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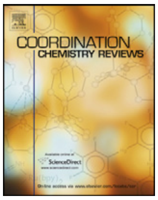

Review

Gallane-coordinated transition metal complexes and related compounds

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ABSTRACT

The gallane-Lewis base adduct $H_3Ga{\cdot}L$ is employed as a σ-Ga–H ligand for the group 6 carbonyl metal complexes $(OC)_5M(H_3Ga{\cdot}L)$ (M = Cr, Mo, W) and the manganese complex $Cp^*(OC)_2Mn(H_3Ga{\cdot}L)$. Group 6 carbonyl metal derivatives $(OC)_5M(H_3Ga{\cdot}L)$ are synthesized by the reaction of $(OC)_5M(THF)$ and $H_3Ga{\cdot}L$. The photochemical reaction of $Cp^*(OC)_3Mn$ and $H_3Ga{\cdot}L$ affords the gallane manganese σ-complex $Cp^*(OC)_2Mn(H_3Ga{\cdot}L)$. The structural properties of these complexes can be understood in terms of the coordination mode of σ-Ga–H bond to $(OC)_5M$ and $Cp^*(OC)_2Mn$ fragments being depicted as η^1-$HGaH_2{\cdot}L$ and η^2-$HGaH_2{\cdot}L$, respectively. The contribution of σ-donation from the Ga–H σ-bond to d_σ orbital on M occurs in both systems, however, the participation of π-back donation from filled d_π orbital to Ga–H σ* orbital is negligible for the $(OC)_5M(H_3Ga{\cdot}L)$ complexes but important for $Cp^*(OC)_2Mn(H_3Ga{\cdot}L)$ complex. Such distinctive characteristics of the σ-$H_3Ga{\cdot}L$ ligand provides a sharp contrast to that of $H_3B{\cdot}L$ and silane ligands.

1. Introduction

Transition metal σ-complexes containing M–H–E 3c2e bonding (M = transition metal, E = H, B, Si, C, etc.) are an essential and fascinating class of compound from both the structural and bonding viewpoint [1]. These complexes are also informative as model compounds for the proper interpretation of E–H bond activation processes, which are relevant in the transition metal-mediated or -catalyzed addition of E–H bond to a variety of organic and inorganic substrates [2]. The M–H–E 3c2e interactions are constructed with σ-donation from σ-E–H bond to empty d_σ orbital on M and π-back donation from filled d_π orbital on M to E–H σ* orbital (Fig. 1). The simplest σ-complex is the dihydrogen-coordinated complex first reported by Kubas et al. in 1984. This first report stimulated this field and H_2 σ-complexes of nearly every transition metal (V to Pt), including one lanthanide metal, have been synthesized [3,4]. The H_2 molecule has electrons only in the H–H σ-bond. The structure and stability of H_2 σ-complexes thus strongly depend on the electronic and steric effect of L_nM (L = ligand). For example, most of the H_2 σ-complexes include a cationic metal center and weakly donating ligands to avoid strong π-back donation from L_nM to the H_2 σ* orbital, otherwise, cleavage of the H–H bond would occur to afford the dihydride complexes H–M–H. Hydrosilanes (H–SiR_3, R = H, alkyl, aryl, etc.) can also bind to L_nM to form stable σ-complexes L_nM(H–SiR_3) [5]. The nature of Si–H bond is different from that of the H–H bond in the following way; the Si–H bond is polarized and the Si atom bears substituents. Structure and stability of silane σ-complexes are thus affected by both metal fragment L_nM and substituents on Si. Hydrosilanes appear to be both better σ-donors and π-acceptors in comparison

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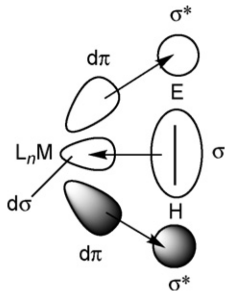
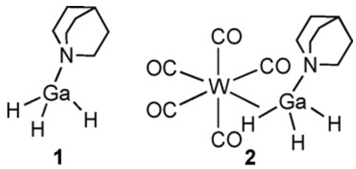


Fig. 1. Bonding model for E–H σ-complex.



1 2

Fig. 3. H_3Ga·quinuclidine (**1**, left) and the first gallane σ-complexes (**2**, right).

to H_2 [5]. In most $R_3Si–H$ σ-complexes isolated so far, the Si–H bond is further along the reaction coordinate toward oxidative addition than for H_2 binding. This situation is well illustrated in $RuH_2\{(HSiR_2)_2X\}(PCy_3)_2$ (Cy = cyclohexyl), $Mo(PP)_2(CO)(H–SiR_3)$ (PP = diphosphine), and $Cp'Mn(CO)(L)(H–SiR_3)$ $Cp' = \eta^5$-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*), η^5-C_5H_4Me (Cp^{Me})) systems [5d,6,7].

Much less attention has been concentrated on σ-complexes with group 13 hydrides except for boron. The coordination chemistry of the tetrahydroborate ion (BH_4^-) has been developed for several decades [8]. Bidentate and tridentate BH_4^- ligands are usually bound in the BH_4^--coordinated complexes and rare examples have been known with a monodentate BH_4^- ligand. The borane-Lewis base adduct $H_3B·L$ is isoelectronic to BH_4^- ion but normally interacts with L_nM through only one σ-B–H bond. The first σ-complexes of a monoborane-Lewis base adduct $(OC)_5M(H_3B·L)$ (M = Cr, W; L = PMe_3, PPh_3, NMe_3) were synthesized in 1994 (Fig. 2) [9]. Experimental and theoretical investigation revealed that σ-B–H coordination for M is dominated by σ-donation from the B–H bond and π-back donation from the metal to B–H σ* orbital is negligible [10]. Hartwig et al. reported the synthesis and bonding structure of σ-B–H complexes with a neutral 3-coordinated borane ligand $Cp_2Ti(HBcat)_2$ (HBcat = catecholborane) and related complexes [11]. In this type of complex, π-back donation from Ti is reported to be important, however, the orbital accepting electrons is an empty boron p orbital rather than B–H σ* orbital [11c]. In contrast to the development of borane σ-complexes, heavier group 13 analogues, alane and gallane σ-complexes have rarely been investigated, although numerous examples are known for transition metal complexes containing penta- and hexacoordinate AlH_n fragments [12]. No reports have appeared on the synthesis of σ-In–H and σ-Tl–H complexes. A practical reason for the σ-Al–H and σ-Ga–H complexes remaining unexplored is that handling of alane and gallane compounds is somewhat troublesome since these compounds are easily decomposed by disproportionation or hydrolysis with a trace amount of H_2O. In 1989, Porschke et al. reported the reaction of $Ni(cdt)_2$ (cdt = cyclododecatriene) with HMe_2Al·quinuclidine affording the first alane σ-complex $(cdt)Ni(HAlMe_2$·quinuclidine) (Fig. 2) [13]. The second alane-coordinated σ-complex Cp_2Zr(2-vipy)(HAl^iBu_2) (2-vipy = 2-vinylpyridine) was prepared by the reaction of zirconium complex Cp_2Zr(2-vipy) and $^iBu_2AlH$ [14]. In this complex, the Al and Zr atoms are bridged by the Zr–H–Al 3c2e bond and the 2-vipy group. For gallane, Atwood and coworkers reported the synthesis of thermally stable gallane-Lewis base adduct H_3Ga·quinuclidine (**1**) in 1991 (Fig. 3) [15]. The isolation and characterization of the first gallane σ-complex was accomplished in 2002 by our group utilizing the gallane **1** as ligand (Fig. 3) [16].

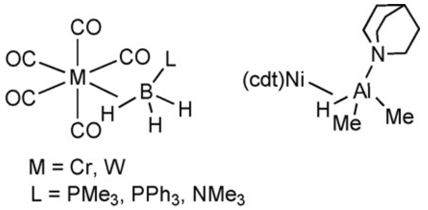


Fig. 2. The first $H_3B·L$-coordinated (left) and alane σ-complex (right).

This review focuses on the synthesis, structure, and reactivity of σ-complexes with gallane-Lewis base adduct **1** and borane-Lewis base adducts and related σ-complexes. In this review, the coordination mode of σ-E–H bond to L_nM is noted as η^n (n = 1 or 2), in which η^1 is applied for σ-complexes with weak or negligible M–E interaction and η^2 is appropriate for those with a strong M–E interaction (Fig. 4). The σ-Si–H bond and σ-B–H bond in $H_3B·L$ ligand generally coordinate with η^2- and η^1-fashion, respectively, while σ-Ga–H bond in $H_3Ga·L$ ligand shows both η^2- and η^1-coordination depending on the electronic and steric properties of the metal fragments used. In Tables 1–4, we summarize ^1H NMR chemical shifts of bridging and terminal hydrogen atoms and ν(CO) in the IR spectrum of gallane σ-complexes and other E–H σ-complexes with $(OC)_5M$ (M = Cr, Mo, W) and $Cp'(OC)_2Mn$ fragments (Cp′ = Cp, Cp*, Cp^{Me}).

2. Gallane σ-complexes

2.1. Synthesis and structure of monometallic gallane σ-complexes

The first gallane σ-complex $(OC)_5W(H_3Ga$·quinuclidine) (**2**) was synthesized by photochemical reaction of $W(CO)_6$ and H_3Ga·quinuclidine (**1**) in low yield (9%) [16]. The yield of **2** was improved to 39% by the thermal reaction of $(OC)_5W(THF)$ with **1** in THF (Eq. (1)). In a similar manner, molybdenum and chromium complexes $(OC)_5M(H_3Ga$·quinuclidine) (**3**; M = Mo, **4**; M = Cr) were obtained from the reaction of the corresponding $(OC)_5M(THF)$ and **1** in 38 and 23% yield, respectively (Eq. (1)) [17]. Crystal structure analysis revealed that H_3Ga·quinuclidine (**1**) coordinates to $(OC)_5M$ fragment via a Ga–H bond to form the M–H–Ga 3c2e bond (Fig. 5). The M–Ga interatomic distances in **2** (3.0194(5) Å) and **3** (3.0252(7) Å) are longer than the usual M–Ga single bonds (W; 2.71–2.76, Mo; 2.58–2.73 Å) [32,33]. The Cr–Ga interatomic distance in **4** (2.8969(9) Å) is longer than the sum of the metallic radii of Cr and Ga (2.68 Å) [34]. The long M–Ga separations imply a weak interaction between M and Ga. These observations revealed that the coordination mode of σ-Ga–H bond in **1** to the group 6 carbonyl metal fragment $(OC)_5M$ is η^1-Ga–H. The small M–H–Ga bond angles in **2**–**4** (125(4), 119(3), and 126(4)°, respectively) compared to that observed in

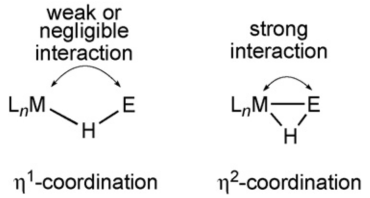


Fig. 4. Coordination mode of σ E–H bond to L_nM.

Table 1

Selected data for certain isolable $(OC)_5M(\sigma\text{-ligand})$ complexes (M = Cr, Mo, W).

Complex	^1H NMR (ppm)		$\nu(CO)$ (cm^{-1})	Ref.
	Brid.[a]	Term.[a]		
$(OC)_5Cr(H_3Ga{\cdot}quinuclidine)$ (**4**)	−10.95	4.98	1961	[17]
$(OC)_5Mo(H_3Ga{\cdot}quinuclidine)$ (**3**)	−6.99	5.06	1954	[17]
$(OC)_5W(H_3Ga{\cdot}quinuclidine)$ (**2**)	−7.32	5.51	1948	[16]
$(OC)_5Cr(H_3B{\cdot}PPh_3)$	−2.8		1920	[10]
$(OC)_5Cr(H_3B{\cdot}PMe_3)$ (**8**)	−3.8		1930	[10]
$(OC)_5Cr(H_3B{\cdot}NMe_3)$	−3.3		1950	[10]
$(OC)_5Cr(H_3B{\cdot}quinuclidine)$	−3.3		–[b]	[18]
$(OC)_5W(H_3B{\cdot}PPh_3)$	−1.2		1918	[10]
$(OC)_5W(H_3B{\cdot}PMe_3)$	−2.1		1925	[10]
$(OC)_5W(H_3B{\cdot}NMe_3)$	−1.5		1940, 1920	[10]
$(OC)_5W(H_3B{\cdot}quinuclidine)$	−1.6		–[b]	[18]
$[(OC)_5W]_2(H_3Ga{\cdot}quinuclidine)$ (**6**)	−6.80	7.20	1930, 1892	[17]
$[(OC)_5W]_2\{HGa(THF)(quinuclidine)\}$ (**7**)	−4.61	–	1930, 1909	[17]

[a] The bridging and terminal hydrogen atoms are abbreviated as brid. and term., respectively.

[b] The data was not reported in the literature.

Table 2

Selected data for spectroscopically detected $(OC)_5M(\sigma\text{-ligand})$ complexes (M = Cr, Mo, W).

Complex	^1H NMR (ppm)		$\nu(CO)$ (cm^{-1})	Ref.
	Brid.[a]	Term.[a]		
$(OC)_5Mo(H_3B{\cdot}PPh_3)$	−1.0		–[b]	[10]
$(OC)_5Mo(H_3B{\cdot}PMe_3)$	−2.0		–[b]	[10]
$(OC)_5Mo(H_3B{\cdot}NMe_3)$	−1.4		–[b]	[10]
$(OC)_5W(H_3B{\cdot}pyridine)$	−0.1		–[b]	[10]
$(OC)_5Cr(HSiEt_3)$	−13.5	–	1951	[19]
$(OC)_5Cr(HSiPh_3)$	−11.7	–	–[b]	[19b]
$(OC)_5Cr(HSiHPh_2)$	−11.2	6.02	–[b]	[19b]
$(OC)_5Mo(HSiEt_3)$	−8.36	–	1957	[19b]
$(OC)_5Mo(HSiHPh_2)$	−6.49	6.40	–[b]	[19b]
$(OC)_5W(HSiEt_3)$	−8.55	–	1951	[19b]
$(OC)_5W(HSiPh_3)$	−6.38	–	–[b]	[19b]
$(OC)_5W(HSiHPh_2)$	−6.40	6.50	–[b]	[19b]
$(OC)_5Cr(H_2)$	−7.45	–	2094, 1974	[20]
$(OC)_5Mo(H_2)$	–[b]	–	2098, 1979	[20d]
$(OC)_5W(H_2)$	−3.88	–	2098, 1972	[20d,e,21]

[a] The bridging and terminal hydrogen atoms are abbreviated as brid. and term., respectively.

[b] The data was not reported in the literature.

Table 3

Selected data for certain isolable $Cp'(OC)_2Mn(\sigma\text{-ligand})$ complexes ($Cp' = \eta^5\text{-}C_5H_5$ (Cp), $\eta^5\text{-}C_5Me_5$ (Cp*), $\eta^5\text{-}C_5H_4Me$ (Cp^{Me})).

Complex	^1H NMR (ppm)		$\nu(CO)$ (cm^{-1})	Ref.
	Brid.[a]	Term.[a]		
$Cp^*(OC)_2Mn(H_3Ga{\cdot}quinuclidine)$ (**5**)	−13.1	5.44	1936, 1876	[22]
$Cp(OC)_2Mn(H_3B{\cdot}quinuclidine)$ (**11**)	−6.24		–[b]	[18]
$Cp(OC)_2Mn(H_3B{\cdot}NMe_3)$ (**10**)	−6.10		1927, 1820	[23]
$Cp(OC)_2Mn(H_3B{\cdot}PMe_3)$ (**9**)	−6.30		1918, 1839	[23]
$Cp^{Me}(OC)_2Mn\{HBClSi(SiMe_3)_3\}$	−15.32	–	1978, 1913	[24]
$Cp^{Me}(OC)_2Mn(HBcat)$	−14.46	–	1995, 1937	[11d]
$Cp^*(OC)_2Mn(HSiHPh_2)$	−11.2	5.9	1975, 1918	[7j,l]
$Cp(OC)_2Mn(HSiCl_3)$	−9.70	–	2028, 1977	[7a,25]
$Cp^{Me}(OC)_2Mn(HSiHPh_2)$	−11.5	6.7	1994, 1935	[7j–l,o,26]
$Cp^{Me}(OC)_2Mn(HSiHPhC_{10}H_7)$	−11.23	–[c]	1978, 1918	[7f,g]
$Cp^{Me}(OC)_2Mn(HSiMePhC_{10}H_7)$	−11.97	–	1965, 1903	[7c–e,g,i]
$Cp^{Me}(OC)_2Mn(HSiPh_3)$	−11.44	–	1983, 1926	[7a,g]
$Cp^{Me}(OC)_2Mn(HSiPh_2SiHPh_2)$	−10.71	5.69	1978, 1921	[7m]
$Cp^{Me}(OC)_2Mn\{HSiPhC_{10}H_7(OMe)\}$	−12.03	–	1972, 1910	[7f,g]
$Cp^{Me}(OC)_2Mn(HSiPh_2F)$	−11.0	–	2004, 1947	[7h,j]
$Cp^{Me}(OC)_2Mn(HSiPhC_{10}H_7F)$	−11.70	–	1988, 1930	[7f,g]
$Cp^{Me}(OC)_2Mn(HSiPhC_{10}H_7Cl)$	−10.68	–	1990, 1934	[7f,g]
$Cp^{Me}(OC)_2Mn(HGePh_3)$	−9.08	–	1965, 1910	[7i]
$Cp^{Me}(OC)_2Mn(HSnPh_3)$	−8.9	–	1983, 1925	[27]

[a] The bridging and terminal hydrogen atoms are abbreviated as brid. and term., respectively.

[b] The data was not reported in the literature.

[c] Terminal Si–H signal could not be detected owing to overlapping with other signals.

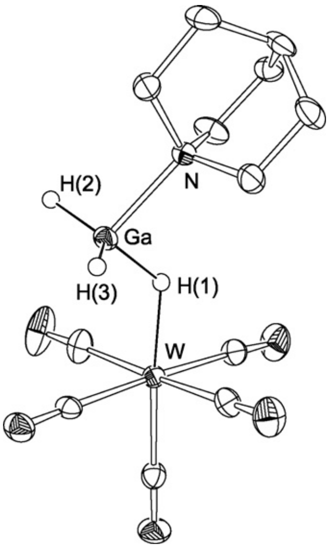
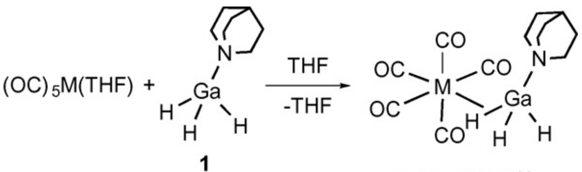


Fig. 5. ORTEP drawing (50% probability level) of $(OC)_5W(H_3Ga{\cdot}quinuclidine)$ (**2**). Hydrogen atoms of quinuclidine are omitted for clarity.

GaH_4^--coordinated compound (pmdeta)ClZn(η^1-GaH_4) (177(3)°, pmdeta = N,N,N′,N″,N″-pentamethyldiethylenetriamine) [35] clearly demonstrate the intrinsic dissimilarity of bonding between the neutral $H_3Ga{\cdot}$quinuclidine (**1**) and L_nM and that of anionic GaH_4^-. As coordination of GaH_4^- ion to L_nM fragment is dominated largely by ionic interaction between H^- and Zn^+, the GaH_4^- ligand is arranged with the linear Zn–H–Ga conformation to attain the least steric repulsion between L_nM and GaH_4^-. In σ-Ga–H complexes **2**–**4**, the interaction of **1** and $(OC)_5M$ is mainly composed of σ-donation from Ga–H bond, thus tilting of Ga–H σ-bond toward M would be necessary for maximizing interaction between σ-electrons in the Ga–H bond and d_σ orbital on $(OC)_5M$ fragment. The ^1H NMR spectrum of **2** showed the signals assignable to terminal and bridging GaH at 5.51 and −7.32 ppm, respectively, in addition to the signals assignable to quinuclidine fragment at 2.24, 0.97 and 0.75 ppm (Table 1). The terminal GaH signal was observed as a broad singlet due to the quadrupolar relaxation by Ga, whereas bridging GaH signal appeared as a relatively sharp triplet coupled with two terminal GaH signals ($^2J_{HH}$ = 12 Hz) with tungsten satellites ($^1J_{WH}$ = 48 Hz). In the IR spectra of **2**–**4**, the strong ν(CO) absorptions were observed around 1940–1960 cm^{-1} as shown in Table 1 and these are red-shifted ca. 20–40 cm^{-1} than those of $M(CO)_6$ (1980–1985 cm^{-1}) [36]. This shows the stronger electron donating character of the gallane ligand than that of the CO ligand.



1

2; M = W, 39%
3; M = Mo, 38%
4; M = Cr, 23%

(1)

The synthesis of gallane manganese σ-complex $Cp^*(OC)_2Mn(H_3Ga{\cdot}quinuclidine)$ (**5**) was recently achieved by the photochemical reaction of $Cp^*Mn(CO)_3$ and $H_3Ga{\cdot}$(quinuclidine) (**1**) (Eq. (2)) [22]. Similar to the group 6 complexes **2**–**4**, the ^1H NMR spectrum of **5** shows bridging and terminal GaH signals at −13.1 and 5.44 ppm, respectively, and the ν(CO) absorptions (1936 and 1876 cm^{-1}) were red-shifted by ca. 50–80 cm^{-1} than those in $Cp^*Mn(CO)_3$ (2015 and 1925 cm^{-1}) (Table 3) [29,37]. Interestingly, crystal structure analysis of **5** revealed that the interatomic Mn–Ga distance (2.5668(5) Å) is within the range of the usual Mn–Ga single bonds (2.50–2.67 Å) (Fig. 6) [38]. The bond angle of Mn–H–Ga fragment (97(2)°) is also smaller than those of M–H–Ga fragments (M = Cr, Mo, W). These results imply both σ-donation and π-back donation contribute to the interaction between manganese and gallane **1**. The coordination of σ-Ga–H bond to $Cp^*(OC)_2Mn$ fragment is thus depicted as η^2-mode. This result markedly contrasts to that observed in $H_3B{\cdot}L$-coordinated manganese σ-complexes in which the σ-B–H bond is bound to Mn in the η^1-mode (vide infra) [23]. Our preliminary theoretical investigation of model complexes $Cp(OC)_2Mn(H_3E{\cdot}NH_3)$ (E = Ga, B) also supported the η^2-coordination of Ga–H bond to the Mn fragment [22]. The calculated interatomic distances and the Wiberg bond indices of some important bonds are summarized in Fig. 7. The Ga–H bond of the bridging hydrogen (1.85 Å) is substantially longer than that of the terminal ones (1.58 Å) with decrease of the bond index to almost half of that of the terminal Ga–H (0.411 vs. 0.853). The Mn–H distance is shorter for gallane complex (1.57 Å) than that of the borane complex (1.69 Å). The

Table 4
Selected data for spectroscopically detected $Cp'(OC)_2Mn$(σ-ligand) complexes ($Cp' = \eta^5$-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*), η^5-C_5H_4Me (Cp^{Me})).

Complex	ν(CO) (cm^{-1})	Ref.
$Cp^*(OC)_2Mn(HSiEt_3)$	1951, 1893	[28]
$Cp(OC)_2Mn(HSiEt_3)$	1951, 1893	[29]
$Cp^{Me}(OC)_2Mn(HGeHPhC_{10}H_7)$	1960, 1900	[7i]
$Cp^{Me}(OC)_2Mn(HGeCl_3)$	2040, 1980	[7i]
$Cp^*(OC)_2Mn(H_2)$	1963, 1897	[28,30]
$Cp(OC)_2Mn(H_2)$[a]	1986, 1922	[30,31]
$Cp^{Me}(OC)_2Mn(H_2)$	1982, 1922	[28]

[a] In the ^1H NMR spectrum, a signal assignable to H_2 ligand was observed at −12.9 ppm.

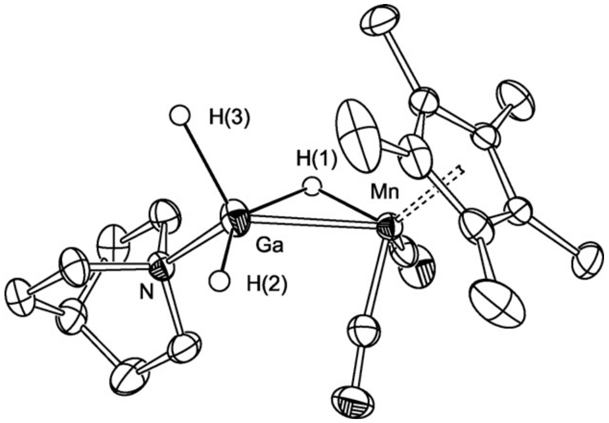


Fig. 6. ORTEP drawing (50% probability level) of $Cp^*(OC)_2Mn(H_3Ga{\cdot}quinuclidine)$ (**5**). Hydrogen atoms of Cp* and quinuclidine are omitted for clarity.

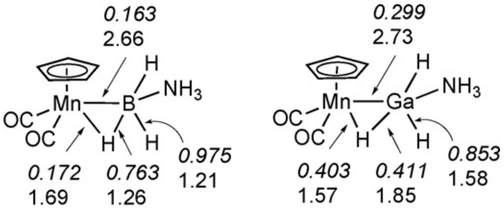


Fig. 7. The calculated interatomic distances (lower) and the Wiberg bond indices (upper, italic) of some important bonds in $Cp(OC)_2Mn(H_3E{\cdot}NH_3)$ complexes (E = B and Ga).

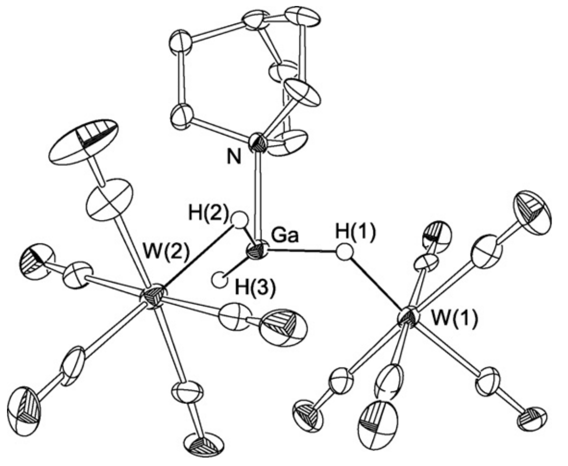
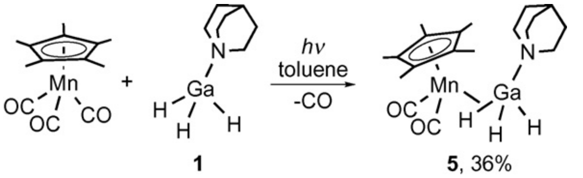


Fig. 8. ORTEP drawing (50% probability level) of $[(OC)_5W]_2(H_3Ga\cdot quinuclidine)$ (**6**). Hydrogen atoms of quinuclidine are omitted for clarity.

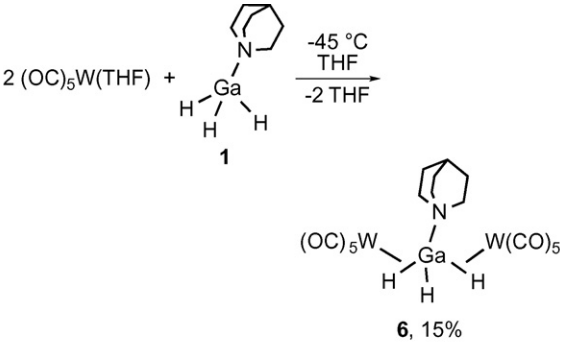
Mn–Ga interatomic distance is also significantly short when the difference of Ga and B covalent radii (1.22 and 0.88 Å, respectively) is taken into account. Bond indices of Mn–Ga and Mn–B bonds (0.403 and 0.299, respectively) also show the stronger interaction in gallane complex. These results imply that considerable π-back donation takes place from Mn to the Ga–H σ* orbital.



(2)

2.2. Synthesis and structure of gallane-bridged dimetallic σ-complex

The reaction of $H_3Ga\cdot$quinuclidine (**1**) and two equivalents of $(OC)_5W(THF)$ afforded the first gallane-bridged dimetallic σ-complex $[(OC)_5W]_2(H_3Ga\cdot quinuclidine)$ (**6**) (Eq. (3)) [17]. The crystal structure analysis of **6** revealed that two $(OC)_5W$ fragments are bridged by **1** via two W–H–Ga 3c2e bonds (Fig. 8). W(1)–Ga and W(2)–Ga interatomic distances in **6** are 3.0698(12) and 2.9284(12) Å, respectively, which are longer than the usual W–Ga single bonds (2.71–2.76 Å) [32]. The ^{1}H NMR spectrum of **6** showed two signals at −6.80 and 7.20 ppm assignable to bridging and terminal GaH, respectively (Table 1). The bridging GaH signal was observed as a doublet coupled with terminal GaH ($^2J_{HH}$ = 24 Hz) with tungsten satellites ($^1J_{WH}$ = 48 Hz). Both bridging and terminal GaH resonances are shifted to a lower magnetic field than those observed in complex **2**. This is attributable to the reduced electron density on the Ga center by the coordination of the gallane to two electrophilic $W(CO)_5$ fragments.



(3)

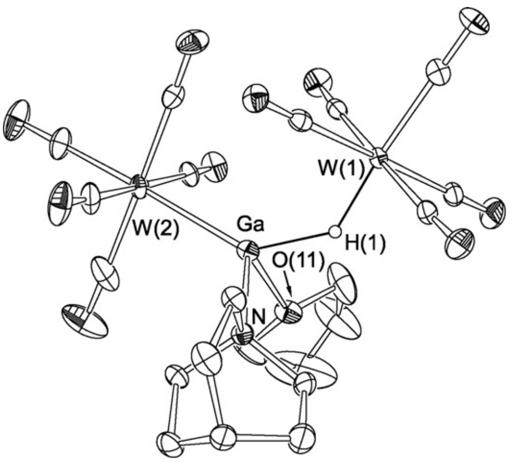
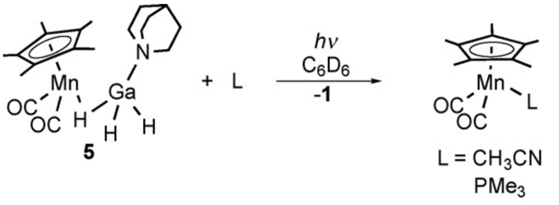


Fig. 9. ORTEP drawing (30% probability level) of $[(OC)_5W]_2\{HGa(quinuclidine)(THF)\}$ (**7**). Hydrogen atoms of quinuclidine and THF are omitted for clarity.

2.3. Reactivity of gallane σ-complexes

The gallane ligand in $Cp^*(OC)_2Mn(H_3Ga\cdot quinuclidine)$ (**5**) was not displaced in the presence of L (L = CH_3CN, PMe_3) under thermal conditions. However, irradiation of a C_6D_6 solution of **5** and L caused substitution of the gallane ligand to give $Cp^*(OC)_2MnL$ in ca. 20% yield with free **1** (Eq. (4)) [22]. Treatment of **5** with H_2O resulted in the decomposition of $H_3Ga\cdot L$ ligand to afford $Cp^*(OC)_2MnH_2$ in 87% NMR yield. The hydride ligands in the product are derived from both of gallane and H_2O since the reaction of **5** with D_2O gave $Cp^*(OC)_2Mn(HD)$. Thermolysis of a C_7D_8 solution of $(OC)_5W(H_3Ga\cdot quinuclidine)$ (**2**) at 80 °C for 0.5 h afforded a mixture of free quinuclidine and unidentified black precipitates, which was ultimately converted to quinuclidine-coordinated tungsten complex $(OC)_5W$(quinuclidine) after 1 week at 80 °C (Eq. (5)) [16]. Gallane-bridged dimetallic complex $[(OC)_5W]_2(H_3Ga\cdot quinuclidine)$ (**6**) was cleanly converted in THF at room temperature for 1 day to complex **7** with evolution of H_2 (Eq. (6)). The ^{1}H NMR spectrum of **7** showed a singlet signal at −4.61 ppm assignable to the W–H–Ga bridging hydrogen and no terminal GaH signal (Table 1). Crystal structure analysis revealed that complex **7** is a hydrogallylene σ-complex. The hydrogallylene tungsten complex $HGa{=}W(CO)_5$ stabilized by coordination of THF and quinuclidine molecules to Ga, interacts with another $W(CO)_5$ fragment, via the terminal Ga–H bond to form a W–H–Ga 3c2e bonding mode (Fig. 9). The bond distance of W(2)–Ga (2.6229(10) Å) is longer than the reported gallylene–tungsten unsaturated bonds ($(OC)_3W(GaCp^*)_3$; 2.52 Å (av.), $(OC)_5W(GaCp^*)$; 2.566(1) Å, $Cp^*(dppe)FeGaW(CO)_5$; 2.5861(8) Å (dppe = $Ph_2P(CH_2)_2PPh_2$)) [39], but still shorter than the W–Ga single bonds (2.71–2.76 Å) [32]. The interatomic distance between W(1) and Ga (3.1784(9) Å) in W–H–Ga bonding is longer than those of **2** (3.0194(5) Å) and **6** (3.0698(12) and 2.9284(12) Å). The IR spectrum shows strong ν(CO) absorption at 1930 and 1909 cm^{-1} which are assignable to Ga–H-coordinated and gallylene-coordinated $W(CO)_5$ fragment, respectively (Table 1).



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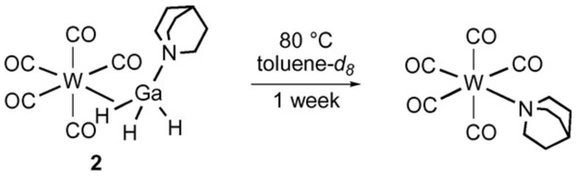

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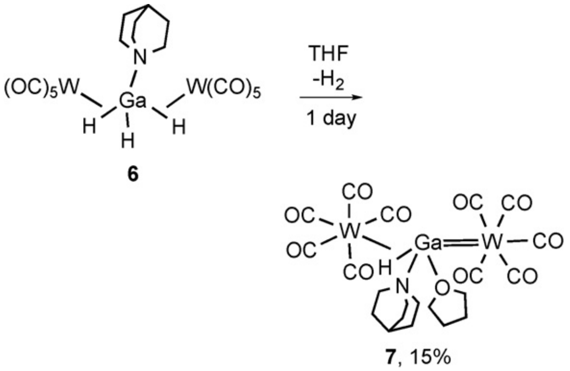
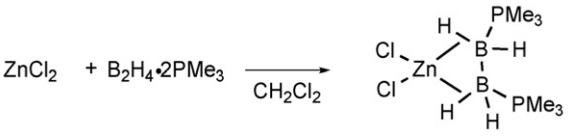


(6)

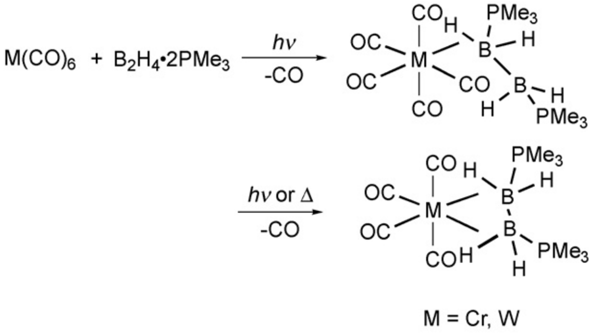
3. Borane σ-complexes

3.1. Synthesis and structure of diborane σ-complexes

The first σ-complex of a neutral borane-Lewis base adduct $ZnCl_2(B_2H_4{\cdot}2PMe_3)$ was synthesized in 1984 by the reaction of diborane $B_2H_4{\cdot}2PMe_3$ with $ZnCl_2$ (Eq. (7)) [40]. The copper phosphine complexes $Cu(PPh_3)(X)(B_2H_4{\cdot}2PMe_3)$ (X = Cl, I) and the nickel carbonyl compound $Ni(CO)_2(B_2H_4{\cdot}2PMe_3)$ were also synthesized in 1990 and 1985, respectively [41]. Crystal structure determinations of these σ-complexes revealed bidentate coordination of the diborane ligand in the complexes; two vicinal H–B bonds in diborane interact with a L_nM fragment. The diborane complexes with group 6 metal fragments $(OC)_5M(B_2H_4{\cdot}2PMe_3)$ and $(OC)_4M(B_2H_4{\cdot}2PMe_3)$ (M = Cr, W), were prepared by irradiation of a solution of corresponding $M(CO)_6$ complex and $B_2H_4{\cdot}2PMe_3$ (Eq. (8)) [42]. The former is the first borane σ-complex with a monodentate borane ligand.



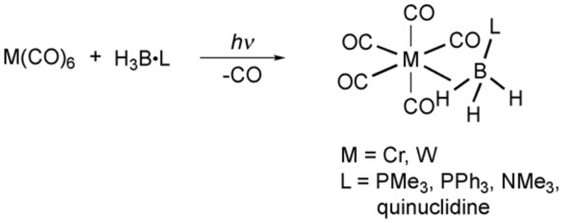
(7)



(8)

3.2. Synthesis and structure of $H_3B{\cdot}L$-coordinated σ-complexes

The first transition metal complexes of the monoborane-Lewis base adduct $(OC)_5M(H_3B{\cdot}L)$ (M = Cr, W; L = PMe_3, PPh_3, NMe_3, quinuclidine) were synthesized by photochemical reaction of $M(CO)_6$ and $H_3B{\cdot}L$ (Eq. (9)) [9,10,18]. Crystal structure analysis of $(OC)_5Cr(H_3B{\cdot}PMe_3)$ (**8**) revealed that the borane-Lewis base adduct interacts with metal center via a B–H bond to give a M–H–B 3c2e bonding. The Cr–B interatomic distance (2.79(1) Å) is much longer than the known Cr–B single bonds (2.16–2.56 Å) [43], indicating the negligible interaction between Cr and B. The ^1H NMR spectrum of **8** showed only one BH signal with integral intensity of three protons at −3.8 ppm (Table 1). Apparently, the bridging and the terminal hydrogen atoms scramble faster than the NMR time scale. Manganese complexes $Cp(OC)_2Mn(H_3B{\cdot}L)$ (**9**; L = PMe_3, **10**; L = NMe_3, **11**; L = quinuclidine) were also prepared by photochemical reaction of $CpMn(CO)_3$ and $H_3B{\cdot}L$, however, these were isolated in only low yield due to the high lability of borane ligands (Eq. (10)) [18,23]. The interatomic Mn–B distance (**9**; 2.682(3) Å and **10**; 2,573(2) Å) is again significantly longer than those observed in usual Mn–B single bonds (2.06–2.16 Å) [44], indicating negligible interaction between Mn and B. Rapid site exchange between the bridging and the terminal hydrogen atoms was also observed in the manganese complexes **9**–**11**. In the IR spectra of complexes **9** and **10**, the ν(CO) absorptions were observed at ca. 100 cm^{-1} lower than those for $Cp(OC)_3Mn$ (2022 and 1934 cm^{-1}) (Table 3) [37b,45]. This indicates that the π-accepting ability of electrons of borane ligand is very weak compared to its σ-donating one, which consequently enhances π-back donation from Mn to carbonyl ligands. These experimental observations revealed that interaction of σ-B–H bond to both $(OC)_5M$ and $Cp(OC)_2Mn$ fragments is with the η^1-mode. Cationic manganese σ-complexes $[(OC)_4(R_3P)Mn(H_3B{\cdot}PMe_3)][B(Ar^f)_4]$ (PR_3 = PMe_2Ph, PEt_3, Ar^f = 3,5-$C_6H_3(CF_3)_2$) and ruthenium σ-complexes $[Cp'(Me_3P)_2Ru(H_3B{\cdot}EMe_3)][B(Ar^f)_4]$ (Cp′ = Cp, Cp*, E = N, P, **12**; Cp′ = Cp, E = P) were also reported to bear η^1-B–H borane ligands [46].



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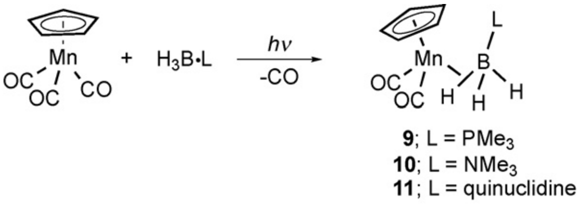
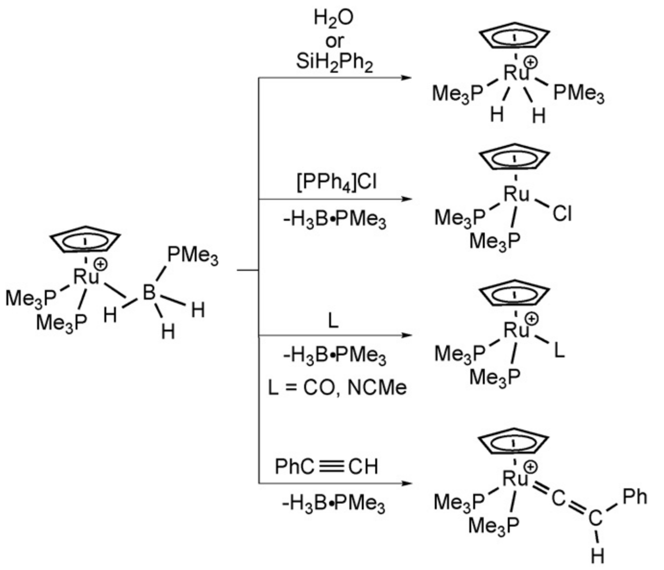


(10)

3.3. Reactivity of $H_3B{\cdot}L$-coordinated σ-complexes

As coordination of $H_3B{\cdot}L$ to a transition metal is weak, substitution of the borane ligand with a two-electron donating ligand takes place easily. Thus, treatment of $CpMn(CO)_2(H_3B{\cdot}NMe_3)$ (**10**) with $SiHPh_3$ or SiH_2Ph_2 caused substitution of $H_3B{\cdot}NMe_3$ ligand with silane to afford the corresponding silane-coordinated σ-complexes in high yield [23]. Substitution of borane ligand in **10** with catecholborane (HBcat) also occurred to afford $CpMn(CO)_2(HBcat)$ [23]. The reactivity of $H_3B{\cdot}L$-coordinated cationic ruthenium σ-complex **12** is summarized in Scheme 1 [46b]. The cationic dihydride Ru complex $[CpRu(PMe_3)_2(H)_2]^+$ was obtained by the reaction of **12** with H_2O or $SiPh_2H_2$. The $H_3B{\cdot}L$ ligand in **12** was easily replaced by Cl^-, CO, MeCN, and phenylacetylene.



Scheme 1. Reactivity of cationic ruthenium complex $[Cp(Me_3P)_2Ru(H_3B{\cdot}PMe_3)][BAr^f{}_4]$ (**12**).

4. Comparison of gallane, borane, and related σ-complexes

The stability of M–H–E 3c2e bonding depends on the strength of σ-donation of electrons in the E–H σ-orbital as well as π-acceptor competence from the filled d_π orbital on M to the E–H σ* orbital. Coordination of dihydrogen molecule to ML_n fragment is clearly definable as the η^2-mode. In this case, both σ-donation and π-back donation contribute to form the $L_nM–H_2$ 3c2e bond [4]. In contrast to the H_2 complexes, the coordination ability of the E–H bond to ML_n (E = Si, C, B, Ga, etc.) is largely affected by the steric and electronic effects of substituents on E. In most of the silane σ-complexes, the electron donating ability of σ-Si–H bond is stronger than that of carbonyl ligand as ν(CO) absorptions in the σ-Si–H complexes are shifted to lower frequencies than those in the original $(OC)_6M$ and $Cp'(OC)_3Mn$ complexes (Tables 2–4, *cf* ν(CO) in $Cp^*(OC)_3Mn$; 2015 and 1925 cm^{-1}, in $Cp(OC)_3Mn$; 2022 and 1934 cm^{-1}, in $Cp^{Me}(OC)_3Mn$; 2023 and 1929 cm^{-1}) [29,37,45,47,48]. The interatomic distance between Mn and Si in Si–H σ-complexes (2.25–2.46 Å) are comparable to those of the usual Mn–Si single bonds (2.32–2.66 Å) [25b,49]. These observations demonstrate the η^2-coordination mode of the Si–H bond and indicate the significant contributions of both σ-donation and π-back donation. In contrast to the silane σ-complexes, borane σ-complexes are categorized to contain η^1-coordination; σ-donation from B–H σ-bond to metal fragment is predominant and the contribution of π-back bonding does not compensate for the σ-donation. A large red-shift of ν(CO) absorptions (ca. 50–100 cm^{-1} in Tables 1 and 3) and significantly long M–B interatomic bond distances demonstrate the negligible contribution of π-back bonding. Shimoi et al. ascribed the negligible π-back donation to the B–H σ* orbital being energetically too high to interact with the d_π orbital on the metal fragment [10,23].

Interestingly, the gallane σ-complex shows η^1- and η^2-mode binding when coordinating to the electron-deficient $(OC)_5M$ fragments and electron-rich $Cp^*(OC)_2Mn$ fragment, respectively. The red-shift of ν(CO) in $Cp^*(OC)_2Mn(H_3Ga{\cdot}quinuclidine)$ (**5**) (ca. 65 cm^{-1}) was comparable to that observed for $Cp'(OC)_2Mn(HSiR_3)$ systems (ca. 50 cm^{-1}) and smaller than that obtained for $Cp(OC)_2Mn(H_3B{\cdot}L)$ complexes (ca. 100 cm^{-1}) (Table 3). M–Ga interatomic bond distances are longer in $(OC)_5M(H_3Ga{\cdot}quinuclidine)$ (**2**; M = W, **3**; M = Mo, **4**; M = Cr) but comparable in complex **5** compared to those of the usual M–Ga single bonds. These observations indicate that π-back donation is important to the $Cp^*(OC)_2Mn$ system. The difference in the coordination mode between σ-Ga–H and σ-B–H complex with the $Cp'(OC)_2Mn$ fragment is attributable to the intrinsic π-accepting ability of Ga–H σ* orbital in $H_3Ga{\cdot}L$ ligand. Preliminary theoretical calculation of the model compounds $H_3E{\cdot}NH_3$ (E = B, Ga) indicates that the energy levels of Ga–H and B–H σ orbitals are practically identical (−9.4 and −9.2 eV), while that of Ga–H σ* orbitals (5.5 eV) is substantially lower than that of B–H σ* orbitals (13 eV). The longer bond length of the Ga–H bond than that of the B–H bond would also be crucial for stabilizing the η^2-Ga–H coordination. The η^2-Ga–H coordination induces close proximity between Ga and L_nM, while the long H-Ga bond could circumvent the interference between Ga and L_nM. Substantial progress could be made by the investigation of σ-complexes of $H_3Ga{\cdot}L$ ligand with other metal fragments and Lewis bases L.

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