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Reversible Coupling of :CO and :BR

Reversible Intramolecular Coupling of the Terminal Borylene and a Carbonyl Ligand of [Cp(CO)$_2$Mn=B–*t*Bu]**

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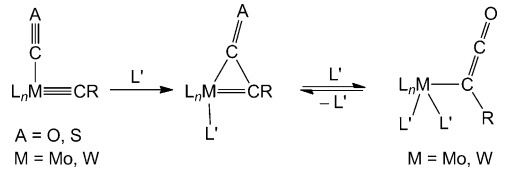
Since the discovery of complexes containing carbon–metal multiple bonds, this area of chemistry has developed at an increasing pace.[1,2] Metal carbyne complexes, following their elder siblings metal carbenes,[3] play a versatile role in many chemical processes, such as alkyne metathesis or polymerization of internal acetylenes.[3b,h,4] One particularly interesting reaction of Group 6 metal carbyne complexes, first reported by Kreissl et al.,[5] involves an intramolecular coupling between the carbido ligand (≡CR) and a neighboring carbonyl ligand to form a ketenyl ligand (Scheme 1). This



Scheme 1. Metal carbyne–carbonyl coupling reactions.

fundamentally interesting and synthetically important carbon–carbon bond formation by intramolecular CO–CR coupling, owing to its similarities to the key step involved in the Monsanto process, has been explored by many research groups, mainly on Group 6 carbyne complexes.[1f,i,5b,6] It was also extended to heavier thio- and seleno-carbonyl analogues.[6c,7]

Metal borylene chemistry, although being much younger,[8] has demonstrated intriguing reactivity.[9] In particular, the terminal Group 7 metal borylene complexes [L$_n$M=B–R] have been shown to undergo [2+2] cycloaddition with unsaturated polar organic substrates. In the case of [Cp(CO)$_2$Mn=B–*t*Bu] (**1**, Cp = η^5-C$_5$H$_5$) and, for example, benzophenone, the resulting cycloaddition product is prone to subsequent cycloreversion to afford otherwise synthetically challenging carbene complexes.[10] This metathesis-type reactivity mirrors that of carbyne complexes. Further exploration of **1** led us to the results presented herein, which include the successful generation and isolation of an unprecedented and electronically unique borylene derivative [Cp(Mes*NC)(OC)Mn{C(O)B(*t*Bu)(CNMes*)}] (**2**, Mes* = 2,4,6-tri(*tert*-butyl)phenyl). The formation of this complex is, to the best of our knowledge, the first structurally characterized example of a reversible, intramolecular CO–BR coupling. Since Group 7 metal terminal borylene complexes such as complex **1** are isoelectronic to Group 6 metal carbyne complexes (Figure 1 A,B), and the borylene ligand (:B–R) is

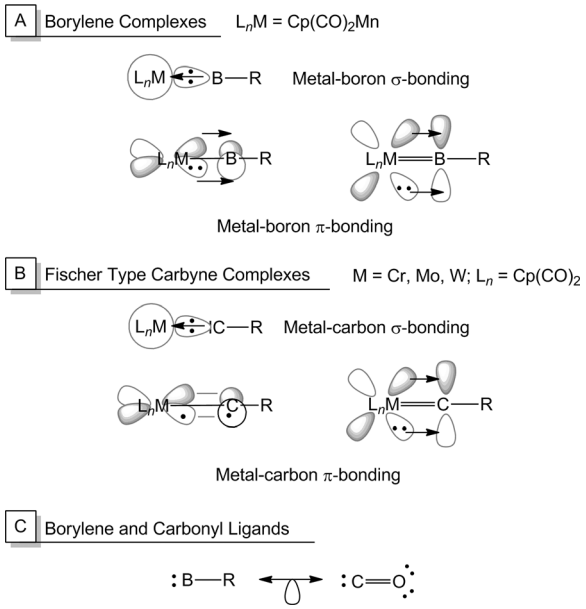


Figure 1. A,B) Bonding descriptions of isoelectronic borylene and carbyne complexes. C) Isolobal borylene and carbonyl ligands.

isolobal to a carbonyl ligand (Figure 1 C), this observed heterocoupling between a borylene and a carbonyl ligand is of great significance as it not only relates closely to the carbyne–CO coupling reactions described above, but also closes a gap between the intramolecular CO–CO homocoupling reactions[11] and the recently disclosed borylene–borylene homocoupling reaction.[12]

The formation of boron–carbon bonds has been a topic of intense interest to synthetic chemists for its fundamental and practical value in metal-assisted catalytic cross-coupling reactions.[13] However, examples that demonstrate a reversible formation of B–C bonds remain rare.[14] Apart from this work, there are only two structurally characterized metal complexes that feature M–C(A)–B (A = O, S) connections,[3a,15] both of which display coordination modes that differ greatly from this study.

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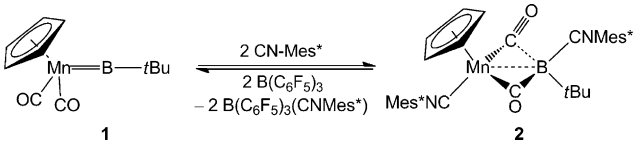
The terminal borylene complex **1** reacted with two equivalents of supermesityl isonitrile (CNMes*) in non-coordinating solvents (*n*-pentane, *n*-hexane, benzene, or toluene) at room temperature to form a dark brown solution, from which the complex [Cp(Mes*NC)(OC)Mn{C(O)B-(*t*Bu)(CNMes*)}] (**2**) precipitated out as a brown crystalline solid quantitatively within minutes. Subsequent treatment of **2** with two equivalents of tris(pentafluorophenyl)borane, which serves as a strong Lewis acid, led to quantitative reformation of the terminal borylene **1**. The reaction of **1** with one equivalent of the isonitrile yielded a mixture of the starting material **1** and the product **2** in a 1:1 ratio. Similarly, addition of one equivalent of tris(pentafluorophenyl)borane to a solution of **2** led to a 50% conversion of **2** into **1** (Scheme 2). No intermediate was detected in either the forward or reverse reactions by ^{11}B or ^{1}H NMR spectroscopy. These observations implied that both isonitrile ligands are essential for formation and stabilization of complex **2**.



Scheme 2. Reversible coupling of the CO and B(*t*Bu) ligands.

Single-crystal X-ray crystallography revealed the unusual molecular structure of **2** as a cyclic complex with one bridging and one semi-bridging carbonyl ligand between the Mn and B atoms (Figure 2).[16] The coordination mode of M–C(O)–E

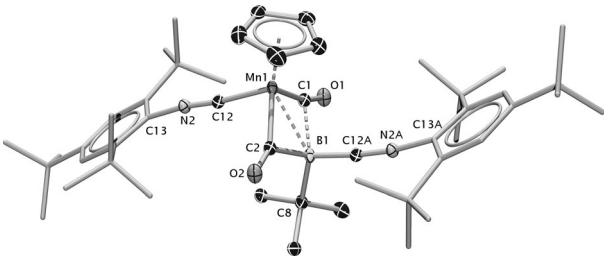


Figure 2. Molecular structure of **2**. Ellipsoids are set at 50% probability. The ellipsoids of supermesityl groups are omitted for clarity. Selected bond lengths [Å] and angles [°] from B3LYP/Def2-SVP calculations: Mn1–B1 2.297, Mn1–C1 1.784, Mn1–C2 1.938, Mn1–C12 1.847, B1–C1 2.229, B1–C2 1.586, B1–C8 1.662, B1–C12A 1.511; Mn1-C1-O1 169.4, Mn1-C2-O2 137.9.

(M = transition metals, E = Group 13 element) was, to the best of our knowledge, unknown prior to this work. We were able to obtain crystals that contained benzene, toluene, or no solvent molecules in the unit cell. However, all three structures show the same type of disorder: an inversion center in the middle of a molecule leads to overlap of a {CpMnCO} moiety with {*t*BuBCO} that causes a problem with deconvolution of atom positions, especially for the Mn/B pair and both carbonyl groups. For this reason, computational studies using density functional theory methods were performed. The IR and NMR calculations of **2** based on optimized geometry are consistent with the experimentally observed values. Therefore, the structural features of **2** will be discussed based on calculated values.[17]

The energy-minimized geometry of **2** revealed two differently bonded bridging carbonyl ligands, which was also reflected by experimental IR data and natural bond order (NBO) analysis of model complexes of **2**. The [C2O2] carbonyl ligand (Figure 2) exhibits strong covalent interactions with both Mn1 and B1 atoms, which involve the π* antibonding orbital of CO, a d_{z^2} orbital of the manganese center, and the p orbital of the boron center (Figure 3). The

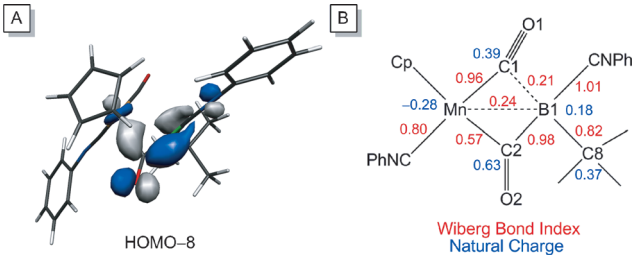


Figure 3. A) Depiction of the HOMO–8 of the model complex [Cp-(PhNC)(OC)Mn{C(O)B(Me)(CNPh)}] ($\mathbf{2}^{H}$), showing the π-type bonding interactions of the bridging carbonyl with the metal and boron centers. B) Calculated Wiberg bond indexes and natural charges of the model complex.

Mn1–C2 separation of 1.938 Å in **1** is noticeably longer than those observed for other related bridging carbonyl-containing derivatives (1.806–1.844 Å).[18] The B1–C2 bond length is 1.586 Å, which lies in the range of a normal B–C single bond.[19] These parameters imply a somewhat stronger interaction between the carbonyl [C2O2] and the boron moiety than the manganese metal fragment, which was also reflected by the Wiberg bond index (WBI) analysis. The Mn1–C2 interaction has a WBI of 0.57, which is significantly lower than that of B1–C2 (0.98). On the other hand, the carbonyl [C1O1] has a quite different bonding situation. The bond lengths of Mn1–C1 (1.784 Å) and C1–O1 (1.168 Å) are not significantly different to those observed for a conventional terminal carbonyl ligand. However, the WBI analysis revealed a small but non-negligible bond order of 0.21 between C1 and B1. An interaction of similar strength was found between Mn1 and B1, with a WBI of 0.24.

The bonding situation of the boron atom in **2** is rather difficult to elucidate in terms of interactions with five neighboring atoms. The covalent bonds B1–C2 and B1–C8 and the dative bond B1–C12A are more conventional, which is also evident from the NBO analysis described above. The third valence electron of boron must be pairing with one from the metal center and forming a more delocalized interaction with both Mn1 and C1. This more diffused, three-center–two-electron bonding mode is also reflected by a remarkable ^{11}B NMR chemical shift of −57 ppm (Table 1), which is shifted by more than 200 ppm upfield from its precursor borylene complex (**1**, 145 ppm).[18b] It lies considerablyfurther upfield than those observed for not only the isonitrile coordinated boron species, $BR_3(CNR')$,[20] but indeed most commonly observed tetracoordinate boron compounds

Table 1: Selected experimental and calculated spectroscopic data of complex **2**.

	IR ($\tilde{\nu}$, cm^{-1})[a]				NMR (δ, ppm)[b]			
	C1O1	C2O2	C12N2	C12AN2A	B1	C1	C2	C12
Expt.	1903	1704	2136	2056	−57.2	260.8		193.1
Calc.	1892	1745	2117	2061	−58.3	241.1	289.7	207.0

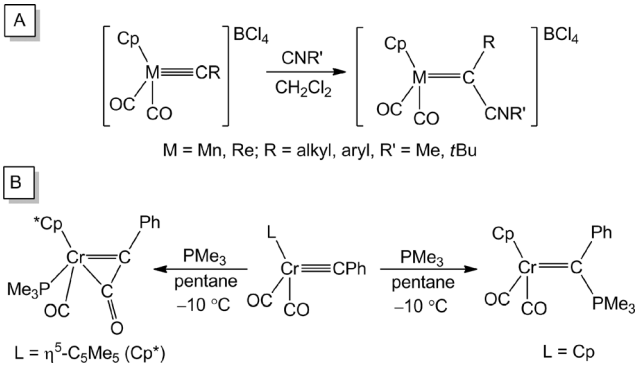
[a] Experimental values were obtained from a toluene solution of **2**. The calculated with B3LYP/Def2-SVP values were scaled with a factor of 0.96. [b] Collected with a Bruker 500 FT-NMR spectrometer at −30 °C from a [D_8]toluene solution.

(BR_3L, BR_4^-, and BH_4^- species, the ^{11}B chemical shifts of which lie in the range of 20 to −45 ppm);[21] it falls in the range expected for boron cluster compounds. The natural chemical shift (NCS) decomposition of shielding tensors computed with GIAO method shows that in **1**, the shielding of the boron core ($\sigma_{core} = 166$ ppm) is essentially reduced by anti-shielding contributions from the Mn–B bond ($\sigma_{Mn\text{-}B} = -137$) and the B–$C_{tBu}$ bond ($\sigma_{B\text{-}C} = -56$ ppm), which lead to total shielding of −44 ppm (re-calculated for the $BF_3{\cdot}Et_2O$ standard: $\delta =$ 151 ppm). As known from earlier IGLO and NCS studies, core contributions are transferable between different compounds,[22] and in **2**, σ_{core} has the same value of 166 ppm. However here, in contrast to its precursor **1**, σ_{core} is little affected by negligible contributions from $\sigma_{Mn\text{-}B^*} = 7$ and $\sigma_{B\text{-}C} =$ −8 ppm, thus resulting in a total shielding of 165 ppm (re-calculated for the $BF_3{\cdot}Et_2O$ standard: $\delta = -58$ ppm).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** are largely unremarkable, showing two sets of signals for the two chemically different isonitrile ligands. The observed proton integrals are consistent with the confirmed structure of **2**. One sharp ^{13}C NMR signal was observed at 260 ppm, attributed to the carbonyl carbon nucleus, which is shifted noticeably downfield from the borylene precursor **1** (224 ppm). The observation of one single CO environment suggests a fluxional process between the two CO ligands that bridge the metal and boron centers. The low-lying transition state of C_s symmetry with $\Delta E = 2$ kJ mol^{-1} supports that hypothesis. Another sharp singlet was observed at 193 ppm, which was assigned to the metal-coordinated terminal isonitrile carbon nucleus. The boron-coordinated terminal isonitrile carbon nucleus was not observed.

The IR spectrum of **2** showed two absorption bands at 2135 (medium) and 2056 cm^{-1} (strong) corresponding to the CN stretches from the two isonitrile ligands. Two less-intense bands were observed at 1903 and 1704 cm^{-1}, corresponding to the semi-bridging (C1–O1) and the bridging (C2–O2) carbonyl ligands between the Mn and B atoms, respectively. These values are significantly lower than those observed for the precursor borylene complex **1** (1968 and 1912 cm^{-1}) and its bridging CO-containing derivatives,[18] which again implies an enhanced π-back-donation from the Mn^-B core. The bridging carbonyl (C2–O2) may be viewed as analogous to those bridging between two transition metals. Furthermore, the low energetic barrier to the fluxional process between the two CO ligands of **2** resembles the exchange of bridging and semi-bridging CO ligands via low energy concerted pathways of complexes containing metal–metal bonds.[23] These points together suggest that the boron in **2** is somewhat metallic in nature, reflecting its high electropositivity.

The mechanism of the formation of **2** calls for discussion. The initial nucleophilic attack could happen either at the manganese or the boron center. Indeed, both cases were observed for the isoelectronic carbyne chemistry (Scheme 3).[6b,h,24] In this study, computational calculations support the proposal that initially one isonitrile molecule approaches



Scheme 3. Selected examples of nucleophilic addition to metal carbyne complexes. A) Fischer's reaction of Group 7 metal carbynes with isonitrile. B) Filippou's selective addition of the trimethylphosphine ligand to $[L(OC)_2Cr{\equiv}CPh]$ ($L = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$).

the boron atom in **1**. The low-lying transition state ($\Delta E =$ 19.8 kJ mol^{-1}) regroups to the marginally bent trigonal geometry intermediate (Int; ∡Mn-B-C 142°). This first step is slightly exothermic ($\Delta E = -77.7$ kJ mol^{-1}). Subsequently, a second isonitrile molecule attacks the manganese atom. The higher-lying transition state ($\Delta E = 74.0$ J mol^{-1}) rearranges then to $\mathbf{2^H}$ ($\Delta E = -204.5$ kJ mol^{-1}). The total enthalpy change for this reaction is −188.3 kJ mol^{-1} (Figure 4).

In conclusion, a cyclic complex **2** with bridging carbonyl ligands was synthesized from an intermolecular carbonyl–borylene ligand coupling reaction involving the borylene complex **1** and two equivalents of supermesitylisonitrile. Upon treatment with a strong Lewis acid, complex **2** loses

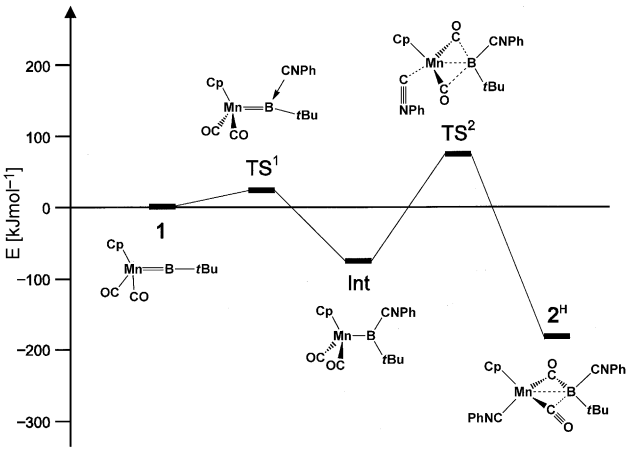


Figure 4. Energy profile for the reaction of **1** with two equivalents of PhNC calculated at the B3LYP/Def2-SVP level.

both isonitrile ligands and reverts back to **1** quantitatively (as observed by NMR spectroscopy). Complex **2** exhibits unique structural and electronic properties, which may result in new reactivity that is of both fundamental and synthetic importance.

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[16] CCDC 898073, 898074, and 898075 contain the supplementary crystallographic data for Compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] Geometry optimization and spectroscopic data were calculated for complex **2**. Calculations on orbital analyses and mechanistic studies were carried out using smaller model compounds. See the Supporting information for details on computations.

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