

Metal-Only Lewis Pairs by Reversible Insertion of Ruthenium and Osmium Fragments into Metal–Boron Double Bonds**

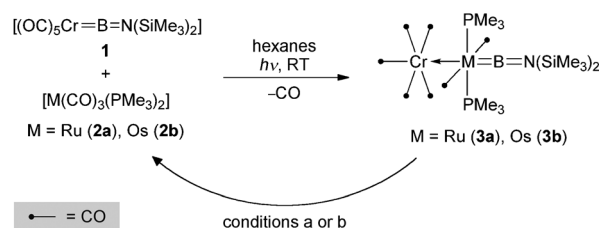
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Abstract: New metal-only Lewis pairs (MOLPs: Ru→Cr and Os→Cr) are prepared by the insertion of a zerovalent ruthenium or osmium complex into chromium–boron double bonds of borylene complexes. The reaction creates new borylene complexes (the first ever for osmium), and is crystallization-controlled; re-dissolving the complexes results in regeneration of the starting materials. A mechanism is proposed based on DFT calculations, along with a computational study of the unusual MOLPs.

Since their first observation in 2003,^[1] borylene transfer reactions from Group 6 borylene complexes to both metallic and non-metallic substrates have provided access to a large range of otherwise-inaccessible bonding motifs.^[2] Intermetallic borylene transfers have allowed the installation of borylene ligands on many metals for which this had otherwise failed. However, two metals that have so far resisted attempts towards borylene transfer have been ruthenium and osmium. Only a few ruthenium borylene complexes are known, including terminal^[3] and bridging neutral,^[4] and terminal cationic^[5] species, while the family of osmium borylenes currently numbers only the base-stabilized examples prepared by Roper a decade ago.^[6] Thus, the number of neutral, terminal borylene complexes of ruthenium and osmium is currently only one; with this work we sought to increase this and prepare the first osmium example by intermetallic borylene transfer.

It is now quite clear that these intermetallic borylene transfer reactions proceed through dinuclear bridging borylene intermediates;^[7] however, once the original metal center (Cr, Mo or W) is completely cleaved from the boron atom, it is invariably lost from the complex. Moreover, intermetallic borylene transfer reactions have never been found to be reversible. Herein, we demonstrate an alternative mechanism in which intermetallic transfer to ruthenium(0) and osmium(0) takes place, albeit with retention of the chromium atom in the product. Astonishingly, this insertion was found to be reversible upon dissolution of the product. The finding marks some very unusual reversible borylene transfer chemistry, a formal insertion of Ru and Os into a metal–borylene bond, and the synthesis of unprecedented metal-only Lewis pairs (MOLPs)^[8,9] featuring borylene ligands. We also present computational evidence for a plausible intermediate in the process and a rationalization of the outcomes based on orbital considerations.

The UV irradiation of a hexane (**2a**) or C₆D₆ (**2b**) solution of borylene complex [(OC)₅Cr{BN(SiMe₃)₂}] (**1**) and the zero-valent Group 8 complexes [M(CO)₃(PMe₃)₂] (M = Ru, **2a**; M = Os, **2b**) led to the isolation of yellow needles in both cases (M = Ru, **3a**; M = Os, **3b**; Scheme 1). Unfortunately,



Scheme 1. Reversible synthesis of **3a** and **3b**. Conditions a: Dissolution in toluene without CO, RT (low yields are observed owing to the need for a sacrificial CO donor). Conditions b: Toluene, RT, excess CO.

the characterization of these compounds by solution NMR spectroscopy was found to be impossible, as dissolution of these compounds, even at low temperatures, induced reversion back to **1** and precursors **2a,b** (Scheme 1, conditions a and b). However, we were able to study compound **3a** by multinuclear solid-state MAS NMR spectroscopy (¹¹B, ¹³C, ¹⁵N, ²⁹Si, and ³¹P). All spectral NMR parameters (δ_{iso} , J , C_{Quad} , η_{Quad}) extracted from the solid-state MAS NMR spectra are in good agreement with the molecular structure deduced from the single-crystal X-ray diffraction experiment (see below). The number of isotropic chemical shifts found for a particular

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[**] We are grateful to the European Research Council for the award of an Advanced Grant to H.B.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201310520>.

nucleus reflects the C1 symmetry of the molecular structure and the cocrystallized solvent hexane. Furthermore, the isotropic chemical shifts of ^{11}B and ^{15}N calculated by DFT match very well with the solid-state NMR data of these nuclei ($^{11}\text{B}_{\text{NMR}}$: $\delta = 84.6$ ppm, $^{11}\text{B}_{\text{DFT}}$: $\delta = 80.3$ ppm, $^{15}\text{N}_{\text{NMR}}$: $\delta = -251.0$ ppm, $^{15}\text{N}_{\text{DFT}}$: $\delta = -256.8$ ppm). The solid-state NMR spectra gave no indication of the presence of compound **2a** or $[\text{Cr}(\text{CO})_6]$, indicating that no decomposition takes place under MAS conditions. The lineshape of the $^{11}\text{B}\{^1\text{H}\}$ MAS NMR spectrum shows a second-order quadrupole MAS powder pattern. The deduced parameters, the quadrupole coupling constant ($C_{\text{Quad}} = 4.07$ MHz), and the quadrupolar asymmetry parameter ($\eta_{\text{Quad}} = 0.21$) reflect both the huge electric field gradient (EFG) due to the linear $\text{N}=\text{B}=\text{Ru}$ bonding situation at the boron site, and the only slight deviation from axial symmetry. This is to be expected from the molecular structure owing to the nearly perpendicular neighboring *trans*-oriented SiMe_3 , CO, and PMe_3 moieties with respect to the $\text{N}=\text{B}=\text{Ru}$ –Cr axis.

The yellow needles of **3a,b** were characterized by single-crystal X-ray crystallography, revealing in both cases an unusual dinuclear connectivity (Figure 1) in which the borylene ligand has been transferred to the Group 8 metal, but a $\{\text{Cr}(\text{CO})_5\}$ fragment is retained in the complex. In both complexes, a metal–chromium bond is present (**3a**: Cr–Ru 3.068(1) Å; **3b**: Cr–Os 3.0857(9) Å), which is assigned as a dative interaction by comparison with similar complexes reported by Pomeroy with osmium–Group 6 metal bonds.^[9] This assumption, that a pair of electrons originally from the ruthenium center is now being donated to the chromium

fragment, is consistent with a valence electron count of 18 for both metals. However, the Cr–Os distance in **3b** is significantly longer than those observed by Pomeroy (2.966–3.0287 Å), which is presumably due to the much higher *trans* influence of the borylene ligand in comparison to the *trans* ligands in the reported compounds (phosphines, CO).^[9] These distances are also much longer than the bond lengths expected from the experimental covalent radii values of the elements (Cr–Ru: 2.85 Å; Cr–Os: 2.83 Å),^[10] making their d_{rel} values (bond length divided by sum of covalent radii; **3a**: 1.08; **3b**: 1.09) significantly higher than those observed by Pomeroy for neutral Group 8→Group 6 MOLPs (1.00–1.07).^[8] In fact, the d_{rel} value for **3b** is the second highest when considered with the MOLPs compiled in our recent review across all metal elements^[8] (the highest, 1.10, being that for a very unusual tricationic Pd→Ag complex),^[11] and is much higher than the average value for neutral MOLPs (0.987).

The Ru–B distance (1.949(5) Å) in the Ru^0 complex **3a** is significantly longer (ca. 9%) than that in the only other known neutral terminal ruthenium borylene complex, the divalent complex *trans*- $[\text{RuHCl}(\text{BMes})(\text{PCy}_3)_2]$ (1.780(4) Å), which is presumably a factor of the vastly different electronic properties of the two borylene substituents (amino/aryl).^[3a] Apart from the effect of the much more π -donating amino group at boron in **3a**, additional reasons for the large Ru–B distance may be that the borylene ligand competes with the strongly Lewis-acidic $\{\text{Cr}(\text{CO})_5\}$ fragment for electron density from the ruthenium atom, along with the higher coordination number and lower oxidation state of the Ru atom in **3a**.

The dissolution of **3a** and **3b** results in their complete decomposition to give **2a,b** and the borylene complex. In the absence of CO, this reaction is presumably a redistribution reaction involving sacrificial $\{\text{Cr}(\text{CO})_5\}$ units that provide the extra CO ligand required to form **2a/b**. However, apart from a very small signal at $\delta = 7$ ppm in the ^{31}P NMR spectrum, we do not observe any other products. In the presence of CO, **1** and **2a,b** are the only products observed in the ^{11}B and ^{31}P NMR spectra, respectively.

To gain a better understanding of the nature of the metal–metal bond in **3a** and the observed reaction outcomes, we performed DFT calculations on **3a** and its heavier Group 6 analogues $[(\text{OC})_5\text{Mo} \leftarrow \text{Ru}(\text{CO})_2(\text{PMe}_3)_2\{\text{BN}(\text{SiMe}_3)_2\}]$ (**3a'**) and $[(\text{OC})_5\text{W} \leftarrow \text{Ru}(\text{CO})_2(\text{PMe}_3)_2\{\text{BN}(\text{SiMe}_3)_2\}]$ (**3a''**) using the gradient-corrected PBE1PBE functional in conjunction with the def2-SVP basis sets (see the Supporting Information for computational details). The optimized geometrical parameters for **3a** are in excellent agreement with experimentally obtained parameters. Apart from the calculated Cr–Ru distance, which is about 5 pm longer than the experimental value, no appreciable differences are found in other geometrical parameters (see Supporting Information). The metal–ruthenium bond constitutes a dative interaction from the ruthenium fragment to the Group 6 metal carbonyl fragment. To check this, we have performed NBO calculations on the separated fragments $[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[\text{Ru}(\text{CO})_2(\text{PMe}_3)_2\{\text{BN}(\text{SiMe}_3)_2\}]$ in their geometry in the complex. The charge at the Ru atom in its mononuclear fragment (−2.1) is more negative than in the dinuclear

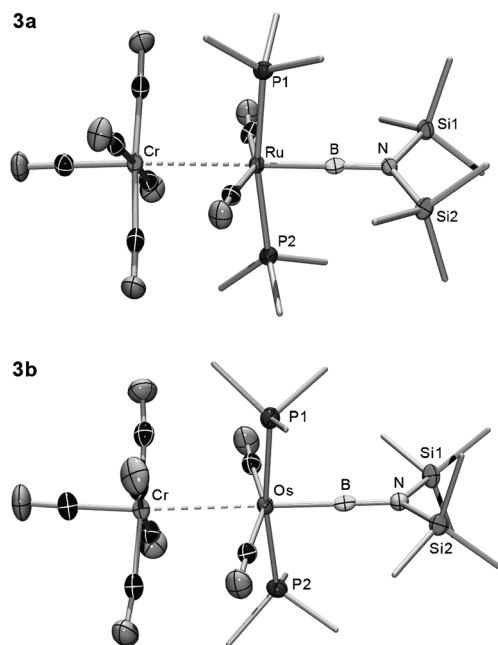


Figure 1. Molecular structures of **3a** and **3b** as derived from X-ray crystallography. Ellipsoids are depicted at 50% probability; hydrogen atoms and some carbon ellipsoids are removed for clarity. Selected bond lengths [Å] and angles [°] for **3a**: Cr–Ru 3.068(1), Ru–B 1.949(5), B–N 1.345(6); B–Ru–Cr 179.1(1). For **3b**: Cr–Os 3.0857(9), Os–B 1.967(6), B–N 1.345(8); B–Os–Cr 178.78(17).

molecules **3a**, **3a'** and **3a''** (−1.9 to −2.0), while the charge at the Group 6 atom is less negative in the fragment than in the MOLP. This indicates a flow of electron density from Ru to the Group 6 metal upon combining the two fragments, and a dative Ru→M bond (see the Supporting Information). The HOMO is the molecular orbital responsible for this interaction (Figure 2). NBO analysis indicates that the metal–metal bond is weaker for **3a** than for **3a'** and **3a''**.

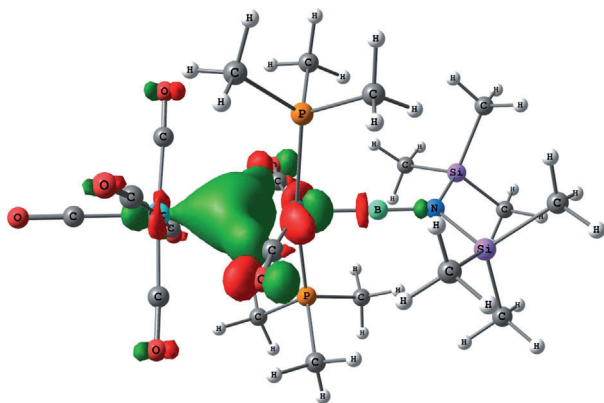


Figure 2. Molecular orbital (HOMO) representing the metal–metal bond in **3a**.

It was observed experimentally that when **3a** was exposed to an atmosphere of CO, the metal–metal bond cleaves, along with transfer of the borylene fragment from ruthenium to chromium and formation of $[\text{Ru}(\text{CO})_3(\text{PMe}_3)_2]$. The thermodynamic preference for attack of CO at the Ru center was evaluated by studying two alternative reactions of **3a**, **3a'**, and **3a''** with CO. For all Group 6 metals, Path A (Figure 3), leading to ruthenium borylene complex $[\text{Ru}=\text{BN}(\text{SiMe}_3)_2](\text{CO})_2(\text{PMe}_3)_2$ and $[\text{M}(\text{CO})_6]$, was found to be less favorable than Path B, which regenerates the precursor Group 6 borylene complexes and $[\text{Ru}(\text{CO})_3(\text{PMe}_3)_2]$. The latter path is favored by about 9.0 kcal mol^{−1} for M = Cr and W, and 6.8 kcal mol^{−1} for M = Mo.

We envisage the following path for transfer of the borylene fragment in **3a**, **3a'** and **3a''** and evaluated the energetics for this process (Figure 4): in the first step, compounds **3** undergo *trans*–*cis* isomerization, effectively exchanging one phosphine ligand with the borylene ligand, to yield **3_{iso}**. This exchange of the strongly *trans*-influencing borylene ligand by the weaker *trans*-influence phosphine has the expected effect on the *trans* M–Ru bond: the M–Ru distances of **3_{iso}** are shorter than those of **3** by

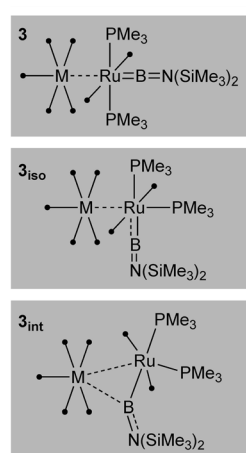


Figure 4. Likely pathway for transfer of the borylene fragment from Ru to the Group 6 metal along with relevant geometrical parameters and relative energies of the molecules. Distances [Å], angles [°], and relative energies [kcal mol^{−1}] are shown.

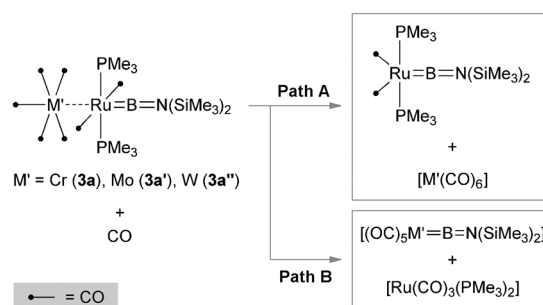


Figure 3. Computed fragmentation pathways for **3a** and hypothetical complexes **3a'** and **3a''**.

5.5–8.2 pm. We also located an intermediate **3_{int}** that shows the formation of an incipient M–B bond. The Ru–B bond lengthens by 6.1–8.8 pm in going from **3** to **3_{int}**. We did not observe any dramatic change in the Ru–B and B–N bond lengths upon changing the Group 6 metal. The relative energy change for this entire rearrangement process is less than 4.0 kcal mol^{−1}, implying that the potential energy surface is rather shallow. This explains the very fast transfer of the borylene fragment from ruthenium to the Group 6 metal upon dissolution of **3** in CO-saturated solvent.

We reasoned that the observation of the bimetallic species **3a** rather than the expected mononuclear species $[\text{Ru}\{\text{BN}(\text{SiMe}_3)_2\}(\text{CO})_2(\text{PMe}_3)_2]$ could originate from a synergic effect in the Cr–Ru–B unit, that is, the Ru–B bond is slightly stronger in the presence of the Cr atom *trans* to the B atom. Indeed we find a slightly shorter Ru–B distance in the optimized geometry of **3a** compared to the hypothetical $[\text{Ru}(\text{PMe}_3)_2(\text{CO})_2\{\text{BN}(\text{SiMe}_3)_2\}]$ complex despite the lower coordination number of the Ru center in the latter. As shown in the Supporting Information, Figure S1, the orbital interactions between the $\{\text{BN}(\text{SiMe}_3)_2\}$ (denoted [B]) and $[(\text{OC})_5\text{Cr}–\text{Ru}(\text{PMe}_3)_2(\text{CO})_2]$ fragments (denoted [Ru–Cr]) show that the HOMO of [B] interacts with the HOMO–4 of [Ru–Cr] to form the HOMO–12 of **3a**. Examination of the

	<i>d</i> (M–Ru)	<i>d</i> (Ru–B)	<i>d</i> (B–N)	<i>∠</i> (M–Ru–B)	<i>E</i> _{rel.}
M = Cr	3.103	1.922	1.378	180.0	0
M = Mo	3.198	1.923	1.379	179.8	0
M = W	3.191	1.925	1.379	179.7	0

	<i>d</i> (M–Ru)	<i>d</i> (Ru–B)	<i>d</i> (B–N)	<i>d</i> (M–B)	<i>∠</i> (M–Ru–B)	<i>E</i> _{rel.}
M = Cr	3.048	1.976	1.374	3.254	77.4	3.86
M = Mo	3.119	1.977	1.378	3.179	73.3	3.67
M = W	3.109	1.981	1.379	3.126	71.9	3.23

	<i>d</i> (M–Ru)	<i>d</i> (Ru–B)	<i>d</i> (B–N)	<i>d</i> (M–B)	<i>∠</i> (M–Ru–B)	<i>E</i> _{rel.}
M = Cr	2.970	2.010	1.40	2.670	61.5	3.80
M = Mo	3.111	1.984	1.385	2.940	75.4	2.83
M = W	3.089	2.0	1.396	2.766	61.5	1.85

— = CO

composition of the frontier orbitals (HOMO to HOMO–4) of **3a** reveal that these orbitals mainly originate from interactions between the Cr and Ru centers (Supporting Information, Table S1). In contrast, in the optimized [Ru{BN-(SiMe₃)₂}(CO)₂(PMe₃)₂] complex (Supporting Information, Figure S2), the boron atom switches to interacting with the higher-energy orbitals of ruthenium (data not shown) to make up the frontier orbitals of the molecule, resulting in a slightly lower Ru–B bond order (weaker bond) in the fragment (1.48) than in **3a** (1.50). Analogously, the Ru–B distance is larger in the fragment (1.960 Å) than in **3a** (1.945 Å) (Supporting Information, Figure S2), indicating a weaker Ru–B bond in the former. Overall, in **3a** the relevant interactions are B_{frontier}–Ru_{low-energy} and Cr_{frontier}–Ru_{frontier}, whereas in [Ru{BN-(SiMe₃)₂}(CO)₂(PMe₃)₂], the interactions are B_{frontier}–Ru_{frontier}.

The decomposition of the interaction energy E_{int} in **3a** is in line with the apparent facile cleavage of the Ru–B linkage (E_{orb} : –141.24, E_{elstat} : –256.97 and E_{Pauli} : 323.70 kcal mol^{–1}), with E_{int} amounting to –74.50 kcal mol^{–1}. Thus the repulsive Pauli interaction constitutes the highest contribution to the bonding energy, the destabilizing interactions between occupied orbitals making the total interaction energy between the [Cr(CO)₅Ru(PMe₃)₂(CO)₂] and [BN(SiMe₃)₂] fragments relatively low and weakening the Ru–B bond. Overall, while the Ru–B bond in **3a** is more stable than in the hypothetical mononuclear Ru borylene, it remains somewhat “metastable” owing to the relatively intense Pauli repulsions from the interactions between filled orbitals, perhaps explaining the reversibility of the reaction.

Our results have uncovered a number of unusual reactivity patterns of Group 8 borylene complexes. The products include the first osmium borylene complex, as well as a rare example of a terminal ruthenium borylene complex, in addition to containing very unusual Ru/Os→Cr dative bonds. Moreover, the reversibility of the borylene transfer reaction is unprecedented. A general feature of borylene ligands is that they have a strong proclivity towards bridging when more than one metal is available. Notably in this case, the products are the first multimetallic borylene complexes in which not all of the transition metal atoms interact with the boron center, suggesting that the Ru/Os→Cr dative bond must be very favorable indeed.

Received: December 4, 2013
Published online: March 12, 2014

Keywords: bimetallic complexes · boron · borylene · metal-only Lewis pairs · transition-metal complexes

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