

σ -Alane Complexes of Chromium, Tungsten, and Manganese

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S Supporting Information

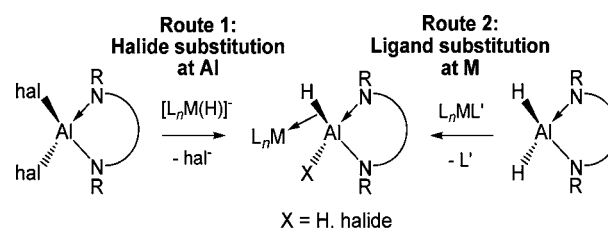
ABSTRACT: Photolytic ligand displacement and salt metathesis routes have been exploited to give access to κ^1 σ -alane complexes featuring Al–H bonds bound to $[\text{W}(\text{CO})_5]$ and $[\text{Cp}^*\text{Mn}(\text{CO})_2]$ fragments, together with a related κ^2 complex of $[\text{Cr}(\text{CO})_4]$. Spectroscopic, crystallographic, and quantum chemical studies are consistent with the alane ligands acting predominantly as σ -donors, with the resulting binding energies calculated to be marginally greater than those found for related dihydrogen complexes.

Transition metal σ -complexes featuring activated but more- or-less intact E–H bonds (E = H, B, or Si) have attracted significant attention since the first dihydrogen complex was reported in 1984.^{1–8} Such efforts reflect not only interest in the fundamental electronic structure of nonclassical bonds, but also the relevance of σ -complexes to E–H oxidative addition,^{2,3} and ultimately to metal catalyzed processes for the addition of E–H bonds to unsaturated substrates.^{9–11} While σ -alkane complexes are relatively uncommon,¹² coordination of H_2 and of libraries of boranes/silanes to unsaturated 16-electron fragments such as $[\text{Cp}^*\text{MnL}_2]$ and $[\text{W}(\text{CO})_3\text{L}_2]$ has allowed for systematic studies of the electronic structure of such systems.^{2–8}

Among Group 13 systems, the coordination and activation of B–H bonds at transition metal centers has been systematically investigated,^{13,14} not least due to applications in hydroboration, borylation, and dehydrocoupling processes.^{11,15,16} By contrast, the interaction of E–H bonds featuring the heavier Group 13 elements is much less well developed despite, for example, reports of transition metal dopants catalyzing dihydrogen cycling from aluminum hydride materials.^{17,18} Thus, while Ueno, Ogino, and co-workers have reported the coordination of an amine–gallane adduct to $[\text{W}(\text{CO})_5]$,¹⁹ the majority of complexes containing coordinated Al–H bonds feature highly electrophilic early transition metals and/or anionic hydroaluminate ligands. Examples of simple, unsupported, charge neutral σ -alane complexes are very rare and those featuring the classical $[\text{Cp}^*\text{MnL}_2]$ and $[\text{W}(\text{CO})_3\text{L}_2]$ fragments are unknown.^{20–24}

In this manuscript, we report two strategies for the synthesis of complexes containing neutral alane donor ligands (Scheme 1). Such approaches mirror the routes used for σ -borane complexes of the type $[\text{Cp}^*\text{Mn}(\text{CO})_2(\kappa^1\text{-HBR}_2)]$ [$\text{Cp}^* = \eta^5\text{-}(\text{C}_5\text{H}_4\text{Me})$],²⁵ but additionally employ sterically imposing ancillary frameworks, in order to minimize the tendency for

Scheme 1. Potential Synthetic Routes to σ -Alane Complexes Exploiting either (1) Halide Substitution at Aluminum by a Nucleophilic Metal Hydride, or (2) Ligand Substitution at a Transition Metal (M) by an Alane



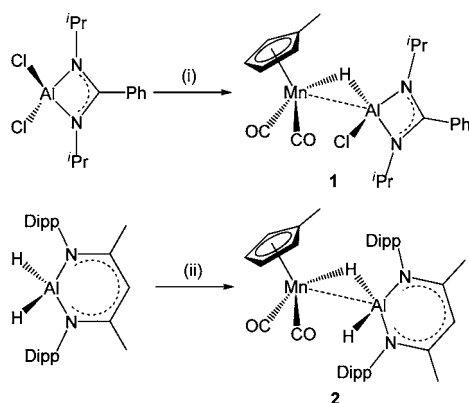
aggregation prevalent among aluminum hydrides.²⁶ Moreover, the transition metal fragments employed, $[\text{Cp}^*\text{Mn}(\text{CO})_2]$ and $[\text{W}(\text{CO})_5]$, permit for the first time comparison of alane σ -complexes with archetypal dihydrogen, borane, and silane systems.^{1–7}

The ready accessibility of amidinate and guanidinate stabilized aluminum dihalides,²⁷ and of the $[\text{Cp}^*\text{Mn}(\text{CO})_2\text{H}]^-$ anion,²⁸ suggests that a halide metathesis approach (Scheme 1, route 1) might offer a convenient synthesis of compounds featuring a Mn–H–Al interaction. Consistently, the reaction between $[\text{Cp}^*\text{Mn}(\text{CO})_2\text{H}]^-$ and $\text{Cl}_2\text{Al}\{(\text{N}^i\text{Pr})_2\text{CPh}\}$ (Scheme 2) leads to the formation of $[\text{Cp}^*\text{Mn}(\text{CO})_2\{\text{HAl}(\text{Cl})\{(\text{N}^i\text{Pr})_2\text{CPh}\}\}]$ (1), which has been characterized by standard spectroscopic methods (see Supporting Information (SI)) and by X-ray crystallography. Particularly indicative of the bridging hydrogen atom is the ^1H NMR resonance at $\delta_{\text{H}} = -13.93$ ppm; the location of H(1) could also be inferred crystallographically in the solid state from the difference Fourier map (Figure 1).

The geometry around Al(2) approximates to trigonal bipyramidal in a manner reminiscent of related manganese silane complexes (with due allowance made for the constraints imposed by the four-membered amidinate ring and the Mn–H linkage).^{4,5,29} Thus, the sum of the angles subtended at Al(2) by the Mn–Al, Al–Cl, and Al–N(6) vectors is $349.1(1)^\circ$, and the H–Al–N(4) angle is $150.6(1)^\circ$. The identification of H(1) as bridging the Mn–Al linkage is consistent with a metal–metal distance [$2.446(1)$ Å] which is markedly longer than the Fe–Al separation measured for the closely related (but non-hydride-containing) Fp system $[\text{CpFe}(\text{CO})_2\{\text{Al}(\text{Cl})\{(\text{N}^i\text{Pr})_2\text{CPh}\}\}]$ [$2.340(1)$ Å; see SI]. Moreover, while the (O)C–M–Al angles in the iron compound are nearly equal [$80.7(1)$, $82.1(1)^\circ$],

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Scheme 2. Syntheses of Manganese σ -Alane Complexes **1** and **2**^a

^aKey reagents/conditions: (i) $K[Cp^*Mn(CO)_2H]$ (1.1 equiv.), Et_2O , 20 °C, 18 h, 17% (as single crystals); (ii) $Cp^*Mn(CO)_3$ (1.0 equiv.), toluene, 20 °C, UV photolysis (Hg arc lamp, 1 kW), 165 min, 13% (as single crystals; ca. 50% as microcrystalline material) (Dipp = 2,6- $iPr_2C_6H_3$).

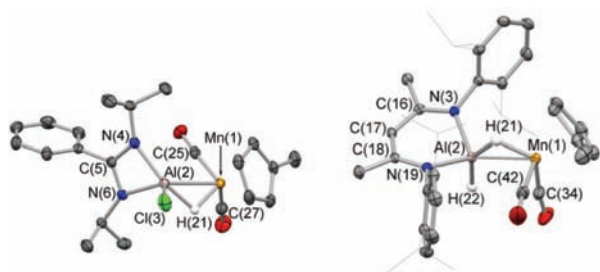
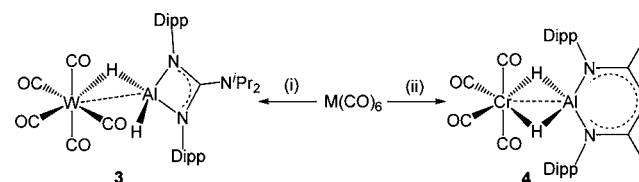


Figure 1. Molecular structures of **1** and **2** in the solid state. H atoms (except metal-bound H's) omitted for clarity and thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (°): (for **1**) Mn(1)···Al(2) 2.446(1), Mn(1)–H(21) 1.56(3), Al(2)–H(21) 1.72(3), Al(2)–Cl(3) 2.156(1), Al(2)–N(4) 1.923(2), Al(2)–N(6) 1.906(2), Mn(1)–H(21)–Al(2) 97(1), N(4)–Al(2)–N(6) 69.6(1); (for **2**) Mn(1)···Al(2) 2.654(1), Mn(1)–H(21) 1.57(3), Mn(1)–C(34) 1.760(3), Mn(1)–C(42) 1.770(3), Al(2)–H(21) 1.70(2), Al(1)–H(22) 1.59(3), Al(2)–N(3) 1.910(2), Al(2)–N(19) 1.925(2), Mn(1)–H(21)–Al(2) 109(2), H(21)–Al(2)–H(22) 143(1).

those for **1** are more disparate [76.0(1), 115.7(1)°], reflecting the accommodation of an additional hydrogen atom within the manganese coordination sphere. A description as a three-legged piano stool complex featuring a coordinated Al–H bond is therefore conceivable. With this in mind, we set out to explore alternative synthetic pathways using starting materials containing preformed Al–H bonds (i.e., route 2).

While simple amidinato derivatives of the type [(amid)AlH₂]_n are not well-known; related dihydrides containing sterically more encumbered heterocycles are readily available. Thus, we probed the reactivity of the dimeric guanidinate-stabilized alane [$\{iPr_2NC(NDipp)_2\}AlH_2\}_2$], and the monomeric β -diketiminato derivative $\{HC(CMeNDipp)_2\}AlH_2$ with metal carbonyl substrates under photolytic conditions (Scheme 3).^{30–33} Such chemistry provides not only a complementary synthesis of $[Cp^*Mn(CO)_2]$ alane σ -complexes, but also access to related systems featuring $[M(CO)_5]$ and $[M(CO)_4]$ fragments, and hence comparison with additional families of archetypal E–H σ complexes. Thus, photolysis of an equimolar mixture of $\{HC(CMeNDipp)_2\}AlH_2$ and $Cp^*Mn(CO)_3$ in

Scheme 3. Syntheses of Group 6 σ -Alane Complexes **3** and **4**^a

^aKey reagents/conditions: (i) M = W, alane (0.5 equiv. of dimer), hexanes, 20 °C, UV photolysis, 100 min, 8% (as single crystals); (ii) M = Cr, alane (1.0 equiv.), toluene, 20 °C, UV photolysis, 90 min, 49% (co-crystallized as a ca. 9:1 mixture with the κ^1 complex).

toluene leads to the formation of $Cp^*Mn(CO)_2[\kappa^1-H_2Al\{(NDipp)CMe\}_2CH]$ (**2**). Consistent with the spectroscopic data determined for **1**, the ¹H NMR spectrum of **2** features a similarly high-field shifted signal ($\delta_H = -15.42$ ppm). Interestingly (and in contrast to reports of related κ^1 -borane complexes),^{34–40} there appears to be slow exchange between the bound and unbound Al–H hydrogens on the NMR time scale at temperatures up to 75 °C. Crystallographically, **2** is characterized by similar Al–H(Mn) and Mn–H distances to **1** [1.57(3), 1.70(2) Å for **2** vs 1.56(3), 1.72(3) Å], although the Mn···Al separation is significantly longer [2.654(1) cf. 2.446(1) Å], reflecting a wider Al–H–Mn angle [109(2) vs 97(1)°] and, presumably, the greater steric requirements of the β -diketiminato skeleton (Figure 1).

The carbonyl stretching frequencies measured for **2** [$\nu_s(CO) = 1947$; $\nu_{as}(CO) = 1879$ cm^{-1}] can be compared to analogous values of 1995–1967 and 1937–1901 cm^{-1} for σ -complexes of tricoordinate boranes (which possess π -acceptor capabilities),^{25a} and 1947–1919, 1858–1820 cm^{-1} for tetra-coordinate boranes.^{34,37} As such, these data are indicative of a dominant σ -donor role for the alane ligand. Also consistent with such a description is the alignment of the $H_2Al\{(NDipp)CMe\}_2CH$ fragment in **2**; a Cp centroid–Mn–Al–H torsion angle of 67.0° is reflective of minimal overlap of the Al–H σ^* orbital with the HOMO of the metal fragment.^{34,37}

Photolytic substitution of carbonyl ligands by Al–H donors can also generate κ^1 alane complexes featuring $[M(CO)_5]$ fragments, and under appropriate conditions, related κ^2 systems by substitution of a second CO ligand. Thus, the reaction of [$\{iPr_2NC(NDipp)_2\}AlH_2\}_2$] with $W(CO)_6$ generates $(OC)_5W[\kappa^1-H_2Al\{(NDipp)_2CN^iPr_2\}]$ (**3**) via substitution of a single CO ligand; for this system at least, the use of more forcing conditions results only in the formation of the known anionic tungsten hydride $[(OC)_5W(\mu-H)W(CO)_5]^-$.^{41,42} A κ^1 mode of coordination for **3** in solution is implied by a lowering of symmetry within the flanking Dipp substituents (four CH₃ and two CH signals in both ¹H and ¹³C NMR spectra) and by the observation of distinct resonances for the terminal and bridging Al–H hydrogens (at $\delta_H = 6.80$ and -7.11 ppm). The former signal is very broad, and could be definitively identified only via ¹H{²⁷Al} experiments; the Al–H–W signal can, however, be resolved as a doublet ($^2J_{HH} = 20.0$ Hz). Moreover, as with **2**, slow fluxional exchange of the aluminum-bound hydrogens is observed at temperatures up to 75 °C, implying that $\Delta G^\ddagger > 17$ kcal mol⁻¹; similar behavior has been reported for a gallane fragment bound to $[W(CO)_5]$.¹⁹ Although experimental coupling constant data for geminal AlH₂ units have not been reported, the value determined for **3** can be compared to quantum chemical estimates for ‘free’ alanes (22.6–29.7 Hz)

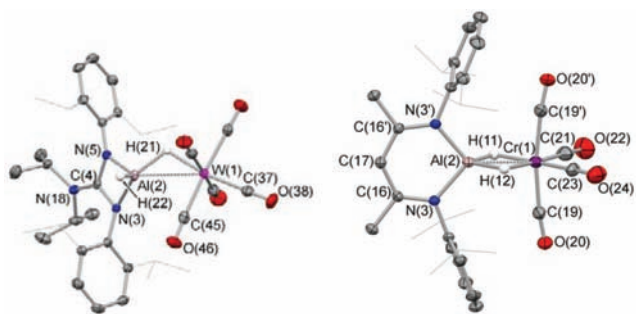


Figure 2. Molecular structures of **3** and **4** in the solid state. H atoms (except metal-bound H's) omitted and Dipp ³Pr groups shown in wireframe format for clarity and thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (°): (for **3**) W(1)⋯Al(2) 2.841(1), W(1)–H(21) 1.80(3), W(1)–C(37) 2.014(4), W(1)–C(45) 2.024(3), Al(2)–H(21) 1.67(3), Al(2)–H(22) 1.46(3), Al(2)–N(3) 1.913(2), Al(2)–N(5) 1.892(2), W(1)–H(21)–Al(2) 110(2), H(21)–Al(2)–H(22) 123(2); (for **4**) Cr(1)⋯Al(2) 2.420(1), Cr(1)–H(11) 1.64, Cr(1)–H(12) 1.69, Cr(1)–C(19) 1.892(2), Cr(1)–C(21) 1.834(3), Cr(1)–C(23) 1.846(3), Al(2)–H(11) 1.51, Al(2)–H(12) 1.65, Al(2)–N(3) 1.856(1), Cr(1)–H(11)–Al(2) 100, Cr(1)–H(12)–Al(2) 93, H(11)–Cr(1)–H(12) 81, H(21)–Al(2)–H(12) 86.

and rationalized in terms of the minor extent of Al–H bond activation.⁴³

Details of the mode of alane binding in **3** in the solid state were established crystallographically (Figure 2). In this case, the structure is characterized by a relatively long M–Al separation of 2.841(1) Å (cf. 2.55 Å for the sum of the respective covalent radii),⁴⁴ which presumably indicates that the predominant binding interaction in this tungsten system is through the bridging hydrogen atom. A κ^1 mode of interaction is consistent with the decidedly nonlinear C(4)⋯Al(2)⋯W(1) angle [136.9(1)°] and with markedly differing Al–H distances [1.46(3) and 1.67(3) Å]. By contrast, the major product of the reaction of {HC(CMeNDipp)₂}AlH₂ with M(CO)₆ (M = Cr, Mo) appears from ¹H NMR spectroscopy to be the κ^2 alane adduct (OC)₄M[κ^2 -H₂Al{(NDippCMe)₂CH}] in each case. Coordination of both Al–H bonds is consistent with the pattern of two Dipp CH₃ and one CH signals observed by ¹H NMR spectroscopy, and with the observation of a single Al–H resonance (at $\delta_{\text{H}} = -10.48$ ppm for M = Cr). In the case of the chromium compound **4**, crystallographic studies confirmed that the major (89%) component in the crystal features a κ^2 -alane ligand bound to a [Cr(CO)₄] moiety (Figure 2).^{45,46} Structurally, this mode of binding is reflected by a linear C(17)⋯Al(2)⋯Cr(1) unit [179.5(1)°], by essentially equivalent Cr–H–Al linkages, and by a Cr⋯Al separation [2.420(1) Å] which is shortened with respect to the W⋯Al separation measured for **3** [2.841(1) Å] by more than would be expected simply on the basis of the differing covalent radii of chromium and tungsten ($\Delta d = 0.23$ Å).⁴⁴ Moreover, **4** also provides a platform on which the relative σ -donor capabilities of CO and alane ligands can be assessed; the respective *trans* Cr–C distances [$d(\text{Cr}–\text{C}) = 1.834(3)/1.846(3)$ (*trans* to alane) and 1.892(2) Å (*trans* to CO)] are consistent with the Al–H bond being a weaker σ -donor.

Density Functional Theory (DFT) calculations have been carried out on κ^1 -alane systems **1–3** (i) with a view to corroborating the positions of metal-bound hydrogen atoms proposed on the basis of spectroscopic/structural studies, and (ii) as a means of comparing the intrinsic thermodynamics of

alane binding with other σ -complexes. Such studies reveal excellent binding agreement with X-ray structural data, and estimate ligand binding energies which are comparable to/greater than those found for H₂, but markedly less than those for CO ($D_0 = 26.9, 25.6, 54.2$ kcal mol⁻¹ for alane, H₂, and CO complexes of [Cp^{*}Mn(CO)₂] and 22.9, 14.3, 36.2 kcal mol⁻¹ for the corresponding [W(CO)₅] systems). Moreover, the relatively similar alane binding energies calculated for these two metal systems (cf. much larger differences for the H₂ and CO complexes) are consistent with the minor role of π -back-bonding in alane coordination.

In summary, we have demonstrated two synthetic approaches to complexes of charge neutral alane donors, and elucidated κ^1 and κ^2 modes of coordination at 16- and 14-electron metal fragments, respectively. Spectroscopic and structural data are consistent with a predominantly σ donor role for the alane, with the marked polarity of the Al–H bond presumably also being important. Further studies targeting broader demonstration of this chemistry, and elucidation of fundamental patterns of reactivity will be reported in due course.

■ ASSOCIATED CONTENT

📄 Supporting Information

Characterizing data for **1–4** and CpFe(CO)₂[Al(Cl){(NⁱPr)₂CPh}]; CIF files for all X-ray crystal structures; details of DFT calculations (including run files). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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