which ligand systems dominate and in which regions, homoleptic systems give as a definite point in this scheme of things.

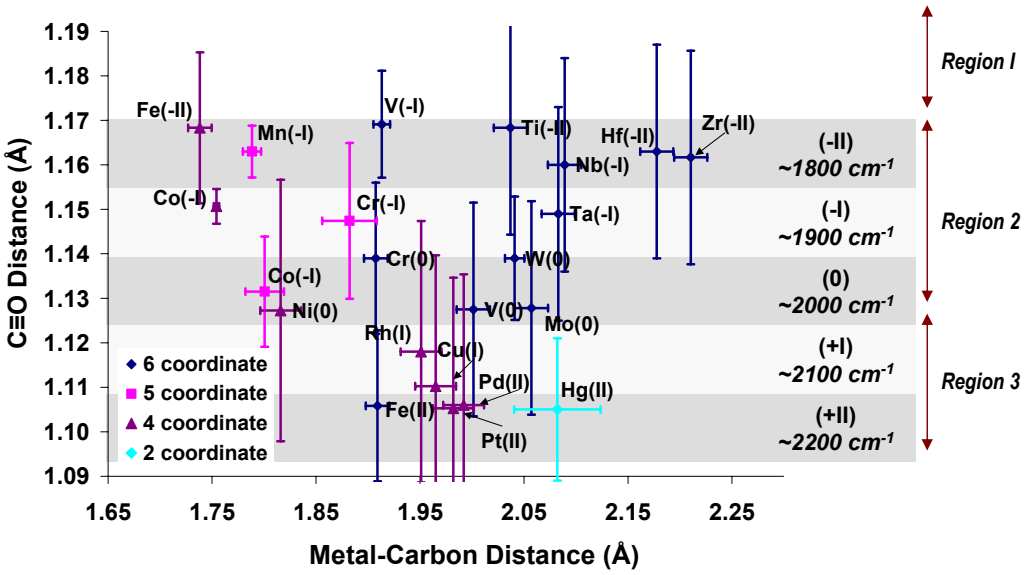

Figure S.17. The Structural Data reported thus far for all Homoleptic Metal-Carbonyl Species. Figure 8.14 illustrates the experimental relationship between C≡O bond-length and the C≡O stretching frequencies, as well as the relationship between oxidation state and vibrational frequencies in homoleptic metal-carbonyl complexes.

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7. The Effect of Other Ligands in the Coordination Sphere

a. *trans*-ligands

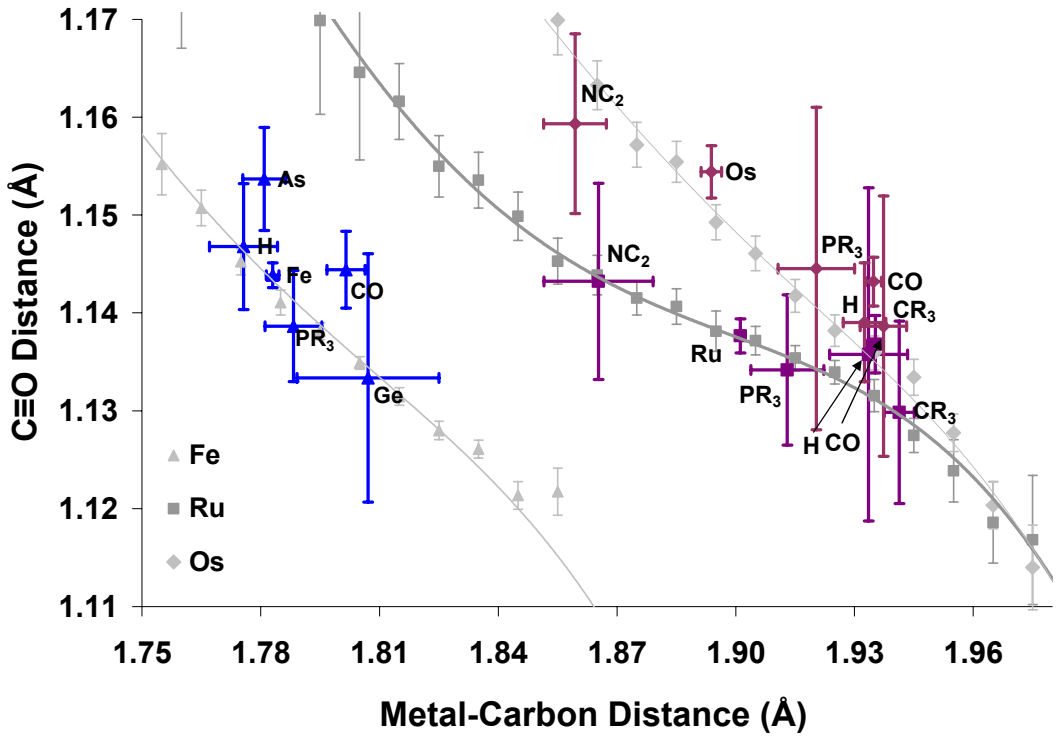

Figure S.18. Effect of *trans*-donors in Group 8 metals Fe, Ru and Os.

Figure S.18 represents the "average" effect of trans donors across the Os data-sets. From this data set the series NC<Os<PR_3<CR_3<H<CO is derived and it represents the average response of the *trans* donor. It does not necessarily mean these donors only exhibit bonding in the observed regions, rather that there is a propensity to observe more of these compounds in certain regions of the curves.

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b. Other Ligands in the Coordination Sphere

i. Effect of Coordination Number

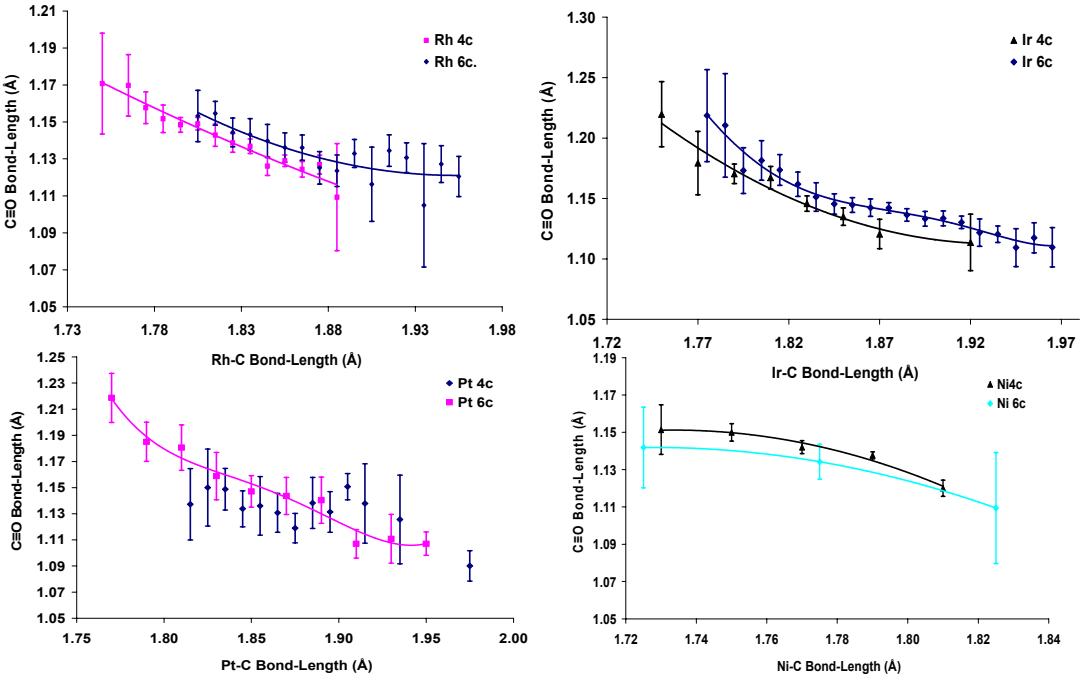

Figure S.19. Comparison of Different Coordination Numbers

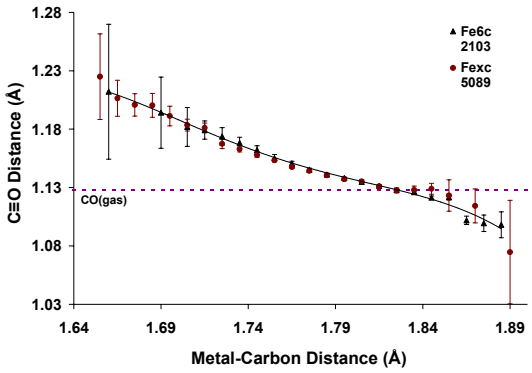

Figure S.20. Comparison of Different Subsets of the Fe-Data Set. With there relative numbers of structures. *Many numbers of different coordination, the datasets used are currently the same size due to array limitations in our programs.

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It is clear from Figure S.6 that whilst the trends are not completely independent of coordination number they are too a good approximation. In all cases we observe 4c. species to have shorter M-C bond lengths than 6c. species, this is probably a steric effect across the series. The difference between 4c and 6c is in each case less than the difference between the elemental centres.

8. The Exclusion of Metal-Metal Bonds

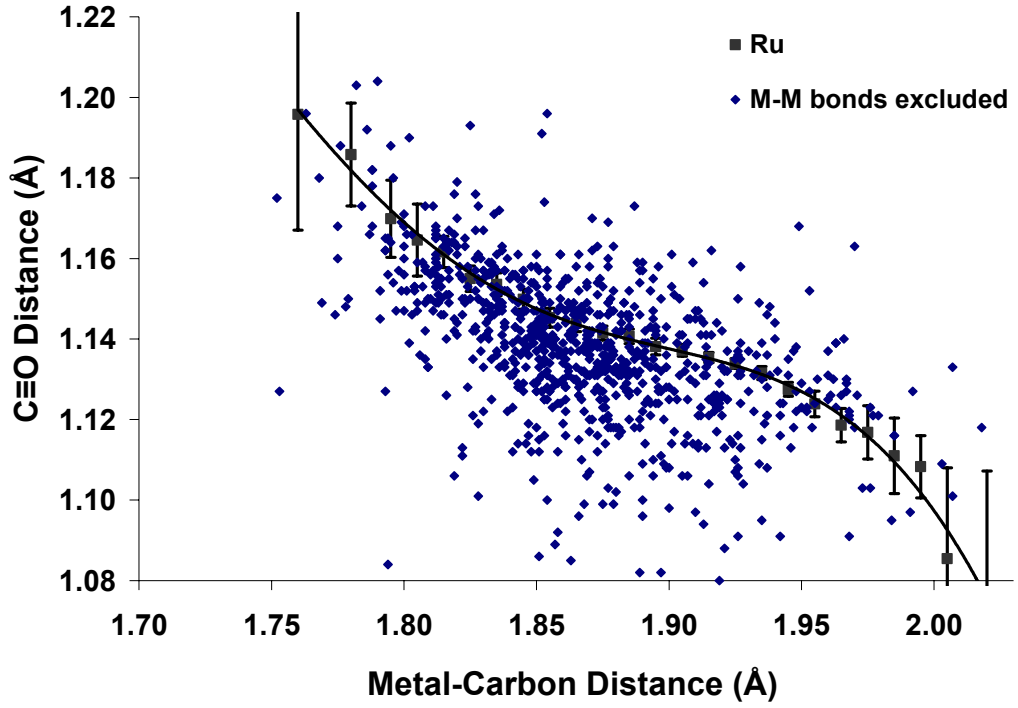

Figure S21. Ruthenium Trend plotted with a scatter plot representing the exclusion of all Metal-Metal bonds.

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9. Tables of Data

Table 3. Data for Homoleptic Metal-Carbonyl Species

Metal Centre	Coordination Number	Oxidation State of Metal Centre	average	median	count	stdev	confidence
Cr1	6	0	1.91	1.91	12	0.0103	0.0058
Fe1	6	2	1.91	1.91	12	0.0052	0.0029
Hf1	6	-2	2.18	2.18	6	0.0029	0.0023
Mo1	6	0	2.06	2.06	6	0.0051	0.0041
Nb1	6	-1	2.09	2.09	6		
Ta1	6	-1	2.08	2.08	6		
Ti1	6	-2	2.04	2.04	6	0.0027	0.0021
V1	6	1	1.91	1.91	24	0.0303	0.0121
V1	6	-1	2.00	2.00	6	0.0058	
W1	6	0	2.04	2.05	18	0.0123	0.0057
Zr1	6	-2	2.21	2.21	6	0.0042	0.0034
Mn	5	-1	1.79	1.80	45	0.0395	0.0115
Fe1	5	0	1.80	1.81	10	0.0163	0.0101
Cr1	5	-1	1.88	1.89	5	0.0239	0.0209
Rh	4	1	1.95	1.95	4	0.0050	0.0051
Pt	4	2	1.98	1.98	4	0.0032	0.0031
Pd	4	2	1.99	1.99	4	0.0105	0.0103
Ni	4	0	1.82	1.82	4	0.0020	0.0020
Fe	4	-2	1.74	1.74	12	0.0209	0.0118
Cu	4	1	1.97	1.97	4	0.0036	0.0035
Co	4	-1	1.75	1.76	228	0.0352	0.0046
Hg	2	2	2.08				
Re2	6	1	1.990	1.999	6	0.062	0.0494

(1) Centre., C. C. D.; 1.2 ed.; CCDC, 2001.

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Spreadsheets containing full sets of data are available by writing to the authors. There are interlinked arrays >60,000 data points long as such it was difficult to appropriately present some of the data as supporting information. r.hocking@chem.usyd.edu.au/t.hambley@chem.usyd.edu.au