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Metallocene Hydrides: Their Didactic Value for Teaching Organometallic Chemistry

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Abstract: Metallocene hydrides, Cp$_2$MH$_n$ (n=1-3), are complexes known for elements of Groups 3 to 8. Their properties can be understood by the use of a common qualitative MO diagram.

Keywords: Acid-base properties · Bent metallocenes · Hydrido complexes · Lewis acids

Metallocene hydrides, complexes of composition Cp$_2$MH$_n$ (Cp = η^5-cyclopentadienyl, n = 1-3) are a special class of metallocenes, known for elements of Group 3, including the lanthanoids, through Group 8. I will argue in this column (almost a tutorial) that these compounds convey a high instructional value. Their reactivities – *e.g.* from highly hydridic to highly acidic, from Lewis acidic, to essentially neutral, to basic – follow clear trends across the corresponding section of the Periodic Table. These trends can be easily understood and rationalized by applying a common qualitative MO diagram.

Metallocenes – MCp$_2$ – are prototypical organometallic compounds, known for the vast majority of the metallic elements. It is therefore obvious that their more or less in-depth treatment in any not only introductory course in organometallic chemistry is a must. Following the serendipitous discovery of ferrocene (FeCp$_2$) in 1951[1] they have soon become the object of intensive research efforts and constitute nowadays a source of disparate (possible) applications, from catalysts to metallodrugs. So-called bent metallocenes were discovered in the 1950's. These are derivatives having typically one to three additional ligands (2e-donors) attached to the metal center of the MCp$_2$ unit, leading to a molecular geometry in which the planes of the two Cp ligands are no longer parallel to each other, hence 'bent'. The additional ligands may be neutral, such as in *e.g.* Cp$_2$Mn(PMe$_3$), or anionic, such as in Cp$_2$TiCl$_2$. The hydrido complexes Cp$_2$ReH, Cp$_2$WH$_2$, Cp$_2$MoH$_2$, and Cp$_2$TaH$_3$ were among the first bent metallocenes, discovered more than 60 years ago.[2]

The electronic structure of bent metallocenes were first analyzed by Lauher and Hoffmann in their classical paper of 1976[3] and were revisited by Jennifer Green in 1998.[4] Starting from an MO description of an undistorted metallocene, the bending results in three new metal-centered frontier orbitals that may then be involved in bonding to up to three additional ligands. Depending on the total number of valence electrons (VE) and the number of additional ligands of Cp$_2$ML$_n$, these orbitals may be bonding or non-bonding and fulfill the role of HOMO or LUMO, respectively. Fig. 1 shows the three key orbitals as in the original paper of Lauher and Hoffmann, leading to the qualitative MO diagrams used in Fig. 2. Fig. 2 further collects examples of known complexes of the type Cp$_2$MH$_n$ with specific key structural parameters, ^{1}H NMR chemical shift of the hydrido ligand(s), and typical reactivity properties, not necessarily mentioned here. It is therefore a summary that can be used when teaching an organometallic chemistry course.

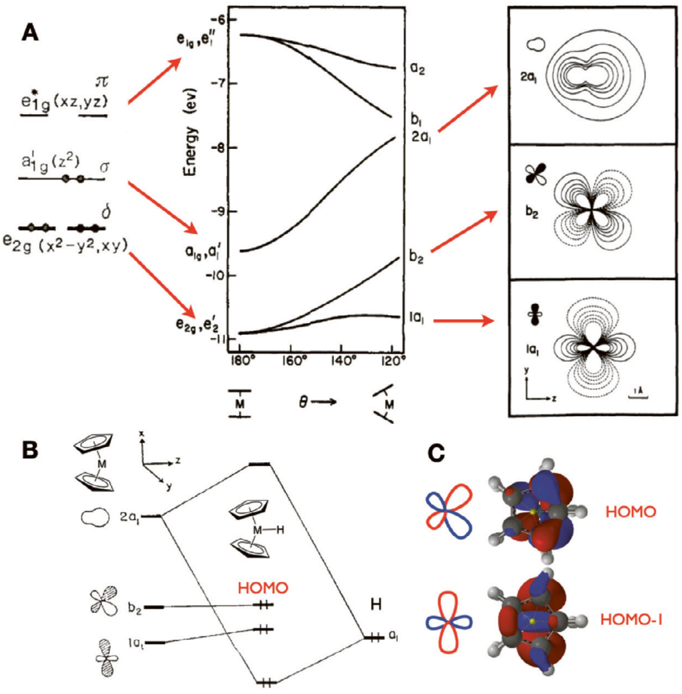


Fig. 1. A: Frontier orbitals in an undistorted metallocene (left), their energy levels as a function of bending (center) and contour plots of the three key orbitals in a bent metallocene. B: MO diagram for Cp$_2$MH. C: shapes of calculated HOMO and HOMO-1 for Cp$_2$ReH (DFT ωB97X-D 6-311G*, Spartan'24, Wavefunction, Inc., Irvine, CA). A and B reproduced with permission and adapted from ref. [3].

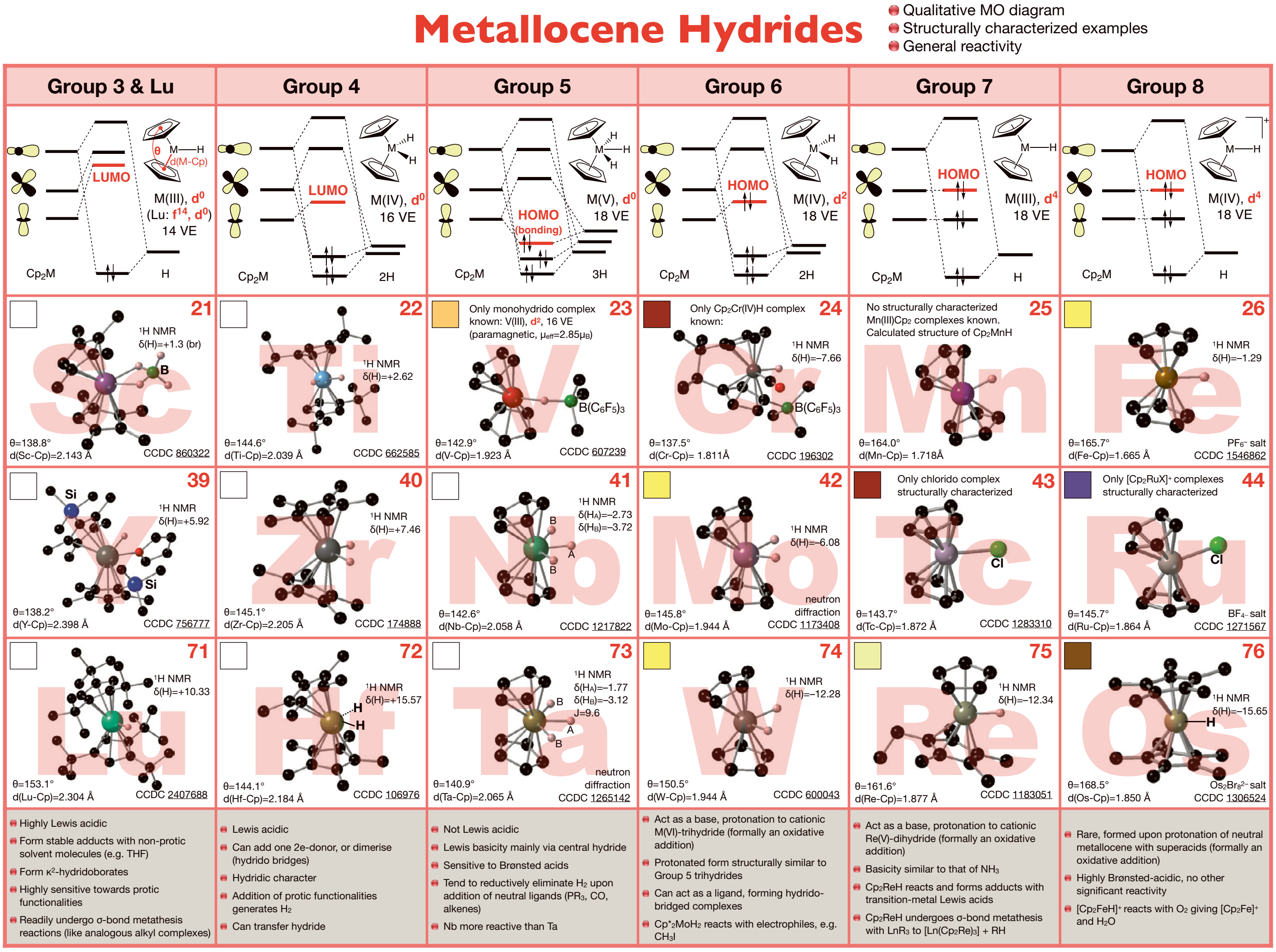
Group 3 metals and the lanthanoids in the formal oxidation state III form d^0, 14 VE complexes of composition Cp$_2$MH, whereas Group 4 elements form d^0, 16 VE complexes of the type Cp$_2$MH$_2$, thus both are coordinatively unsaturated. Hence, by virtue of their a$_1$ molecular orbital being the LUMO, they display Lewis acidic character and may add one additional ligand. In fact, Group 3 and Ln derivatives are highly Lewis acidic and can mostly be isolated only in dimeric form with the hydrido ligands in bridging position.[5] They are also known to voraciously retain coordinating solvent molecules and boro- and aluminohydrides adopt as ligands a κ^2 coordination mode (see examples for Y and Sc, respectively, in Fig. 2). The only way to avoid this is to make the Cp ligands extremely bulky, well beyond the limits of Cp* (pentamethylcyclopentadienyl). Indeed, the only Cp ligand known to stabilize corresponding monomeric 14 VE complexes is 1,2,4-tris(*tert*-butyl)cyclopentadienyl. Thus, as an example, (*t*-Bu$_3$Cp)$_2$LuH has been reported very recently.[6]

For Group 5 metals one can imagine either the d^2, 16 VE $Cp_2M^{III}H$ complexes or the d^0, 18 VE Cp_2MVH_3 species, and both indeed exist.[7] However, the monohydrides of Nb and Ta are only known as coordinatively saturated $Cp_2MH(L)$ complexes, with typical neutral ligands L such as *e.g.* CO or alkenes (for vanadium there is only one complex known, see Fig. 2). These species may form from the trihydrides by reductive elimination of H_2 in the presence of L. The trihydrides have used up the three original frontier orbitals for bonding, hence they no longer possess non-bonding metal-centered orbitals (the HOMO is a bonding and the LUMO is an anti-bonding orbital). Thus, they do not display any specific acidic or basic properties, as compared to their neighbours.

The two Group 6 metals Mo and W form d^2, 18 VE $Cp_2M^{IV}H_2$ complexes. The corresponding Cr species is not known and the only Cr^{IV} chromocene hydrido complex known is the zwitterionic species shown in Fig. 2.[8] Cp_2MoH_2 and Cp_2WH_2 can act as a base and are readily protonated by Brønsted acids, thereby giving the cationic trihydrides $[Cp_2(Mo/W)H_3]^+$, isoelectronic to $Cp_2(Nb/Ta)H_3$. Note that this protonation reaction formally corresponds to an oxidative addition. At first sight, this may seem to be a rather peculiar property. However, this typical reactivity is a consequence of the fact that the two neutral dihydrides now display a non-bonding, occupied metal-centered orbital as the HOMO. This not only explains the observed basicity of Cp_2MoH_2 and Cp_2WH_2 but can also be invoked to understand the behaviour of these two complexes as *ligands* in corresponding hetero bi- and trimetallic complexes, usually formulated as species with bridging hydrido ligands. Scheme 1 shows complexes formed by Cp_2WH_2 with Ag^+[9] and Au^+,[10] as well as with Pt(II)[11] and Ir(I)[12] coordinatively unsaturated fragments. In the latter case, the primary adduct undergoes an intramolecular C-H oxidative addition. Furthermore, it is not surprising that Cp_2WH_2 also reacts with a Lewis acidic metallocene hydride such as the dimeric $[Cp^*_2SmH]_2$.[13] In this case, however, the primary adduct undergoes a σ-bond metathesis leading to a Cp C-H activation under elimination of H_2, also shown in Scheme 1.

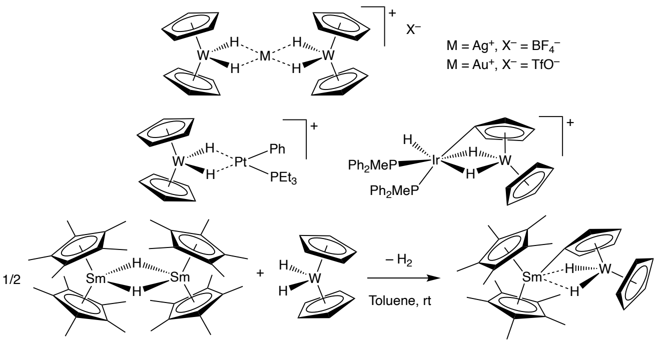
In Group 7 bent metallocene hydrides are only known for Re. In a similar way as to the relatives of Group 6, Cp_2ReH and its substituted derivatives are bases comparable in strength to NH_3 in aqueous systems. Cp_2ReH also forms adducts with a variety of Lewis acids, *e.g.* CuI leading to the formation of the tetranuclear complex $[Cp_2ReHCu(\mu\text{-}I)_2CuHReCp_2]$.[14] Furthermore, it forms Re-Ln bonds upon σ-bond metathesis with lanthanocene alkyl complexes.[15]

Group 8 metallocene chemistry is obviously dominated by ferrocene itself and its innumerable derivatives obtained by in-



Group 3 & Lu	Group 4	Group 5	Group 6	Group 7	Group 8
Highly Lewis acidic Form stable adducts with non-protic solvent molecules (e.g. THF) Form κ²-hydridoborates Highly sensitive towards protic functionalities Readily undergo σ-bond metathesis reactions (like analogous alkyl complexes)	Lewis acidic Can add one 2e-donor, or dimerise (hydrido bridges) Hydridic character Addition of protic functionalities generates H_2 Can transfer hydride	Not Lewis acidic Lewis basicity mainly via central hydride Sensitive to Brønsted acids Tend to reductively eliminate H_2 upon addition of neutral ligands (PR_3, CO, alkenes) Nb more reactive than Ta	Act as a base, protonation to cationic M(VI)-trihydride (formally an oxidative addition) Protonated form structurally similar to Group 5 trihydrides Can act as a ligand, forming hydrido-bridged complexes $Cp^*_2MoH_2$ reacts with electrophiles, e.g. CH_3I	Act as a base, protonation to cationic Re(V)-dihydride (formally an oxidative addition) Basicity similar to that of NH_3 Cp_2ReH reacts and forms adducts with transition-metal Lewis acids Cp_2ReH undergoes σ-bond metathesis with LnR_3 to $[Ln(Cp_2Re)_3]$ + RH	Rare, formed upon protonation of neutral metallocene with superacids (formally an oxidative addition) Highly Brønsted-acidic, no other significant reactivity $[Cp_2FeH]^+$ reacts with O_2 giving $[Cp_2Fe]^+$ and H_2O

Fig. 2. Section of the Periodic Table, Groups 3 (with Lu as a representative of the lanthanoids) to 8, whose elements are known to form bent metallocene hydrido complexes. For each element a known structurally characterized example is given. The structure representations have been generated with Crystal Maker®, omitting for clarity all hydrogen atoms, except hydrido ligands. Following information is provided for each complex: Cp centroid – M – Cp centroid angle (θ), M – Cp centroid average distance (d(M-Cp)), ¹H NMR chemical shift of hydrido ligand(s), observed color, and CCDC deposition number linked to the corresponding journal article. Furthermore, for each Group a qualitative MO diagram and a summary of the typical reactivity are given.[16]



Scheme 1. Hydrido-bridged complexes formed by the reaction of Cp_2WH_2 acting as a ligand for various metal fragments.

troducing substituents onto the Cp rings. However, the cationic M(IV) hydrides $[Cp_2FeH]^+$ and $[Cp^*_2OsH]^+$ (Fig. 2) are known to form under highly acidic conditions and are most likely strong Brønsted acids themself, though measurements of pK_a values have not been reported.

Finally, the key structural parameters used for the description of bent metallocenes, *i.e.* the angle θ formed by the two Cp centroids and the metal center as well as the distance d(M-Cp centroid) nicely follow expected trends. Fig. 3 collects corresponding calculated data for the unsubstituted systems Cp_2MH_n. From Group 3 to Group 8 the Cp_2M unit gradually shrinks and the degree of bending diminishes (angle θ increases).

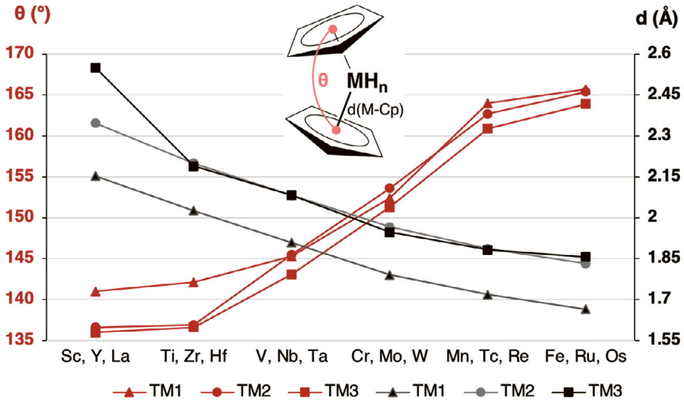


Fig. 3. Calculated values (DFT ωB97X-D 6-311G*, Spartan'24, Wavefunction, Inc., Irvine, CA) of the angle θ ($Cp_{centroid} – M – Cp_{centroid}$) and the distance d($M – Cp_{centroid}$) for unsubstituted Cp_2MH_n complexes; Cp_2MH_3 for Group 5; TM1-3 = transition-metal series 1-3.

In conclusion, metallocene hydrides indeed offer an opportunity to discuss not only specific aspects of their chemistry, but also to make connections to other more general concepts (*e.g.* acidity, basicity, periodicity, hydrido ligands, steric effects, lanthanide contraction, *etc.*). Thus, I think that they may fulfill a central exemplary role in teaching fundamental aspects of inorganic and organometallic chemistry, as they did over several years in my personal case.

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[1] For a very brief review, see: A. Togni, *CHIMIA*, **2021**, *75*, 805, https://doi.org/10.2533/chimia.2021.805

[2] Re: a) M.L.H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.* **1958**, *3916*, https://doi.org/10.1039/JR9580003916. W: b) M. L. H. Green, J. A. McCleverty, L. Pratt, G. Wilkinson, *J. Chem. Soc.* **1961**, 4854, https://doi.org/10.1039/JR9610004854. For an improved synthesis, see: c) M. L. H. Green, P. J. Knowles, *J. Chem. Soc. Perkin Trans. I* **1973**, 989, https://doi.org/10.1039/P19730000989.

[3] J. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 1729, https://doi.org/10.1021/ja00423a017.

[4] J. Green, *Chem. Soc. Rev.* **1998**, *27*, 263, https://doi.org/10.1039/A827263Z.

[5] S.-S. Liu, S. Gao, J. W. Ziller, W. J. Evans, *Dalton Trans.* **2014**, *43*, 15526, https://doi.org/10.1039/C4DT02194K.

[6] E. Papangelis, L. Demonti, I. del Rosal, A. Shephard, L. Maron, G. Nocton, T. Simler, *J. Am. Chem. Soc.* **2025**, *147*, 9752, https://doi.org/10.1021/jacs.4c18416.

[7] A. Antiñolo, F. Carrillo-Hermosilla, M. Fajardo, J. Fernández-Baeza, S. García-Yuste, A. Otero, *Coord. Chem. Rev.* **1999**, *193*, 43, https://doi.org/10.1016/S0010-8545(99)00164-2.

[8] P.-J. Sinnema, P. J. Shapiro, D. M. Jin Foo, B. Twamley, *J. Am. Chem. Soc.* **2002**, *124*, 10996, https://doi.org/10.1021/ja026633q.

[9] H. Brunner, M. Muschiol, T. Neuhierl, B. Nuber, *Chem. Eur. J.* **1998**, *4*, 168, https://doi.org/10.1002/(SICI)1521-3765(199801)4:1<168::AID-CHEM168>3.0.CO;2-N.

[10] L. Rocchigiani, W. T. Klooster, S. J. Coles, D. L. Hughes, P. Hrobárik, M. Bochmann, *Chem. Eur. J.* **2020**, *26*, 8267, https://doi.org/10.1002/chem.202000016.

[11] A. Albinati, R. Nägeli, A. Togni, L. M. Venanzi, *Organometallics* **1983**, *2*, 926, https://doi.org/10.1021/om50001a028.

[12] A. Albinati, A. Togni, L. M. Venanzi, *Organometallics* **1986**, *5*, 1785, https://doi.org/10.1021/om00140a005.

[13] N. S. Radu, P. K. Gantzel, T. D. Tilley, *J. Chem. Soc., Chem. Commun.* **1994**, 1175, https://doi.org/10.1039/C39940001175.

[14] V. K. Bel'sky, V. M. Ishchenko, B. M. Bulychev, G. L. Soloveichik, *Polyhedron* **1984**, *3*, 749, https://doi.org/10.1016/S0277-5387(00)88016-X.

[15] M. V. Butovskii, B. Oelkers, T. Bauer, J. M. Bakker, V. Bezugly, F. R. Wagner, R. Kempe, *Chem. Eur. J.* **2014**, *20*, 2804, https://doi.org/10.1002/chem.201304125.

[16] a) Sc, CCDC 860322: S. Demir, N. A. Siladke, J. W. Ziller, W. J. Evans, *Dalton Trans.* **2012**, *41*, 9659, https://doi.org/10.1039/C2DT30861D; b) Y, CCDC 756777: Y. Takenaka, Z. Hou, *Organometallics* **2009**, *28*, 5196, https://doi.org/10.1021/om900453j; c) Lu, CCDC 2407688: See ref. [6], https://doi.org/10.1021/jacs.4c18416; d) Ti, CCDC 662585: M. D. Walter, C. D. Sofield, R. A. Andersen, *Organometallics* **2008**, *27*, 2959, https://doi.org/10.1021/om7012315; e) Zr, CCDC 174888: B. M. Kraft, R. J. Lachicotte, W. D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 10973, https://doi.org/10.1021/ja016087l; f) Hf, CCDC 106976: P. J. Chirik, M. W. Day, J. E. Bercaw, *Organometallics* **1999**, *18*, 1873, https://doi.org/10.1021/om9810293; g) V, CCDC 607239: R. Choukroun, C. Lorber, L. Vendier, C. Lepetit, *Organometallics* **2006**, *25*, 1551, https://doi.org/10.1021/om050965x; h) Nb, CCDC 1217822: R. D. Wilson, T. F. Koetzle, D. W. Hart, A. Kvick, D. L. Tipton, R. Bau, *J. Am. Chem. Soc.* **1977**, *99*, 1775, https://doi.org/10.1021/ja00448a016; i) Ta, CCDC 1265142: See ref. [16 h], https://doi.org/10.1021/ja00448a016; j) Cr, CCDC 196302: See ref. [8], https://doi.org/10.1021/ja026633q; k) Mo, CCDC 1173408: A. J. Schultz, K. L. Stearley, J. M. Williams, R. Mink, G. D. Stucky, *Inorg. Chem.* **1977**, *16*, 3303, https://doi.org/10.1021/ic50178a063; l) W, CCDC 600043: M. H. Chisholm, J. C. Gallucci, C. B. Hollandsworth, *Inorg. Chem. Commun.* **2006**, *9*, 982, https://doi.org/10.1016/j.inoche.2006.04.035; m) Tc, CCDC 1283310: C. Apostolidis, B. Kanellakopulos, R. Maier, J. Rebizant, M. L. Ziegler, *J. Organomet. Chem.* **1990**, *396*, 315, https://doi.org/10.1016/0022-328X(90)85473-C; n) Re, CCDC 1183051: R. A. Paciello, P. Kiprof, E. Herdtweck, W. A. Herrmann, *Inorg. Chem.* **1989**, *28*, 2890, https://doi.org/10.1021/ic00313a037; o) Fe, CCDC 1546862: M. Malischewski, K. Seppelt, J. Sutter, F. W. Heinemann, B. Dittrich, K. Meyer, *Angew. Chem. Int. Ed.* **2017**, *56*, 13372, https://doi.org/10.1002/anie.201704854; p) Ru, CCDC 1271567: M. Watanabe, I. Motoyama, M. Shimoi, H. Sano, *J. Organomet. Chem.* **1996**, *517*, 115, https://doi.org/10.1016/0022-328X(96)06119-0; q) Os, CCDC 1306524: C. L. Gross, S. R. Wilson, G. S. Girolami, *Inorg. Chem.* **1995**, *34*, 2582, https://doi.org/10.1021/ic00114a015.

Addition/Correction: July 24, 2025

The statement "However, the cationic M(IV) hydrides $[Cp_2FeH]^+$ and $[Cp^*_2OsH]^+$ (Fig. 2) are known [...], though measurements of pK_a values have not been reported." (top of p. 453) is partly incorrect. It has been brought to my attention by Prof. Robert H. Morris that pK_a values for $[Cp^*_2OsH]^+$ and $[Cp^*_2RuH]^+$ have in fact been reported. See: A. Pedersen, V. Skagestad, M. Tilset, *Acta Chem. Scand.* **1995**, *49*, 632, https://doi.org/10.3891/acta.chem.scand.49-0632. See also: R. H. Morris, *Chem. Rev.* **2016**, *116*, 8588, https://doi.org/10.1021/acs.chemrev.5b00695.