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Structural insights into transition-metal carbonyl bonding†

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An examination of the relationship between TM–C and C≡O bond lengths using more than 20,000 crystal structures has revealed three novel observations relating to TM–carbonyl interactions.

Transition metal (TM) carbonyl compounds form a class of compounds that is one of the most widely studied in chemistry.[1–5] These compounds have diverse applications ranging from catalysts to functional species in biochemistry.[6] The strength of a TM–carbonyl bond is generally thought to arise from the synergistic effects of σ- and π-bonding.[7,8] σ- and π-bonding have opposite effects on carbonyl bond order; σ-bonding increasing the bond order and π-bonding decreasing it. Thus, changes in TM–C bonding can be detected by monitoring the carbonyl bond order, usually through the use of IR spectroscopy.[2,9]

It is the general consensus amongst chemists that crystallographic determinations of individual C≡O bond lengths are too imprecise to provide useful insight into the nature of bonding.[10,13] Whilst this may be true for an individual observation, analysis of large data sets can provide insights not available from such observations.[11,12,14] Over 20,000 crystal structures containing a TM–carbonyl bond have been reported to the Cambridge Structural Database (CSD)[15] and in this study we have applied database analysis techniques in order to gain new insights into TM–carbonyl bonding.

All reported unique terminal‡ 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.[16] Where sufficient data existed, subsets with different coordination numbers, oxidation states, and *trans* ligands were analyzed. To identify any 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 on the mean calculated, using methods detailed elsewhere.[10,11] The nature of this analysis means that uncertainty increases if there are fewer observations.§

Two expected observations emerge from plots of C≡O *vs.* TM–C bond lengths, Fig. 1 and 3. Firstly, as TM–C bond lengths become shorter, the C≡O bond lengths become longer; this is consistent with the effects of increasing π-overlap as TM–C bond length decreases. Secondly, the derived trends in bond length are periodic, (Fig. 1 and 3).[17] These observations are expected based on both experimental[2] and theoretical work.[5]

In addition to these expected observations of TM–carbonyl bonding, the curves in Figs. 1 and 3 reveal a number of characteristics not seen before experimentally. Firstly, the curves representing plots of TM–C *vs.* C≡O bond lengths are chair shaped, having three distinct regions of gradient, illustrated schematically in Fig. 2. The steeper gradient in region 1, with very short TM–C bond lengths is consistent with the effects of π-bonding dominating over those of σ-bonding. This is presumably because the effects of σ-bonding plateau at very short TM–C bond lengths. The shallowest gradient occurs in region 2, with intermediate TM–C distances. In this region the σ- and π- contributions to bonding have largely counteracting effects. Finally, an increase in gradient is again observed in Region 3, where C≡O bond lengths are shorter than those of gaseous carbon monoxide.[18] In this region the σ and ionic contributions to the bonding dominate and are not balanced by the effects of π-bonding presumably because it is weak at these long TM–C bond lengths.[18]

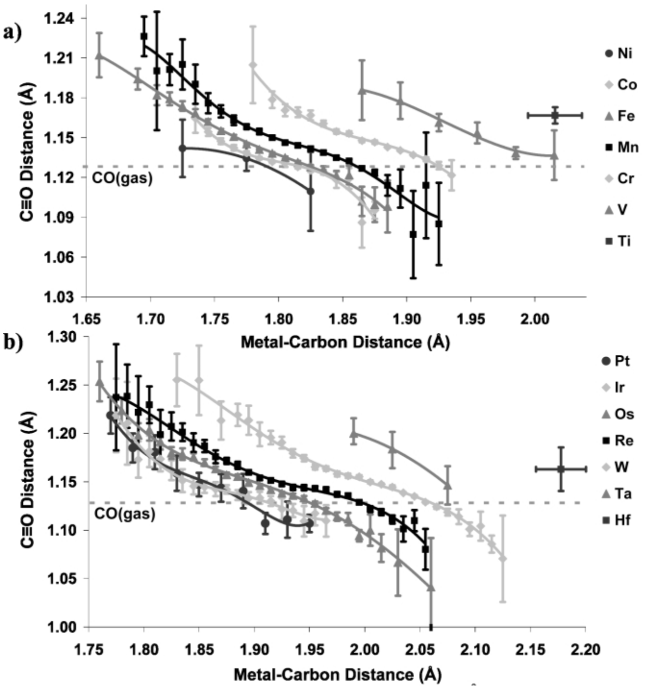

Fig. 1 Plots of C≡O bond length *vs.* TM–C bond length (Å) for **a**) first-row, and **b**) third-row six-coordinate TM–carbonyl complexes (error bars represent the 95% confidence intervals on the mean). Both second row and colour versions of these figures are given in the ESI.†

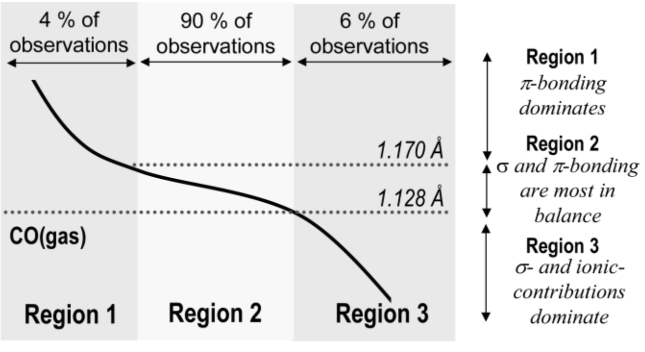

Fig. 2 Schematic illustration of the relationship between TM–C and C≡O bond lengths.

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† Electronic supplementary information (ESI) available: search criteria and data retrieval, bond distances, datasets and statistics, details on oxidation state, homoleptic metal–carbonyl species and exclusion of metal–metal bonds. See http://www.rsc.org/suppdata/cc/b3/b303271j/

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The second novel observation is that a region of large gradient change is coincident with the C≡O bond length being equal to that in carbon monoxide gas. This corresponds in Fig. 2 to the division between Regions 2 and 3, and is most obvious from the curves when plotted as groups (Fig. 3). The coordinated C≡O bond length will equal the free gas bond length when the effects of σ and π bonding are equal and opposite. Above this point the effects of π-bonding dominate, below this point the effects of σ- and ionic- bonding dominate.

Carbonyl compounds whose average stretching frequencies are greater than those of gaseous carbon monoxide are often referred to as "non-classical" metal carbonyls, as they have bonding features measurably different to other carbonyl complexes. Where there are crystallographic observations of such complexes they fit into region 3.[5] Computational studies show that non-classical metal carbonyls are the result of an effect of ligands (particularly those *trans* to the carbonyl) or an effect of oxidation state.[1,5] A change in oxidation state or a change in *trans* ligand has the common effect of changing the occupation of the d-orbitals of the metal and it is this occupation that determines the TM–C bond length. Complexes with the largest amount of back bonding, or very short TM–C bond-lengths, (Fig. 2, Region 1) are relatively rare making up only ~ 4% of observations and are a consequence of highly occupied d-orbitals. This can be due to low oxidation states or a situation where the electronic requirements of the other ligands in the system mean that the carbonyl group back bonds unusually strongly. Most of the compounds in this region have metal–metal bonds (Fig. S21, see ESI†). Complexes with the smallest amount of back bonding are also rare making up only 6% of observations. In these complexes the d-orbitals are less available to take part in back bonding, either because the carbonyl is *trans* to a ligand which is more strongly electron withdrawing, or the metal is in a high oxidation state.[5] The increasing steepness of the slope as TM–C bond length increases is more consistent with an increasing ionic component rather than a σ-contribution as the latter must tend to zero at long TM–C distances.[1–5]

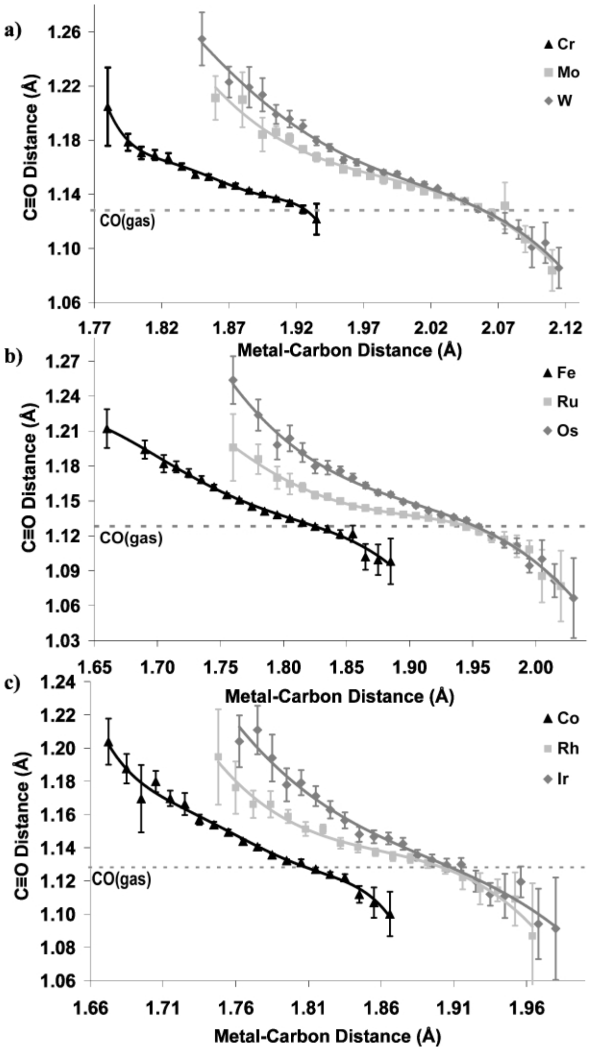

Fig. 3 Plots of C≡O bond length *vs*. TM–C bond length for groups 6 (a), 8 (b) and 9 (c) (error bars represent the 95% confidence intervals on the mean). Colour versions of these figures as well as the data for the other triads are given in the ESI.†

The final novel observation emerges from a comparison of the results for 2nd and 3rd row elements of the same triad, (Fig. 3, Fig. S6–9†). The curves overlap in region 3 but increasingly diverge through regions 2 and 1. The overlap in region 2 is consistent with the similarity of the ionic radii of 2nd and 3rd row elements and with the bonding in this region being dominated by σ and electrostatic contributions. The divergence in regions 1 and 2 begins where the C≡O bond length is the same as in gaseous carbon monoxide or as the contribution of π-bonding begins to have a net effect. This suggests that π-bonding is weaker in the 2nd row elements than either the third or the first, consistent with both experimental[19] and calculated[20,21] bond dissociation energies. This has been attributed to the destabilisation of the 5d orbitals by the relativistic contraction of the inner orbitals in third row elements, which increases the strength of π-bonding to these metals.[22]

From this data analysis we are able to extract the relationship between TM–C and C≡O bond lengths and this relationship has given us new insights into TM–carbonyl bonding.

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Notes and references

‡ Details of how other binding modes were excluded are in the supporting information.†

§ Further plots of TM–C *vs.* C≡O bond lengths are available for subsets of the original data, as are homoleptic complexes. Excel spreadsheets containing full sets of data are available by writing to the authors.

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