

Reply to the Comment on “Hydride, gold(I) and related derivatives of the unsaturated ditungsten anion $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$ ” by M. Green, Dalton Transactions, 2018, 47, DOI to be confirmed

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Abstract

The half-electron and CBC representations of the hydride-bridged complexes $[\text{M}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PR}_2)(\text{CO})_2]$ are analyzed. It is shown that the former gives a picture in good agreement with the physicochemical properties of these species, while keeping simplicity.

Reply

In his comment to our 2014 article, Prof. Green proposes a new CBC description of the tricentric M_2H interaction in our hydride-bridged complexes $[\text{M}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PR}_2)(\text{CO})_2]$ (**1**) ($\text{M} = \text{Mo}, \text{W}$) that now recognizes the bonding nature of these interactions with respect to the intermetallic connection.

The principal problem with earlier versions of the CBC treatment of tricentric interactions was that these 3-centre, 2-electron interactions were generally supposed to make no contribution to the intermetallic bond. In contrast with this, our first DFT calculations on the dimolybdenum complex led us to conclude that the intermetallic bond in this molecule would involve two bicentric (Mo_2) and one tricentric Mo_2H interaction, with the latter being of bonding nature.¹ The half-electron representation (**A** in Figure 1) of our hydride-bridged complexes **1** was considered to give a view of this situation more accurate than the CBC representation at the time (**B**), since three (and not just two) bonding orbital interactions actually keep the metal atoms in close proximity.

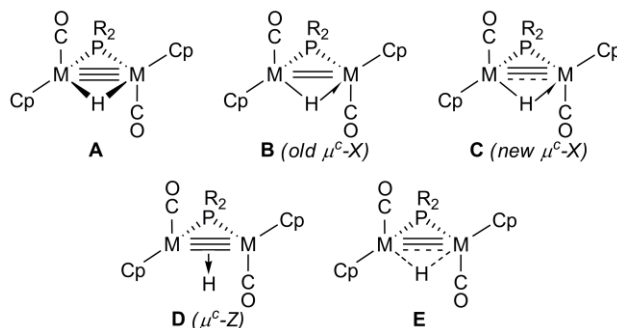


Figure 1. Different representations of complexes $[\text{M}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PR}_2)(\text{CO})_2]$ ($\text{M} = \text{Mo}, \text{W}$) (see text).

The new representation now proposed by Prof. Green for the closed $\mu^c\text{-X}$ bond, by including a dotted $\text{M}\cdots\text{M}$ line, recognizes the bonding nature of these tricentric

interactions as concerning the intermetallic connection, and therefore represents an improvement of the model (**C** in Fig. 1). However, a drawback of this representation is that it would seem to involve an asymmetric interaction of the bridging hydrogen atom with otherwise equivalent metal fragments. To circumvent this, we would rather favour the use of the closed μ^c -Z bond as an alternative CBC description for our compounds (**D**), which incidentally is in line with the experimental preparation of many hydride-bridged complexes via protonation of suitable precursors having a metal-metal bond. Tricentric interactions have been also represented in the past by using dotted lines (**E** in Fig. 1) and in other ways,² but their use in structural diagrams did not last, perhaps because of conflict with stereochemical indicators and one-electron bonds (dotted lines are also used to these purposes). Similarly, arrows are not commonly used in structural diagrams of metal complexes, except for emphatic purposes, so to keep drawings as simple as possible. Yet everyone understands the difference between a M–Cl bond and a M–PR₃ bond, even if the latter is also drawn with a single line instead of an arrow.

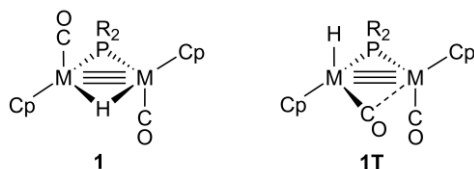


Figure 2. The isomeric forms of complexes $[M_2Cp_2H(\mu\text{-}PR_2)(CO)_2]$ ($M = Mo, W$).

It is beyond doubt that none of the above schemes gives an exact description of the tricentric interaction taking place at $M_2(\mu\text{-}H)$ moieties. Then the question is which one is more useful in a particular context. We trust that, in the case of our 30-electron complexes, the half-electron method still gives a picture in good agreement with the physicochemical properties of these species, while keeping simplicity. Without entering into a lengthy discussion on the matter, we would like to note that the unsaturated compounds **1** can display, depending on M and R , a second isomer (**1T**) having a terminal hydride and a linear semibridging carbonyl (Figure 2). Isomer **1T** coexists in solution with the hydride-bridged isomer when $M = W$ and $R = Cy$,^{3,4} while it is fully dominant when $M = Mo$ and $R = tBu$.⁵ The representation of the intermetallic interaction for this second isomer is a triple bond under all schemes, including the CBC method. Interestingly, the DFT-computed $M\text{-}M$ lengths and electron densities at the intermetallic bond critical point of isomers **1T** are almost identical to those of the corresponding hydride-bridged structures **1** (Table 1). Moreover these electron densities are comparable to the values computed for the respective $[M_2Cp_2(CO)_4]$ complexes at the same level of theory ($0.576 \text{ e}\text{\AA}^{-3}$ (Mo) and $0.652 \text{ e}\text{\AA}^{-3}$ (W)). All of the above points to the retention of substantial $M\text{-}M$ bonding character in the tricentric M_2H interaction at the hydride-bridged isomers, therefore the

formulation of M–M triple bonds seems a sensible choice for all these hydride complexes irrespective of the particular coordination (bridging or terminal) of the hydride ligand. In the end, if the properties of the hydride-bridged isomers **1** are similar to those of molecules with a conventional triple bond, why not draw three lines between the metal atoms?

Table 1: Selected DFT-data for isomers **1** and **1T** of hydride complexes $[M_2Cp_2H(\mu-PR_2)(CO)_2]$ (M = Mo, W).^a

<i>M, R</i>	Isomer 1		Isomer 1T	
	<i>M–M</i>	ρ	<i>M–M</i>	ρ
Mo, Cy	2.535	0.582		
Mo, ^t Bu	2.526	0.573	2.550	0.568
W, Cy	2.545	0.644	2.536	0.629

^a M–M distances in Å; electron densities at the intermetallic bond critical point (ρ) in eÅ⁻³. Data are taken from refs. 1, 3, 4 and 5.

References

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