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Structural preference in complexes containing both double-face and single-face π-acceptor ligands

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Abstract

The development of the Dewar–Chatt–Duncanson model has a great impact on coordination/organometallic chemistry in terms of understanding the structure and bonding in metal complexes containing π-accepting ligands. The majority of π-acceptor ligands can be categorized into two types: double-face and single-face π-accepting ligands. Metal complexes containing both single-face and double-face π-accepting ligands show unique structural preferences. In this paper, the structural consequence for these complexes will be discussed with the aid of density functional theory calculations. Examples include η^1-alkenyl, η^2-silane, η^2-alkene and boryl octahedral complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Competition for π-backdonation; Metal–alkene complexes; Metal–alkenyl complexes; Metal–boryl complexes; Metal–silane complexes

1. Introduction

Nearly 50 years ago, the Dewar–Chatt–Duncanson model was developed to describe the bonding in metal–alkene complexes [1]. Over the last half century, the bonding model has played an extremely important role in understanding the structure and bonding in coordination/organometallic compounds [2–4]. The Dewar–Chatt–Duncanson type of interaction emphasizes both a σ-type donation from the alkene's filled π orbital to an empty metal d orbital and a concomitant π-type backdonation from a filled metal d orbital to the alkene's empty π* orbital. In addition to the metal–alkene complexes, metal–carbonyl interactions also overwhelmingly involve the ligand-to-metal σ bonding and metal-to-ligand dπ backdonation because CO is a strong π-accepting ligand. The difference between carbonyl and alkene ligands is that carbonyl has two π* orbitals capable of having backbonding interactions with the metal center while an η^2-alkene ligand has only one. Ligands having two perpendicular π* orbitals that are capable of backbonding interactions with metal d orbitals have been called as double-face π-accepting ligands such as CO, NO, and CN^-, etc. Ligands such as η^2-olefin and η^1-alkenyl have only one π* orbital available for π-interaction with the metal center and are defined as single-face π-accepting ligands.

A great number of metal complexes containing both types of ligands have been synthesized and structurally characterized. Because of the presence of both types of π-accepting ligands, for these complexes optimal π-backbonding interactions are expected in order to achieve structural stability. In this paper, we wish to discuss the structural consequences for complexes containing both single-face and double-face π-accepting ligands. Examples used for our discussion include η^1-alkenyl, η^2-silane, η^2-alkene and boryl octahedral complexes having d^6 electron configuration of the metal center. Sections related to the η^1-alkenyl and η^2-silane complexes summarize our previous studies [5,6] while sections related to the metal–η^2-alkane and boryl complexes are dealt with in the present study.

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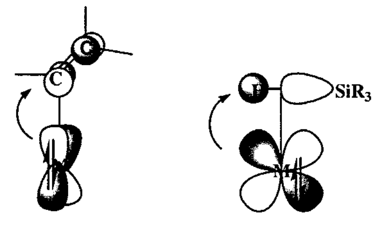
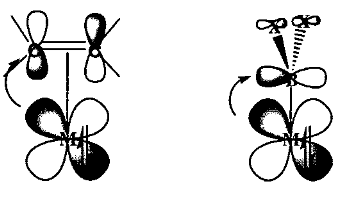
2. Computational details

In Sections 3.1 and 3.2, we summarize our previous studies reported in the literature [5,6]. These studies were based on calculations at the MP2 level. In Sections 3.3 and 3.4, we report the current studies based on density functional theory (DFT) calculations at the B3PW91 level. The Hay and Wadt effective core potentials (ecp) with a double-zeta valence basis were used to describe the transition metal atoms and main group atoms of period three, while the standard 6-31G basis set was used for all the other atoms. All calculations were performed with the use of gaussian 98 [7].

The reasons for the use of DFT instead of MP2 calculations can be described as follows. Several testing studies reported previously [8] showed that both DFT and MP2 calculations give similar results in terms of structural parameters and relative energies in systems that we have been interested in. As it is well known, MP2 calculations are more demanding in computational resources. Therefore, it is preferable to perform DFT calculations. Within the DFT methods, we found that the B3PW91 level gives slightly better results in the calculated structural parameters for some systems containing metal–boron interactions [9].



(a) Metal-η^1-alkenyl (b) Metal-η^2-silane



(c) Metal-η^2-alkene (d) Metal-boryl

Fig. 1. The π symmetry fragment orbitals of (a) alkenyl; (b) η^2-silane; (c) η^2-alkene and (d) boryl ligands for metal backbonding interactions.

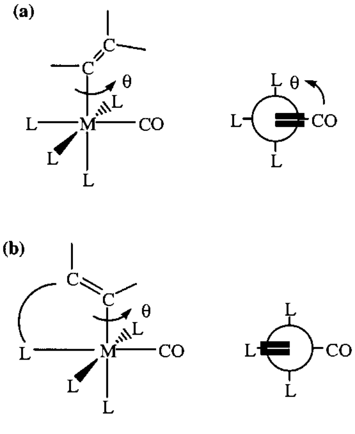


Fig. 2. A Newman projection diagram for the definition of θ in coplanar orientation: (a) $\theta = 0°$; (b) $\theta = 180°$ with chelating ligand (adapted from Ref. [5]).

3. Discussion

Ligands such as η^1-alkenyl, η^2-silane, η^2-alkene and boryl are typical examples of single-face π-accepting ligands. Each of these ligands has only one low-lying empty orbital having π-symmetry with respect to the metal d orbitals. Fig. 1 illustrates how these empty orbitals interact with the relevant metal d orbitals. Since all the complexes discussed in this paper are pseudooctahedral and 18-electron species, they have the filled 't_{2g}' orbitals corresponding to d^6 electron configurations. These filled 't_{2g}' orbitals are responsible for the backbonding interactions with the low-lying empty ligands' orbitals mentioned above. In the following sections, we will develop specific examples according to the types of single-face π-accepting ligands.

3.1. Metal–η^1-alkenyl complexes

Carbonyl-containing η^1-alkenyl complexes are examples having both types of π-accepting ligands. These complexes are important because of their relevance to organometallic synthesis and catalysis [10]. In a previous study [5], it was found that the majority of the alkenyl complexes prefer a coplanar orientation of the alkenyl and carbonyl ligands. There is a general trend for alkenyl complexes containing one or two carbonyl ligands to adopt structures with θ close to 0° (see Fig. 2a) unless a chelating ligand is present in the complex, in which case θ is close to 180° (see Fig. 2b).

The preference for coplanarity has been explained by maximum utilization of metal d orbitals for backbonding interaction with both the alkenyl and carbonyl ligands. Fig. 3 shows that with the coplanar orientation, the d_{yz} and d_{xy} orbitals from the metal center interact with the two perpendicular π* orbitals of the CO ligand, while the d_{xz} orbital interacts with the alkenyl π* orbital. This orientation provides an optimal situation for the maximum backbonding interactions between the metal center and both the alkenyl and carbonyl ligands. Deviation from such a coplanar orientation leads to the sharing of d orbitals for backbonding interactions between the alkenyl and carbonyl ligands, results in competition for backdonation, and consequently gives rise to the structural instability.

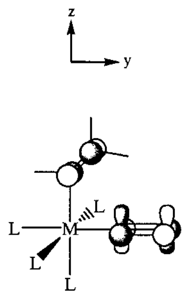


Fig. 3. Coplanar orientation (only $\theta = 0°$ is shown) of the π^* orbitals of the alkenyl and carbonyl ligands relative to the metal atom (adapted from Ref. [5]).

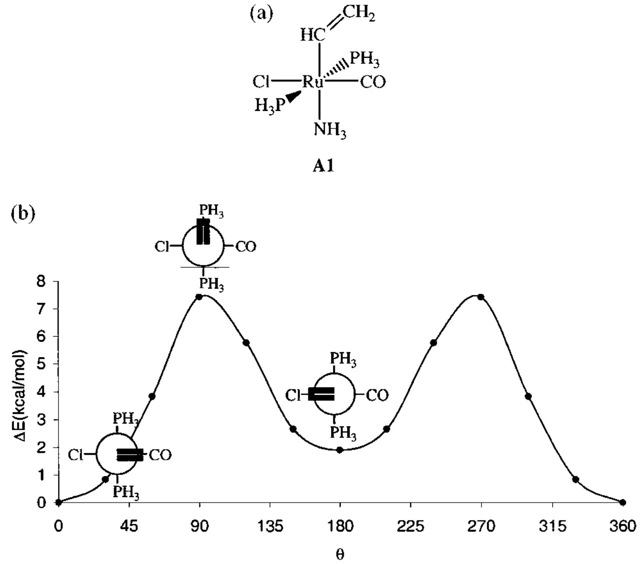


Fig. 4. (a) Structure of **A1**. (b) Potential energy surface for **A1** showing the change in relative energy ΔE (kcal mol^{-1}) with respect to θ (°) (adapted from Ref. [5]).

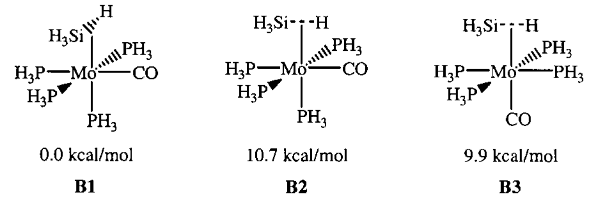


Fig. 5. The structure of $(PH_3)_4Mo(CO)(H\cdots SiH_3)$ **B1**, its orientational isomer **B2** and its *trans* isomer **B3** and their relative energy.

Indeed, the energetics of alkenyl rotation reported for the model complex *cis*-$(PH_3)_2RuCl(NH_3)CO(CH{=}CH_2)$ **A1**, shown in Fig. 4, give two minima corresponding to the coplanar orientations ($\theta = 0$ or 180°) and two maxima corresponding to the perpendicular orientations ($\theta = 90$ or 270°). The barrier to rotation is approximately 7.4 kcal mol^{-1} [5].

Theoretical studies on alkenyl complexes with more than one CO ligands have also been done [5]. The preference for coplanarity is largest when the complex contains only one or two carbonyl ligands. As the number of carbonyl ligands is increased, no orientation of the alkenyl ligand results in overall favorable interactions as the carbonyl ligands essentially compete with each other for the metal 't_{2g}' orbitals. In these complexes steric factors dominate and the alkenyl ligand adopts a position which results in minimized steric interactions with other ligands [5].

3.2. Metal–η^2-silane complexes

Silane complexes with the H–Si σ bond coordinated to the metal center have long been suggested as possible intermediates of hydrosilation [11]. The existence of the H···Si interaction in hydrosilyl complexes has been recognized since 1969 [12]. An extended Hückel theoretical study on the model system $MnCp(CO)_2(H\cdots SiH_3)$ [13] suggested that the metal–η^2-silane interaction is similar to the Dewar–Chatt model for the well-known π complexes, the Si–H filled σ bonding orbital donation to a metal empty d orbital and metal filled d orbital backdonation to the Si–H σ^* antibonding orbital. On comparing with the non-classical η^2-H_2 complexes, the η^2-silane ligand is rather a strong σ^* acceptor due to the presence of the low-lying σ^* orbital and can be viewed as a single-face π-accepting ligand.

Previous study [6] showed that the orientation of the Si–H bond is affected by the presence of other π acceptor ligands (e.g. CO). Theoretical calculations on the model complex *cis*-$Mo(CO)(PH_3)_4(\eta^2\text{-}H\cdots SiH_3)$ **B1** (see Fig. 5) have been done [6]. The calculated structure reproduces its corresponding experimental complex *cis*-$Mo(CO)(dppe)2(\eta^2\text{-}H\cdots SiHPh_2)$ quite well [14] in which the H···Si moiety and CO are mutually perpendicular to each other. A hypothetical orientation isomer **B2** (see Fig. 5) in which the H···Si moiety is coplanar with the CO bond has been studied. Structure **B2** has an energy 10.7 kcal mol^{-1} higher than that of **B1** [6].

The destabilization of the coplanar orientation can be explained by the presence of competition for metal(d)-to-ligand π-backdonation between the CO and

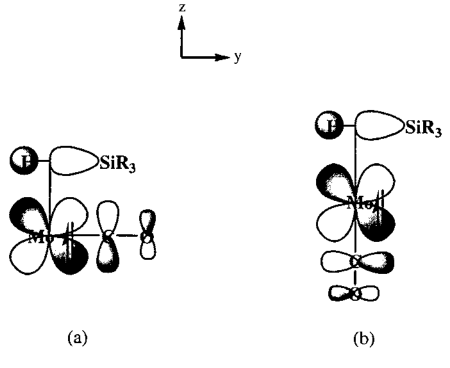


Fig. 6. Competition of the metal 't_{2g}' set of d orbital in (a) the orientation isomer **B2** and (b) the *trans* isomer **B3**.

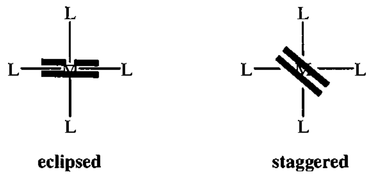


Fig. 7. Eclipsed and staggered conformations in pseudooctahedral ethylene metal complexes $ML_5(CH_2{=}CH_2)$. The eclipsed conformation is the preferred structure.

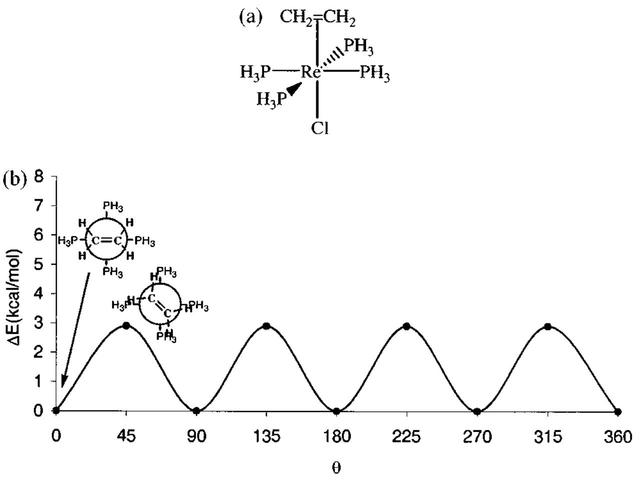


Fig. 8. (a) Structure of $(PH_3)_4ReCl(\eta^2\text{-ethene})$. (b) Potential energy surface for $(PH_3)_4ReCl(\eta^2\text{-ethene})$ showing the change in relative energy ΔE (kcal mol^{-1}) with respect to θ (°) (adapted from [17]).

η^2-H···Si ligands. Fig. 6a shows the sharing of d_{yz} in the π-interaction with both the σ* orbital of the η^2-H···Si ligand and one component of the carbonyl's π* orbitals, i.e. the competition for π-backdonation.

The perpendicular orientation gives no sharing of d orbitals in the π-interactions, having an optimal situation in which all the three 't_{2g}' orbitals interact with different empty orbitals of the two ligands (two with CO and one with H···Si). In contrast, if the H···Si moiety lies coplanar to the CO bond, the σ* orbital of the H···Si moiety will be forced to share one of the metal d orbitals (d_{yz}) with carbonyl. Indeed, the optimized structure of **B2** shows signs to a lesser extent of the Mo → H···Si σ* backbonding relative to the orientation isomer **B1** [6]. The carbonyl bond length and the H···Si distance are 0.01 and 0.06 Å shorter, respectively, than those of the isomer **B1** [6]. Theoretical study on another hypothetical *trans* isomer **B3** (see Fig. 5) has also been done [6]. This isomer is 9.9 kcal mol^{-1} higher in energy than the *cis* form **B1**. The destabilization of the *trans* isomer can be again explained by sharing the same d orbital for metal(d)-to-ligand backdonation between the carbonyl and H···Si ligands (see Fig. 6b).

3.3. Metal–η^2-alkene (metal–olefin) complexes

Zeise's salt $K[PtCl_3(CH_2{=}CH_2)]$ was the first metal–alkene complex that was synthesized. Since then, a lot of metal–alkene complexes have been studied and structurally characterized. These complexes have been proposed as intermediates in many catalytic reactions [15]. Previous theoretical studies [16,17] focused on the discussion of the structural preference for an eclipsed orientation (the C–C vector of the η^2-alkene ligand eclipses one of the L–M–L axes) rather than the staggered one (see Fig. 7). The structural preference has been explained through the stronger metal–alkene interaction [17] and the absence of having $4e^-$ destabilization interaction [16,18] in the eclipsed conformation.

In the eclipsed conformation, the mixing of metal p orbitals into d orbitals due to the metal–ligand distortion (L–M–L bends away from the η^2-alkene ligand) enhances the metal(d)-to-η^2-alkene (π*) backdonation [17]. In the staggered conformation, there is a $4e^-$ destabilization interaction between the alkene π bonding electrons and electrons from the d_{xy} orbital [16,18]. This is because the two orbitals (the π bonding orbital of the alkene ligand and the d_{xy} orbital of the metal center) accommodating the four electrons have the same symmetry in the staggered conformation. Fig. 8 illustrates the potential energy curve corresponding to the alkene's rotation in the model complex $(PH_3)_4ReCl(\eta^2\text{-ethene})$, clearly showing that the eclipsed conformations are preferred [17].

Fig. 9 shows several pseudooctahedral alkene complexes containing one or more than one carbonyl ligand [19–25]. In the presence of one carbonyl ligand (**C1** [19] and **C2** [20]), the alkene ligand prefers to lie perpendicular to the metal–CO bond ($\theta = 90°$) and eclipse the P–M–P unit. In the perpendicular orientation, each low-lying empty π* orbital of the CO and η^2-alkene ligands interacts with one d orbital, allowing the use of different d orbitals in the metal(d)-to-ligand π-backbonding interactions between the two π-accepting ligands [19,21–23]. Theoretical calculations have been carried on model complexes $(PH_3)_2OsH(OH)(CO)(CH_2{=}CH_2)$ **C2a** to study the structural preference. The calculated geometry is in good agreement with its corresponding experimental complex $(PPr^i_3)_2OsH(OH)(CO)[CH_2{=}CH(COOCH_3)]$ **C2** (see Fig. 10). The potential energy curve corresponding to the η^2-alkene rotation of **C2a** is shown in Fig. 10. The rotation barrier is about 7.8 kcal mol^{-1}. The maxima are found when the ethene ligand lies coplanar with the CO ligand ($\theta = 0$ and 180°).

In the complexes having three carbonyl ligands (**C3** [21], **C4** [22], **C5** [23]), the preference for a perpendicular orientation between the alkene's C–C vector and the OC–M–CO axis can also be observed. Model complex $(PH_3)_2(CO)_3W(CH_2{=}CH_2)$ **C3a** has been optimized and the calculated geometry is in good agreement with its corresponding experimental complex $(PCy_3)_2(CO)_3W(CH_2{=}CH_2)$ **C3** (see Fig. 11). The potential energy curve corresponding to the η^2-alkene rotation of **C3a** is shown in Fig. 11. Interestingly, we found that the potential energy curve differs significantly from the one shown in Fig. 10 for the case having one carbonyl ligand. Maxima are found when the C–C vector of the η^2-ethene ligand is in a staggered orientation with respect to the equatorial plane, instead of the coplanar orientations with the CO ligands ($\theta = 0$ and 180°).

To understand the different characteristics between the two potential energy curves shown in Figs. 10 and 11, we recall the potential energy curve in Fig. 8, showing the preferred eclipsed conformations which have stronger metal–alkene π-backdonation interactions. Fig. 11 represents a case in which all the eclipsed conformations correspond to a minima, and eclipsing the P–W–P axis (perpendicular to metal–carbonyl) is more preferred. In fact, one can view the potential energy curve of Fig. 11 as a result of summing the two curves of Figs. 8 and 10.

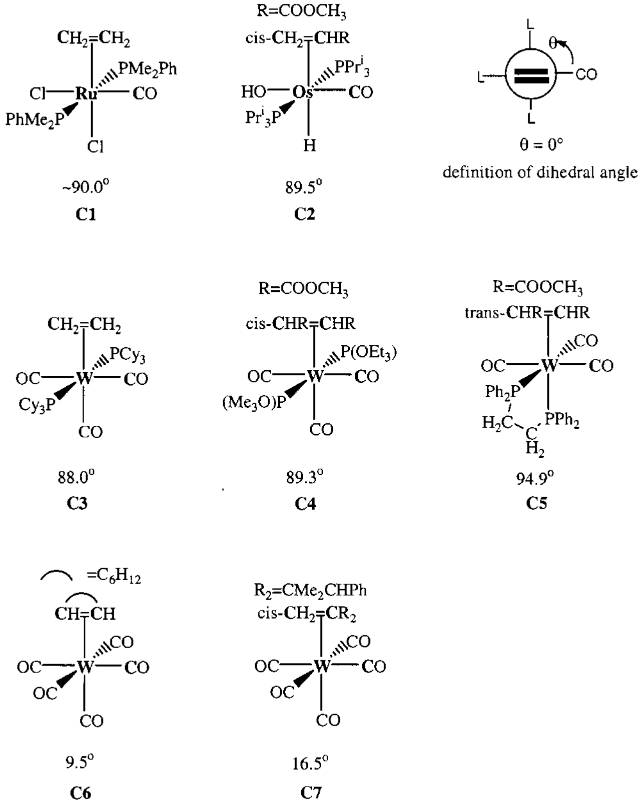


Fig. 9. Examples of transition metal–alkene complexes containing one or more than one carbonyl ligands and their corresponding alkene–carbonyl dihedral angle θ. The carbonyl used for the definition of θ corresponds to the one in the right side of each structural diagram.

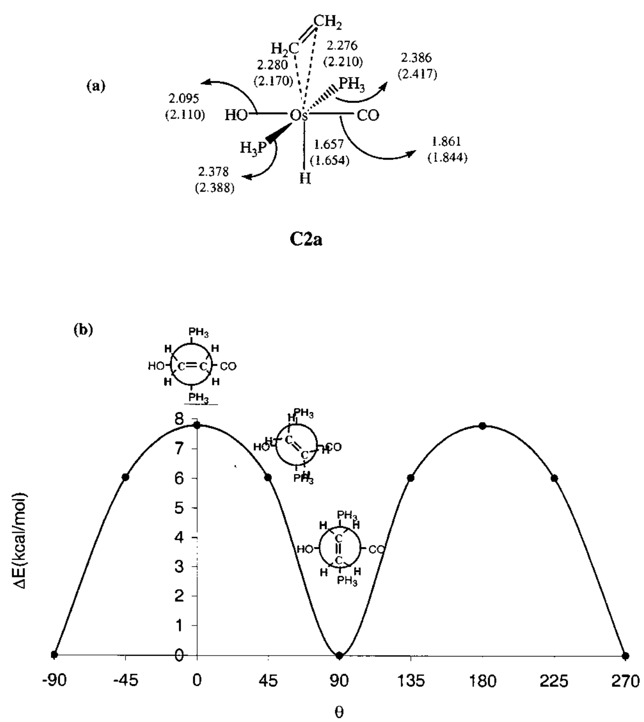


Fig. 10. (a) Structure of **C2a** together with selected calculated structural parameters. Data in parentheses are from the X-ray crystal structure of $(PPr^i_3)_2OsH(OH)(CO)[CH_2{=}CH(COOCH_3)]$ **C2** [14]. (b) Potential energy surface for **C2a** showing the change in relative energy ΔE (kcal mol^{-1}) with respect to θ (°).

Here, one might ask why $(PH_3)_2(CO)_3W(CH_2{=}CH_2)$ **C3a** shows different characteristics in the rotational potential energy curve in comparison to $(PH_3)_2OsH(OH)(CO)(CH_2{=}CH_2)$ **C2a**. Because of the presence of the *trans*-CO in **C3a**, it is expected that the metal–alkene bonding interactions are weaker. Therefore, the rotational barrier is reduced, leading to the observation that conformations in which the alkene ligand eclipses the OC–W–CO axis ($\theta = 0$ and 180°) also correspond to minima in the alkene's rotational potential energy curve. Careful examination of the potential energy curve for **C2a** (see Fig. 10) reveals substantial flattening in the ranges of $\theta = -45$ to 45° and $\theta = 135$ to 225°, indicating the tendency for the eclipsed conformations ($\theta = 0$ and 180°).

From the two examples discussed above, we can see that different ligand environments affect the alkenes' rotational behavior significantly. The extent of the metal–alkene backbonding interactions can also be affected by the substituents on the alkene ligand as well as the metal center. Previous D-NMR measurements of the barriers of rotation of the olefin ligands in tungsten–alkene complexes showed that the rotation barrier of methylmaleate is nearly double as that of ethylene [22]. For complexes having more than four carbonyls such as **C6** [24] and **C7** [25] in Fig. 9, the alkene ligand in each complex tends to eclipse one of the OC–W–CO axes as the competition factor no longer plays the role.

3.4. Metal–boryl complexes

The transition metal–boryl complexes $L_nM\text{–}BX_2$ have also attracted considerable interest [26] because of their role in metal catalyzed hydroborations [27] of unsaturated organic substrates and in the functionalization of unreactive C–H bonds [28]. It is generally accepted that the metal–boryl interaction is similar to the metal–carbene one, including σ bonding between an sp^2-hybridzed orbital in boron and a metal fragment orbital with appropriate symmetry as well as π backdonation from a filled metal fragment d orbital to the empty p orbital in boron [26]. However, the boron atom in a given boryl complex interacts not only with the metal center but also with substituents attached such as alkoxy or amino groups. It is believed that the boron-substituent (π donor) interaction is dominant and the donation from the alkoxy/amino groups destabilizes the empty p orbital [26a].

Fig. 12 shows several pseudooctahedral boryl complexes containing one or more than one carbonyl ligand [29–33]. Nearly half of the boryl complexes (**D1**–**D4**) orient the boryl ligand coplanarly with the *cis* CO ligand ($\theta = 0°$, see Fig. 12). The preference for the coplanarity can be explained by preventing the empty boryl ligand π* orbital and carbonyl ligand π* orbital from the use of the same d orbital in the metal(d) backbonding interaction. It should be noted that the preference is also expected if one considers the steric effect of the bulky phosphine ligands. For those complexes that do not show the similar structural preference, a possible explanation is as follows. The boryl ligand is probably not a strong π-accepting ligand because the empty p orbital in boron has been used to interact with the boron-substituents. The X-ray structure of the five-coordinate $(PMe_3)_4Rh(Bcat)$ complex [34] indicates that the Bcat ligand prefers an axial rather than equatorial site in a trigonal-bipyramidal geometry. Based on this structural arrangement, the Bcat ligand is believed to be a poor π-acceptor [34]. Theoretical calculations on model complexes $(PH_3)_2Os(CO)_2I[BO_2C_2H_2]$ **D5a** have been done. However, we fail to reproduce the experimental geometry of **D5**, instead the energy minimum corresponding to the perpendicular orientation ($\theta = 90.0°$) is found. Attempts at using different DFT methods did not change

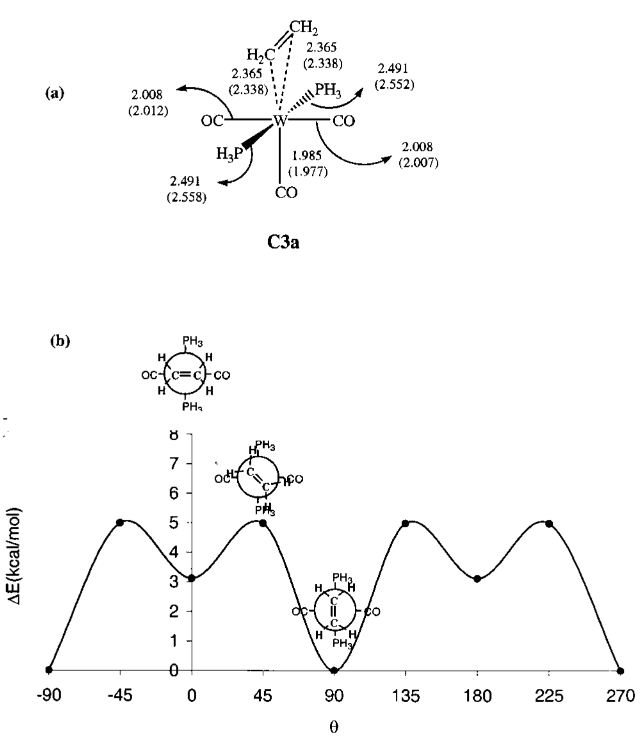


Fig. 11. (a) Structure of **C3a** together with selected calculated structural parameters. Data in parentheses are from the X-ray crystal structure of $(PCy_3)_2(CO)_3W(CH_2{=}CH_2)$ **C3** [15]. (b) Potential energy surface for **C3a** showing the change in relative energy ΔE (kcal mol^{-1}) with respect to θ (°).

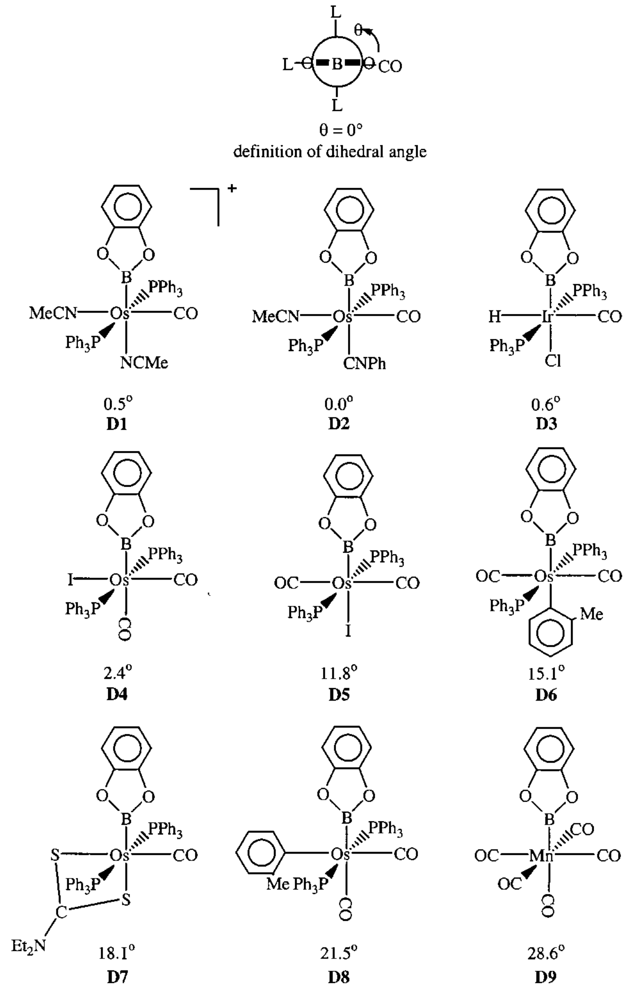


Fig. 12. Examples of transition metal–boryl complexes with one or more than one carbonyl ligands and their corresponding boryl–carbonyl dihedral angle θ. The carbonyl used for the definition of θ corresponds to the one in the right side of each structural diagram.

the results of our calculation. Currently, we do not have an explanation for the discrepancy between our theoretical calculations and the experimental observations. More studies are underway to understand the problem.

4. Summary

The Dewar–Chatt–Duncanson model has played an extremely important role in understanding the structure and bonding in coordination/organometallic compounds. The model describes the interaction between metal and π-acceptor ligands, emphasizing both ligand-to-metal σ bonding and metal(d)-to-ligand π backdonation. A variety of metal complexes containing both single-face and double-face π-accepting ligands show unique structural preferences. Examples of η^1-alkenyl, η^2-silane, η^2-alkene and boryl octahedral complexes involving both types of π accepting ligands have been discussed. The structural characteristics of these various types of complexes can be rationalized in terms of maximizing metal(d)-to-ligand π-backdonations. In order to achieve the maximum π-backdonation, the single-face ligand in a given complex tends to orient itself in such a way that the competition for backbonding interaction between π-accepting ligands can be avoided.

Acknowledgements

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