The Role of Saturated Transition Metal Carbonyl Complexes as π-Acid Ligands; a Theoretical Investigation of the Bonding in [Cr(μ-CO)$_2$(CO)(η-C$_6$H$_6$)Rh(CO)(η-C$_5$Me$_5$)] and [Co(μ-CO)$_2$(η-C$_5$H$_5$)Rh(PH$_3$)(η-C$_5$H$_5$)]

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E.H.M.O. Calculations on [Cr(μ-CO)$_2$(CO)(η-C$_6$H$_6$)Rh(CO)(η-C$_5$Me$_5$)] and [Co(μ-CO)$_2$(η-C$_5$H$_5$)Rh(PH$_3$)(η-C$_5$H$_5$)] indicate that the saturated [Cr(CO)$_3$(η-C$_6$H$_6$)] and [Co(CO)$_2$(η-C$_5$H$_5$)] moieties are excellent π-acid ligands for the electron-rich [Rh(L)(η-C$_5$R$_5$)] fragments; bonding takes place through the semi-bridging carbonyls with little net metal–metal interaction.

The metal–metal donor–acceptor bond formalism has recently been invoked in simple valence-bond descriptions of bimetallic transition-metal complexes for which the electron count at the two metal centres would otherwise be unequal.[1—3] Many of these species[1,2] possess a pair of non-compensating semi-bridging carbonyl ligands.[1] Because alternative representations of the bonding in these compounds have appeared [*viz.* (A),[4] (B),[2b] and (C)[2c]], we felt that a theoretical investigation was necessary to elucidate their electronic structure. Presented here are the results of E.H.M.O. calculations[5] on two members of this class; [Cr(μ-CO)$_2$(CO)(η-C$_6$H$_6$)Rh(CO)(η-C$_5$Me$_5$)] (**1**),[2c] and [Co(μ-CO)$_2$(η-C$_5$H$_5$)Rh(PH$_3$)(η-C$_5$H$_5$)] (**2**), a model for [Co(μ-CO)$_2$(η-C$_5$Me$_5$)Rh(PMe$_2$Ph)(η-C$_5$Me$_5$)] (**3**).[6] Geometrical parameters for (**1**) and (**2**) were taken from the crystal structures of (**1**)[2c] and (**3**).[6]

A fragment analytical approach was employed in which the complexes were partitioned such that the semi-bridging carbonyl groups were attached to the metal to which they show a greater degree of terminal character.‡ Cleavage of (**1**) and (**2**) in this fashion yields a co-ordinatively unsaturated 16 electron [RhL(η-C$_5$R$_5$)] moiety in each case and a saturated 18 electron species namely [Cr(CO)$_3$(η-C$_6$H$_6$)] for (**1**) and [Co(CO)$_2$(η-C$_5$H$_5$)] for (**2**). The frontier orbitals of (**1**) and its fragments (**4**) and (**5**) are depicted in Figure 1. These are classified according to the symmetry of (**1**) (C_s) and furthermore as having σ, π, or δ pseudo-symmetry with respect to the metal–metal axis.

The frontier orbitals of the d^8 rhodium(I) fragment [Rh(CO)(η-C$_5$Me$_5$)] (**4**) are qualitatively similar to those described by Hofmann[7] for [Rh(CO)(η-C$_5$H$_5$)]. They consist of three low lying metal based orbitals [1a″(π), 1a′(π), and 2a′(σ)] and a filled π-donor orbital, 2a″(π), at higher energy, which is the HOMO for the fragment. The LUMO 3a′(σ) is well separated from the other virtual orbitals and is a potential σ-acceptor.

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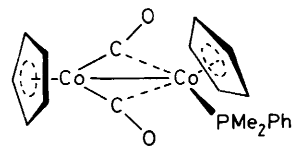
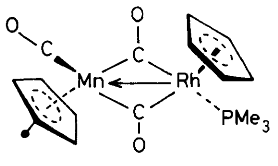
‡ Evidence for the degree of terminal character is derived from structural and spectroscopic studies on (**1**), (**3**), and related molecules.



(A)



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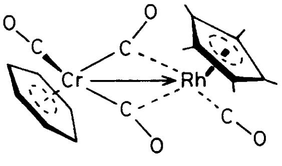


(C)

Table 1. Fractional fragment orbital occupancies for (**1**).

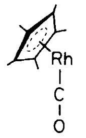
Fragment (4)		Fragment (5)	
3a′	0.20		
2a″	0.66	2a″	0.43
2a′	0.94	2a′	0.94
1a′	0.96	1a′	0.94
1a″	0.92	1a″	1.00

The d^6-[Cr(CO)$_3$(η-C$_6$H$_6$)] moiety, (**5**), has three filled metal based orbitals [1a″(δ), 1a′(π), and 2a′(σ)]. These are similar in energy and lie well below the 2a″(π) LUMO. This LUMO is principally composed of the in-plane μ-CO π* orbitals which are heavily localised on the carbon atoms. The perturbation of the geometry of fragment (**5**) from its ground state[8] upon co-ordination to (**4**) parallels that of alkenes[9] in that rehybridisation occurs to produce a more efficient π-acceptor function.

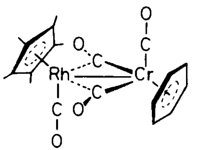
The important interactions between the fragments (**4**) and (**5**) which comprise molecule (**1**) are shown in Figure 1. The dominant interaction is between the two 2a″(π) orbitals, the HOMO of (**4**) is perfectly hybridised to overlap with the μ-C(O) based LUMO of (**5**). There is a net charge transfer of *ca.* 0.7 electrons from (**4**) to (**5**), which is largely due to this interaction as reflected in the fractional orbital occupancies of 0.66 for 2a″(π) of (**4**) and 0.43 for 2a″(π) of (**5**) (see Table 1). Here we have a demonstration of the π-acid capabilities of fragment (**5**) (the relatively accessible LUMO) and the electron rich nature of (**4**) (the high lying HOMO). The semi-bridging nature of the μ-CO ligands in (**1**) is reflected in the atomic overlap population for Cr–μ-C(O) and Rh–μ-C(O) of 0.80 and 0.37, respectively [*cf.* Cr–C(O) terminal = 1.00 and Rh–C(O) terminal = 1.01]. In comparison, other interactions between the fragments are minor.

Whilst there is some charge transfer in the other direction from (**5**) to (**4**) by interaction of 2a′(σ) with 3a′(σ) of (**4**) (the in-phase combination consititutes the metal–metal 'donor-acceptor' bond) this merely serves to offset the two destabilising 4e$^-$ a′(σ) and a′(π) interactions. As the a″(δ) interaction is also of minor importance, we find *no significant net metal–metal bond;* the Cr–Rh atomic overlap population is only 0.03. The Cr–Rh distance of 2.757(2) Å found in the *X*-ray study[2c] is therefore not a sufficient criterion on which to assess the degree of direct metal–metal bonding. Similar conclusions have been reached by others in their theoretical[10] and experimental[11] studies of binuclear complexes containing symmetrical carbonyl bridges.

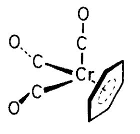
The analysis for (**2**) shows a qualitatively similar bonding pattern. The principal interaction between the two fragments



(**4**)



(**1**)



(**5**)

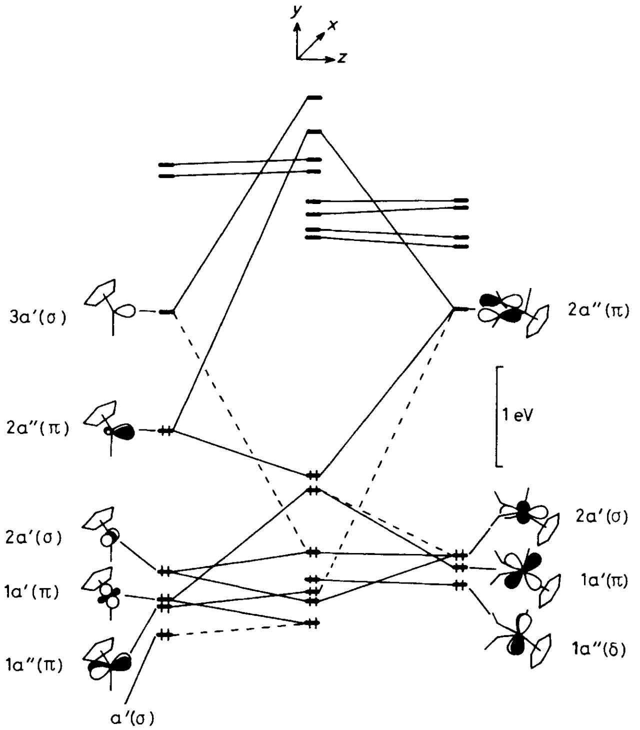


Figure 1. Molecular orbital interaction diagram for compound (**1**). The orbitals for the fragment [Rh(CO)(η-C$_5$Me$_5$)] are depicted at the left and for the fragment [Cr(CO)$_3$(η-C$_6$H$_6$)] at the right of the figure.

is that of the high-energy π-donor orbital on [Rh(PH$_3$)(η-C$_5$H$_5$)] with the π-acceptor function of the [Co(CO)$_2$(η-C$_5$H$_5$)] analogous to 2a″(π) of (**5**). The in-phase combination of these two does not, however, constitute the molecular HOMO in (**2**); the two highest filled levels in (**2**) are reversed in order compared with (**1**). Thus the HOMO of (**2**) consists of the out-of-phase a′(π) interaction.

A bonding scheme for this class of compound thus emerges. The major interaction is the stabilisation of the high-lying filled π-donor on the unsaturated fragment by the out-of-phase combination of the in-plane π* orbitals of the η-CO ligands.§ Although orbitals of appropriate symmetry for M → M bonding exist, other unfavourable M–M interactions counterbalance this producing a net bond order close to 0 between the metal atoms.

Moving the metal centres closer to each other would be expected to result in stabilisation of the in-phase a′ (π) interaction and concomitant destabilisation of the corresponding out-of-phase combination, to the extent that the latter may become the HOMO [as in (**2**) which has a Co–Rh internuclear separation of 2.587(1) Å, from (**3**)[6]]. Removal of a pair of

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§ Certain molecules related to (**2**) have a different ground-state geometry in which there is one terminal and one bridging carbonyl ligand, *e.g.* [Rh$_2$(μ-CO)(CO){P(OPh)$_3$}(η-C$_5$H$_5$)$_2$] (**6**) (ref. 12). We suggest that the [Rh{P(OPh)$_3$}(η-C$_5$H$_5$)] fragment is not sufficiently electron rich to warrant the π-back bonding interaction. Interconversion between these two structural types constitutes a viable mechanism for CO site exchange in (**6**) (ref. 12) and related molecules (ref. 13).

$[Co(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)Rh(PH_3)(\eta\text{-}C_5H_5)]$

(2)

$[Co(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)Rh(PMe_2Ph)(\eta\text{-}C_5Me_5)]$

(3)

$[Rh_2(\mu\text{-}CO)(CO)\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2]$

(6)

electrons in such a case should result in a net M–M bond. Calculations on other molecules for which M → M dative interactions have been postulated {*e.g.* the unsupported osmium dimer, $[Os(CO)_5Os(CO)_3(GeCl_3)Cl]$,[3a] and $[Mo(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)Rh(PPh_3)_2]$[14]} will be reported elsewhere.

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