Journal of Organometallic Chemistry, 336 (1987) C9–C12
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

On the relationship between M–M bond length and the presence of bridging CO ligands in $M_4(CO)_{12}$ complexes (M = Co, Rh, Ir)

Dario Braga * and Fabrizia Grepioni

Dipartimento di Chimica "G. Ciamician", Universita' di Bologna, Via F. Selmi, 2, 40126 Bologna (Italy)

(Received August 12th, 1987)

Abstract

The M–M bond shortening effect, usually attributed to the presence of bridging COs in metal clusters, and the relationship between bridged and unbridged Ir_4 derivatives, are discussed in terms of the balance between M–CO, CO..CO and M–M interactions.

It is commonly believed that in transition metal cluster compounds the M–M bonds spanned by bridging COs are generally shorter than unbridged ones [1]. The shortening effect has been attributed to the bridging CO causing slight M–M bonding character of the polycentric M–M bond [2], and this view has been supported by the observation of progressive decrease of the M–M distance upon increase of the number of bridging ligands [3]. The fact that this behaviour is not found in several cases has been accounted for by invoking special electronic and/or steric effects in the compound under consideration or discounted on the ground of scarce structural data reliability. This is the case, for instance, for many derivatives of $Ir_4(CO)_{12}$, that are known to possess the "C_{3v}-like" arrangement of CO ligands with three bridging COs around a triangular face [4], rather than the "T_d-like" arrangement with only terminal ligands characteristic for the parent molecule [5].

We now provide clear evidence that for the family of substituted M_4 tetrahedral species (M = Co, Rh, Ir), substantial shortening of the bridged M–M bonds with respect to the unbridged ones is observed only for M = Co, and that for M = Rh or Ir the general trend is for longer, or at most equivalent, M–M bonds to accompany the presence of μ_2-COs. A brief comparison of all the known tetrahedral species is given in Table 1 [6]. The few Ir_4 derivatives which have been shown to preserve a "T_d-like" structure are also listed, and will be discussed separately. The differences between the mean bond lengths for unbridged and CO-bridged bonds (Δs in Table 1) have values of 0.068, −0.027, −0.019 Å for Co, Rh and Ir, respectively. Since the standard deviations for M–M bond lengths usually fall in the range 0.001–0.003 Å,

0022-328X/87/$03.50

Table 1

Comparison of averaged structural parameters for substituted derivatives of $M_4(CO)_{12}$ species (M = Co, Rh, Ir)

	$(M-M)_{nb}$	$(M-M)_b$ ^{a}	Δ	$M-C_t$	$M-C_b$	Ref. ^{b}
$Co_4(CO)_{12}$	2.494(14)	2.485(12)	0.009	1.87(5)	2.06(5)	6
$[Co_4(\mu_2\text{-}CO)_3(CO)_8C(O)Me]$	2.562(1)	2.461(1)	0.101	1.78(4)	1.94(4)	1s
$[Co_4(\mu_2\text{-}CO)_3(CO)_8I]^-$	2.521(2)	2.467(2)	0.054	1.76(1)	1.94(1)	2s
$Co_4(\mu_2\text{-}CO)_3(CO)_8PPh_3$	2.530(1)	2.482(1)	0.048	1.797(5)	1.937(4)	3s
$Co_4(\mu_2\text{-}CO)_3(CO)_8PMe_3$	2.530(2)	2.469(2)	0.061	^{c}		4s
$Co_4(\mu_2\text{-}CO)_3(CO)_7[P(OMe)_3]_2$	2.528(1)	2.454(1)	0.074	1.784(7)	1.929(6)	3c
$Rh_4(CO)_{12}$	2.715(8)	2.749(8)	−0.034	1.96(7)	1.99(7)	7
$Rh_4(\mu_2\text{-}CO)_3(CO)_7(PPh_3)_2$	2.707(2)	2.750(2)	−0.043	1.88(2)	2.09(2)	5s
$Rh_4(\mu_2\text{-}CO)_3(CO)_6[P(OPh)_3]_3$	2.694(2)	2.719(2)	−0.025	1.85(3)	2.06(2)	5s
$Rh_4(\mu_2\text{-}CO)_3(CO)_5[P(OPh)_3]_4$	2.709(8)	2.741(8)	−0.032	1.83(c)	2.00(c)	6s
$Rh_4(\mu_2\text{-}CO)_3(CO)_5(dppm)_2$	2.706(1)	2.715(1)	−0.009	1.91(2)	2.09(2)	7s
$Rh_4(\mu\text{-}PPh_2)_4(\mu_2\text{-}CO)_3(CO)_2(PPh_3)$	^{d}	2.876(2)		+ ^{c}	^{c}	8s
$Rh_4(\mu\text{-}PPh_2)_4(\mu_2\text{-}CO)_2(CO)_4$	^{d}	2.816(1)		+ 1.86(7)	2.08(6)	9s
monoclinic						
triclinic	^{d}	2.828(1)		+ ^{c}	^{c}	9s
$Ir_4(\mu_2\text{-}CO)_2(CO)_9(\mu_2\text{-}SO_2)$	2.694(1)	2.731(3)	−0.037	1.93(2)	2.11(2)	10s
$[Ir_4(\mu_2\text{-}CO)_3(CO)_8]_2{}^{2-}$	2.721(1)	2.752(1)	−0.031	1.88(2)	2.13(2)	11s
$[HIr_4(\mu_2\text{-}CO)_3(CO)_8]^-$	2.706(2)	2.727(2)	−0.021	1.84(2)	1.98(5)	12s
X-ray						
neutron	2.714(1)	2.736(1)	−0.022	1.894(6)	2.02(2)	12s
$[Ir_4(\mu_2\text{-}CO)_3(CO)_8Br]^-$	2.696(1)	2.725(1)	−0.029	1.89(3)	2.10(3)	13s
$[Ir_4(\mu_2\text{-}CO)_3(CO)_8(COOR)]^-$	2.726(2)	2.717(2)	0.009	* 2.00(6)	2.14(4)	14s
$[Ir_4(\mu_2\text{-}CO)_3(CO)_8PhPPPhIr_4(\mu_2\text{-}CO)(CO)_8(AuPEt_3)_2]$	2.711(2)	2.746(2)	−0.035	^{c}	^{c}	15s
$Ir_4(\mu_2\text{-}CO)_3(CO)_7(Me_2PCH_2CH_2PMe_2)$	2.736(2)	2.739(2)	−0.003	1.84(3)	2.07(2)	16s
$Ir_4(\mu_2\text{-}CO)_3(CO)_7(diars)$	2.726(1)	2.720(2)	0.006	* 1.88(3)	2.11(3)	17s
$Ir_4(\mu_2\text{-}CO)_3(CO)_7(diop)$	2.723(2)	2.764(2)	−0.041	1.84(3)	2.07(3)	18s
$Ir_4(\mu_2\text{-}CO)_3(CO)_6(PMe_2Ph)nbd$	2.726(1)	2.720(1)	0.006	* 1.89(3)	2.07(2)	19s
$Ir_4(\mu_2\text{-}CO)_3(CO)_6(PPh_3)nbd$	2.713(1)	2.757(1)	−0.044	1.83(3)	2.06(2)	19s
$Ir_4(\mu_2\text{-}CO)_3(CO)_6(PPh_3)Ph_2P(CH_2)_3PPh_2$	2.728(1)	2.745(1)	−0.017	1.84(2)	2.07(2)	20s
$Ir_4(\mu_2\text{-}CO)_3(CO)_5(PMe_3)_4$	2.737(1)	2.745(1)	−0.008	1.85(2)	2.10(2)	21s
$Ir_4(\mu_2\text{-}CO)_3(CO)_5(PH_2PCH_2PPh_2)$	2.726(1)	2.725(1)	0.001	* 1.86(2)	2.12(2)	22s
$Ir_4(\mu_2\text{-}CO)_3(CO)_5(dpp)_2$	2.686(2)	2.725(2)	−0.039	1.89(4)	2.05(4)	23s
$Ir_4(\mu_2\text{-}CO)_3(CO)_5(PPhMe_2)_4$	2.730(3)	2.748(3)	−0.018	1.77(5)	2.07(5)	24s
$HIr_4(\mu_2\text{-}CO)_3(CO)_4(dpp)(PhC_6H_4PCH{=}CHPPh_2)$	2.757(1)	2.719(1)	0.038	+ 1.83(3)	2.07(3)	23s
$[H_2Ir_4(\mu_2\text{-}CO)_3(CO)_7]^{2-}$	2.789(2)	2.711(2)	0.078	+ 1.80(4)	2.03(3)	24s
$Ir_4(\mu_3\text{-}PPh)(\mu_2\text{-}CO)_3(CO)_3(PPh_3)_4$	2.894(1)	2.747(1)	0.147	+ 1.85(1)	2.09(1)	26s
$Ir_4(CO)_{12}$	2.693(7)			1.87		5
$Ir_4(CO)_9[(Ph_2P)_3CH]$	2.689(3)			^{c}		27s
$Ir_4(CO)_{11}CN(t\text{-}Bu)$	2.685(1)			1.86(3)		28s
$[Ir_4(CO)_{11}SCN]^-$	2.684(1)			1.91(2)		29s

[a] Only CO-bridged M–M bonds were averaged. [b] *n*s refers to the supplementary reference list. [c] Not reported. [d] No unbridged M–M bonds.

these values, though not derived from isostructural species, appear to be meaningful. It should be pointed out that some compounds (marked by a + in Table 1) were not included in these comparisons because of some "abnormal" bond lengths, undoubtedly caused by the presence of unusual ligands or by an unusual ligand distribution. The parent $M_4(CO)_{12}$ species were also omitted because of the known problems of disorder and twinning in their crystals [5,7,8]. It should also be emphasized that the few positive Δ-values (a* in Table 1) for Ir_4 derivatives are very small, indicating that there is more likely equivalence of M–M interactions rather than inversion of the trend. A further point of interest is the fact that the trend appears to be irrespective of: (a) the degree of substitution, (b) the presence of ionic charge, (c) the actual involvement of the apical atom in polysubstitution, and (d) the type of substituent. Although M–C and C–O structural parameters are known with lower accuracy, and also depend strongly on the refinement procedure employed [9], it is noteworthy that the difference in the average M–C lengths between terminal and bridging ligands shows a slight increase on going from Co to Rh and Ir ($(M{-}C_b) - (M{-}C_t) = 0.16$, 0.19, 0.21 Å, respectively), and the increase does not seem to depend on whether the bridged M–M bonds are shorter or longer than the unbridged ones. The understanding of the relationship between bridged and unbridged M–M bonds seems to require recognition of the difference in repulsive interactions and steric demands between terminal and bridging COs bound to the same metals, and between COs bound to different metals. Thus the inversion of the bridged/unbridged ratio on passing from Co to Rh and Ir, can be tentatively explained by regarding the metal atom polyhedron within the ligand coverage as the "soft-core" of the molecule, capable of adapting itself to the demand of the surrounding ligands. In other words, lengthening or shortening of M–M bonds may be the indirect consequence of the compromise between optimization of M–CO interactions and minimization of non-identical CO_t–CO_t and CO_t–CO_b intramolecular repulsions, which also reflect differences between the electronegativities of the metals and the electronic effects of the substituents. On this basis it seems that models assuming equivalence between CO_t and CO_b must be reassessed [10,11].

One more consideration arises from a comparison of M–M bond lengths between the "C_{3v}-like" Ir_4 derivatives and the few "T_d-like" species. Although speculation about such a small data set must be somewhat uncertain, it is noteworthy that the metal polyhedron in "T_d-like" species is always smaller than in the "C_{3v}-like" species (see Table 1).

Substitution of COs by poorer π-acceptor or sterically more demanding ligands may well be the cause of the "T_d-C_{3v}" switch [10]. However it appears that, once the "C_{3v}-like" structure is established and the homogeneous distribution of CO_t..CO_t interactions perturbed by CO-bridge formation, Ir–Ir bond lengthening occurs in order to adapt the metal frame to the new ligand distribution. In other words, M–M bonding energy is lost first when ligand reorganization is required as implied by the thermodynamic evidence for stronger M–CO and weaker M–M bonds in polynuclear carbonyls [12]. Conversely, when steric or electronic perturbations are small, the more stable "T_d-like" structure, with optimum M–M bonding, is preferred [13].

However the problem may be more complex, and the present analysis does not yet explain the fact that $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ adopt the bridged structure while $Ir_4(CO)_{12}$ does not. Nevertheless it seems that the balance between bridge formation and M–M bond lengths is, for Ir, in favour of shorter bonds.

We believe that all these point will be clarified by a careful structural analysis of isostructural substituted species of Co, Rh and Ir, and this is in progress.

We thank prof. V.G. Albano for helpful discussions.

References

1 R. Colton and M.J. McCormick, Coord. Chem. Rev., 31 (1980) 1.
2 P. Chini, Inorg. Chim. Acta Rev., 2 (1968) 31.
3 F.A. Cotton, and J.M. Troup, J. Am. Chem. Soc., 96 (1974) 4155.
4 P.R. Raithby, in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, New York, 1985, p. 5.
5 M.R. Churchill and J.P. Hutchinson, Inorg. Chem., 17 (1978) 5328.
6 A complete reference list is available from the authors.
7 C.H. Wei, Inorg. Chem., 8 (1966) 2384; F.H. Carré, F.A. Cotton, and B.A. Frenz, Inorg. Chem., 15 (1976) 380.
8 C.H. Wei, G.R. Wilkes, and L.F. Dahl, J. Am. Chem. Soc., (1967) 4792.
9 D. Braga, and T.F. Koetzle, J. Chem. Soc., Chem. Commun., (1987) 144.
10 B.F.G. Johnson and R.E. Benfield, Inorg. and Organomet. Stereochem., 12 (1981) 253 and ref. therein.
11 J.W. Lauher, J. Am. Chem. Soc., 108 (1986) 1521.
12 P. Chini, G. Longoni, and V.G. Albano, Adv. Organomet. Chem., 14 (1976) 285; P. Chini and B.T. Heaton, Topics Curr. Chem., 71 (1977) 1; J.A. Connor, in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, New York, 1980, p. 345.