

Preliminary communication

THE NATURE OF BRIDGING AND SEMI-BRIDGING CARBONYL GROUPS

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Summary

Calculations indicate the existence of "semi-bridging" bonding in $\text{Mn}_2(\text{CO})_{10}$ but not in $\text{Re}_2(\text{CO})_{10}$.

It has been suggested [1] that in polynuclear transition metal carbonyl complexes, a metal atom with a surfeit of electron density may transfer some of it to carbonyl groups coordinated to other metal atoms which are relatively deficient in this respect. The overlap of the filled metal orbitals with π^* orbitals of these "adjacent" CO groups results in "semi-bridging" CO ligands.

Previously reported calculations from these laboratories [2] have shown that for $\text{Mn}_2(\text{CO})_{10}$ there appears to be considerable bonding interaction between each metal atom and "adjacent" equatorial CO groups coordinated to the other metal (see Table 1). Thus, although the carbonyl groups in this compound have been regarded as being strictly terminal, it is clear that they have considerable "semi-bridging" character. This has no appreciable effect on the molecular geometry, and it seems likely that such interactions are common in polynuclear metal carbonyls although there may be no overt structural evidence for them.

An intriguing feature of our calculations is that they show that the

TABLE 1

$\text{M}_2(\text{CO})_{10}$ OVERLAP POPULATIONS

M	M—M	M(1)—L(2)	L(1)—L(2)
Mn	0.0162	0.0490	-0.0080
Tc	0.1887	0.0025	-0.0068
Re	0.2103	0.0056	-0.0056

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“adjacent” metal—CO interactions are very much less important for $\text{Re}_2(\text{CO})_{10}$ than for $\text{Mn}_2(\text{CO})_{10}$. If these conclusions may be extended to transition metals other than those of Group VII then they are consistent with the generally observed phenomenon of the greater importance of bridging CO ligands in the complexes of the first row transition metal than for those of the third.

References

- 1 F.A. Cotton and J.M. Troup, *J. Amer. Chem. Soc.*, 96 (1974) 1233.
- 2 D.A. Brown, W.J. Chambers, N.J. Fitzpatrick and R.M. Rawlinson, *J. Chem. Soc., A* (1971) 720.