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Authors: Ian Fairlamb, James D. Firth, L. Anders Hammarback, Thomas J. Burden, Jonathan B. Eastwood, James R. Donald, Chris S. Horbaczewskyj, Matthew T. McRobie, Adam Tramaseur, Ian P. Clark, Michael Towrie, Alan Robinson, Jean-Philippe Krieger, and Jason M. Lynam

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Light- and Manganese-Initiated Borylation of Aryl Diazonium Salts: Mechanistic Insight on the Ultrafast Time-Scale Revealed by Time-Resolved Spectroscopic Analysis

James D. Firth,^[a] L. Anders Hammarback,^[a] Thomas J. Burden,^[a] Jonathan B. Eastwood,^[a] James R. Donald,^[a] Chris S. Horbaczewskyj,^[a] Matthew T. McRobie,^[a] Adam Tramaseur,^[a] Ian P. Clark,^[b] Michael Towrie, ^[b] Alan Robinson,^[c] Jean-Philippe Krieger,^[c] Jason M. Lynam^{*[a]} and Ian J. S. Fairlamb^{*[a]}

[a] Prof. Dr. I. J. S. Fairlamb, Drs. J. M. Lynam, J. D. Firth, L. A. Hammarback, J. R. Donald, C. S. Horbaczewskyj, Mr. T. J. Burden, Mr. J. B. Eastwood						
	M. T. McRobie, Mr. A. Tramaseur					
	Department of Chemistry					
	University of York					
	Heslington, York, YO10 5DD, United Kingdom					
	E-mail: ian.fairlamb@york.ac.uk; jason.lynam@york.ac.uk (joint corresponding authors)					
[b]	Dr. I. P. Clark, Prof. M. Towrie,					
	Central Laser Facility					
	Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, Oxfordshire, OX11 0QX, United Kingdom.					
[c]	Drs. A. Robinson, JP. Krieger					
	Syngenta Crop Protection AG					
	Münchwilen, Breitenloh 5, 4333, Switzerland.					

Supporting information for this article is given via a link at the end of the document (full experimental details).

Abstract: Manganese-mediated borylation of aryl/heteroaryl diazonium salts emerges as a general and versatile synthetic methodology for the synthesis of the corresponding boronate esters. The reaction proved an ideal testing ground for delineating the Mn species responsible for the photochemical reaction processes, *i.e.* involving either Mn radical or Mn cationic species, which is dependent on the presence of a suitably strong oxidant. Our findings are important for a plethora of processes employing Mn-containing carbonyl species as initiators and/or catalysts, which have much potential in synthetic applications.

Introduction

Aryl boronates are important building blocks within organic synthesis, without question due to the ubiquity of the Suzuki-Miyaura reaction, which ranks in the top-five most used reactions in target-orientated synthesis,^[1] across the pharmaceutical and agrochemical industries.^[2,3] The most common methods for their preparation involve either the stoichiometric metalation (to organo-lithium or Grignard reagents) or the Miyaura borylation^[4] of aryl halides. The former approach suffers from limited functional group tolerance and the need for anhydrous conditions and controlled reagent addition, whereas the latter requires Pd catalysis. Inexpensive and abundant transition metals including Cu, Ni, Zn and Fe can also be employed.^[5,6]

Alternative practical approaches to aryl boronates include C-H activation / borylation, often using earth abundant metals^[7,8] and the visible light-induced borylation of aryl radical precursors, including aryl iodides,^[9] aryl *N*-hydroxyphthalimido esters,^[10] and aryl azo-sulfones.^[11] Indeed, aryl diazonium salts have been employed extensively as aryl radical precursors^[12–15] due to their relatively low reduction potential and the ease of synthesis from widely available anilines. Photoreduction to the desired aryl radicals can be simply achieved using a photo-initiator, resulting in many reports over the past decade of the photoredox-catalysed arylation of unsaturated systems.^[14] For example, Yan and coworkers demonstrated the eosin Y catalysed borylation of aryl diazonium salts to generate aryl pinacol boronates (Scheme 1).[16] In some cases, such processes proceed via photoinitiated radical chain mechanisms, as was observed for arylation with aryl diazonium salts.^[17] However, it has been shown that the use of broadband visible light irradiation can lead to the direct photolysis of aryl diazonium salts, generating the aryl boronates via aryl cations.[13,18,19] These findings therefore show that it is critical to understand how the photochemical activation is being executed, under specific conditions, as radical and cationic pathways might be similarly energetically feasible. Furthermore, other research teams have developed non-photoinduced processes for the synthesis of aryl boronates from aryl diazonium salts,[20-25] including the one-pot diazotization/borylation of anilines,[26-30] proceeding via both radical and cationic intermediates.



Scheme 1. Light mediated borylation of aryl diazoniums.

A versatile Mn precursor complex, namely dimanganese(0) decacarbonyl, $Mn_2(CO)_{10}$, readily undergoes photo-induced

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homolysis to generate a manganese-centered radical [Mn(CO)₅][•] (BDE of Mn-Mn bond ~15 kcal mol⁻¹).^[31] Facile generation of this reactive species has been employed in several distinctive organic transformations, which often proceed through the abstraction of a halogen from an alkyl halide in reactions involving light.^[32–41] Despite this precedent there has been little reported confirming that $Mn_2(CO)_{10}$ generates reactive aryl radicals.^[42]

Given our interest in initiating chemical transformations with Mn^I-carbonyl complexes,^[43-45] we envisaged that the facile reduction of aryl diazonium salts to aryl radicals could be achieved with Mn₂CO₁₀, leading to generation of aryl pinacol boronates upon treatment with B₂pin₂. Credibility for this proposal comes from Ackermann and co-workers' recent study, with the synthesis of an exemplar aryl boronate (Scheme 1), using Mn₂(CO)₁₀ and blue LEDs through a Mn^I-mediated process.^[42] We recognized that this single example could be broadened out into a general synthetic methodology, but that the reaction manifold allowed us to ask arguably a more fundamentally important question about the involvement of Mn species in a raft of low oxidation state Mnmediated transformations,^[42,46,55–62,47–54] particularly those invoking redox neutral Mn^I species.

It is evident that initiators derived from Mn₂(CO)₁₀ could be either radical (Mn⁰), cationic (Mn¹) or anionic (Mn⁻¹) in nature. Knowing which species form, particularly under activation by light, and under what reaction conditions, is vitally important in exploiting downstream breakthroughs in synthetic chemistry, particularly with an eye on cascade processes. Answering this question is not straight-forward. However, in recent years we have demonstrated exactly how time-resolved multiple probe spectroscopy (TR^MPS) with infra-red detection can be used to interrogate reaction steps pertinent to catalysis, from the picotimescale.[43,63-65] micro-second Following second to photochemical activation of the pre-catalyst, the vibrational modes of the Mn-CO moiety provide the perfect spectroscopic handle for monitoring the accumulation of new species and intermediates as well as their final fate. Thus, in this paper we firstly describe the innovation of the Mn-mediated borylation of aryl/heteroaryl diazonium salts into a general synthetic methodology. The reaction proved ideal for generating mechanistic detail and extraordinary insight into the Mn species involved in the photochemical reaction processes, the findings of which are globally important for a plethora of processes employing Mn-containing carbonyl initiators / catalysts.

Results and Discussion

Our investigation began with the borylation of aryl diazonium tetrafluoroborate salt **1a** with B_2pin_2 and $Mn_2(CO)_{10}$ initiator in MeCN, irradiating with a 60 W blue LED lamp (Table 1 and Table S1 in the Supporting Information). Aryl boronate **2a** was formed in quantitative yield and isolated in 96% yield when 4 mol% $Mn_2(CO)_{10}$ and 3 equivalents of B_2pin_2 were irradiated in MeCN, for 2 h (Table 1, entry 1). Reducing the stoichiometry of the $Mn_2(CO)_{10}$ or B_2pin_2 resulted in lower yields (Table 1, entries 2-4). Control experiments without either $Mn_2(CO)_{10}$ or light confirmed the essential role of both the former (presumed to be the initiator vide *infra*) and latter (Table 1, entries 5-6). Further reaction optimisation studies showed that reducing reaction concentration by five-fold had a negligible effect on product **2a** yield (96%, Table 1, entry 7) and that acetonitrile was the optimal solvent (Table 1,

With optimal reaction conditions in hand, we investigated the robustness and reproducibility of the protocol (for the synthesis of **2a**) using a Glorius sensitivity assessment (Scheme 2, top right, for full details see Supporting Information).^[66] This method is a quick means to gain an overview of the reaction condition based sensitivity of a given synthetic method. Our protocol showed little sensitivity to water content, concentration or light intensity and only a moderate sensitivity to the presence of oxygen. Furthermore, the reaction was easily scaled, giving **2a** in 90% yield (2.10 g) on a 10 mmol scale (Scheme 2).



[a] Reaction Conditions: **1a** (0.5 mmol), B₂pin₂ (1.5 mmol) and Mn₂(CO)₁₀ (4 mol%) in MeCN (0.5 mL) were irradiated with 60W blue LEDs at room temperature under Ar for 2 h. [b] Yield determined by GC using mesitylene (0.25 mmol) as an internal standard. Isolated yield in parentheses. [c] Vial wrapped in foil. [d] 1.0 mL of solvent used.

Next, the substrate scope of the transformation was investigated (Scheme 2). The Mn-initiated borylation tolerated ethers giving **2a** (*vide supra*) and biaryl ether **2b** in excellent yield. Simple alkyl groups were also tolerated giving **2c–f** in moderate yield (43–75%). Sterically demanding mesityl and *ortho*-biphenyl substrates gave **2g** and **2h** in 63% and 61% yield respectively. Potentially reactive functional groups were also found compatible; halogenated aryl diazonium salts gave borylated haloarenes (**2i–m**) in moderate to excellent yields (44–99%), as well as trifluoromethyl aryl boronate **2n** in 71% yield. Ester (**2o**), amide

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(2p) and ketone (2q) functionality were tolerated, as were phenol (2r) and nitro groups (2s and 2t), albeit in poorer yields. Furthermore, heteroaryl substituents gave the corresponding pinacol boronates in moderate yield, including quinoline (2u), pyridine (2v) and benzofuran (2w). Pleasingly, more complex drug-derived substrates were accommodated well by the methodology, with boronates 2x and 2y being formed in 88% and 63% yield respectively.



Scheme 2. Borylation of (hetero)aryl diazonium salts 1.

We examined the feasibility of a continuous photo-flow method; irradiating a 0.35 M solution of **1a**, with 4 mol% of initiator $Mn_2(CO)_{10}$ and 3 equivalents of B_2pin_2 for 2.5 h led to a 93% conversion to aryl boronate **2a**. A preliminary mechanistic investigation involving irradiating **1n** in the presence of $Mn_2(CO)_{10}$

Mechanistic insight provided by TR^MPS. Previous work on the photochemistry of [Mn₂(CO)₁₀] (summarized in Figure 1) has demonstrated that irradiation at low energy ($\lambda \ge 400$ nm) results in Mn–Mn bond cleavage to give [Mn(CO)₅]^{•.[67]} The radical may undergo different fates in non-donor solvents including (a) dimerization to regenerate Mn₂(CO)₁₀ (b) in MeCN strong oxidising agents result in the conversion to 18-electron [Mn(CO)₅(NCMe)]^{+,[68]} and (c) in the absence of an exogenous oxidant, **CO-substitution** by MeCN affords [Mn(CO)₃(NCMe)₃][Mn(CO)₅]. This latter process likely proceeds via 19-electron [Mn(CO)₃(NCMe)₃][•] which is then oxidised by Mn₂(CO)₁₀ to [Mn(CO)₃(NCMe)₃][Mn(CO)₅], with concomitant formation of [Mn(CO)₅][•].^[69,70]



Figure 1. Previously reported fates of photochemically generated $[Mn(CO)_5]^{\bullet}$. (a) dimerization to reform $Mn_2(CO)_{10}$ (b) oxidation and solvent addition to form $[Mn(CO)_5(NCMe)]^+$ (c) formation of $[Mn(CO)_3(NCMe)_3][Mn(CO)_5]$ corresponding for a formal disproportionation of $Mn_2(CO)_{10}$.

TR^MPS was used to gain insight into the mechanistic process underpinning the formation of pinacol boronates **2**. In these experiments, the sample was irradiated with an ultrafast laser pulse ($\lambda = 400$ nm) to activate the Mn₂(CO)₁₀. Insight into the nature and dynamic behavior of the photoproducts was obtained by monitoring the subsequent changes in the infra-red spectrum between 1900 and 2100 cm⁻¹ with pump-probe delays between 1 ps and 1 ms.^[71] The resulting data are shown in Figures 2 and 3 as difference spectra, with negative peaks corresponding to material consumed on photolysis, typically Mn₂(CO)₁₀, and positive peaks due to the photoproducts.

Photolysis of Mn₂(CO)₁₀ in MeCN solution (*ca.* 1.36 mmol dm⁻³) resulted in the formation of [Mn(CO)₅][•] in *ca.* 100 ps (Figure 2a). As expected, the majority of the Mn-radical recombined to give Mn₂(CO)₁₀ as evidenced by the decrease in intensity of the negative bleach bands for the dimer. A single long-lived photoproduct, identified as [Mn(CO)₃(NCMe)₃]⁺ by comparison to literature data,^[72] was formed ($k_{obs} = (1.88 \pm 0.09) \times 10^5 \text{ s}^{-1}$).

Experiments performed in the presence of PhN₂BF₄ **1c** showed concentration-dependent behavior. At a PhN₂BF₄ **1c** concentration of 40.7 mmol dm⁻³ the initially formed [Mn(CO)₅][•] converted to [Mn(CO)₅(NCMe)]⁺ (Figure 2b) and evidence for the reformation of Mn₂(CO)₁₀ was again obtained. However, experiments performed at lower concentrations of PhN₂BF₄ **1c** afforded [Mn(CO)₃(NCMe)₃]⁺ as the sole long-lived photoproduct (Figure 2d). Furthermore, experiments performed with PhN₂BF₄ **1c** at high concentrations of Mn₂(CO)₁₀ resulted in the formation of [Mn(CO)₅(NCMe)]⁺ whereas at lower dimer concentrations [Mn(CO)₃(NCMe)₃]⁺ was formed (Figure 1e).

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Figure 2 TR^MPS-IR data for the reaction between $Mn_2(CO)_{10}$ and PhN₂BF₄1c and/or B₂pin₂. Top: Reaction scheme showing proposed mechanistic pathways. Bottom: TR^MPS-IR data in the metal carbonyl region. The y-axis shows the change in absorbance (mOD, milli-optical density). The negative peaks correspond to the bleach of the bands for $Mn_2(CO)_{10}$. The positive bands show the growth and change of intermediates. Data were acquired in a sealed flow system under ambient conditions. (a) $Mn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL), (b) $Mn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and PhN₂BF₄1c (40.7 mmol dm⁻³), (c) $Mn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.36 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.06 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (1.06 mmol dm⁻³) in MeCN (10 mL) and $Nn_2(CO)_{10}$ (NCMe)_3]⁺, spectra recorded after 8.8 µs; (e) effect of changing concentration of $Mn_2(CO)_{10}$ on the extent of the formation of $[Mn(CO)_{5}(NCMe)_{1}]^{+}$ and $[Mn(CO)_{3}(NCMe)_{3}]^{+}$, spectra recorded after 8.8 µs; (f) effect of changing concentration of B₂pin₂ on the extent of the formation of $[Mn(CO)_{3}(NCMe)_{3}]^{+}$, spectra recorded after 8.8 µs;

These data are consistent with the mechanism outlined in Figure 2. At high concentrations, one-electron oxidation of [Mn(CO)₅][•] by the diazonium salt results in the formation [Mn(CO)₅]⁺, which undergoes rapid solvation to give [Mn(CO)₅(NCMe)]⁺. Reduction of the diazonium salt results in the formation of phenyl radicals and dinitrogen. In the synthetic reaction the phenyl radicals then react with B₂pin₂ to give 2c. The irreversible reduction of PhN₂BF₄ 1c occurs at a potential of -0.16 V (versus SCE in MeCN),^[73] given that the corresponding reduction of [Mn(CO)₅(NCMe)]⁺ has a potential of -0.455 V then this process is clearly thermodynamically viable.^[74] At lower concentrations of PhN₂BF₄ 1c the data are consistent with solvent substitution of $[Mn(CO)_5]^{\bullet}$ to give $[Mn(CO)_3(NCMe)_3]^{\bullet}$ and subsequent oxidation by the diazonium salt to give [Mn(CO)₃(NCMe)₃]⁺ – a viable process as [Mn(CO)₃(NCMe)₃][•] is a strong reducing agent (E < -3 V^[69]).

At lower concentration conditions, the second order rate of oxidation of $[Mn(CO)_5]^{\circ}$ by PhN_2BF_4 **1c** is slower than the rate of solvent substitution and oxidation of $[Mn(CO)_3(NCMe)_3]^{\circ}$.

Consistent with the Marcus theory of electron transfer which predicts a faster reduction of the diazonium salt by $[Mn(CO)_3(NCMe)_3]^{\bullet}$ than by $[Mn(CO)_5]^{\bullet}$. These data show that PhN_2BF_4 **1c** can be reduced through two different pathways, following the photochemical activation of $Mn_2(CO)_{10}$.

Photolysis of $Mn_2(CO)_{10}$ in the presence of B_2pin_2 resulted in the initial formation of $[Mn(CO)_5]^{\bullet}$ followed by conversion to $[Mn(CO)_3(NCMe)_3]^{+}$ (Figure 2c). Experiments performed at variable concentrations of B_2pin_2 demonstrated that at higher concentrations of B_2pin_2 more $[Mn(CO)_3(NCMe)_3]^{+}$ was formed at the expense of the recovery of $Mn_2(CO)_{10}$. The observation of $[Mn(CO)_3(NCMe)_3]^{+}$ in these experiments is remarkable, for which two explanations are possible. Firstly, the presence of B_2pin_2 increases the rate of solvent substitution at $[Mn(CO)_5]^{\bullet}$ to give greater amounts of $[Mn(CO)_3(NCMe)_3]^{\bullet}$ which is then quenched by $Mn_2(CO)_{10}$ to give $[Mn(CO)_3(NCMe)_3]^{\bullet}$. Secondly, and more plausibly, $[Mn(CO)_3(NCMe)_3]^{\bullet}$ reduces B_2pin_2 . The reduction of B_2pin_2 is predicted to occur at a potential of $< -3 V^{[75]}$ supported by the ability of the 19-electron $[Mn(CO)_3(NCMe)_3]^{\bullet}$ species to act

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as a powerful reducing agent. No evidence was obtained for the known boryl complex, $Mn(CO)_5(Bpin)$ (bands at 2012.06 and 1959.74 $cm^{\cdot1}).^{[76]}$

In order to gain insight into the mechanistic process which occurred under the reaction conditions used in the development of the synthetic methodology vide supra, the TR^MPS experiments were performed with Mn₂(CO)₁₀ in the presence of both PhN₂BF₄ 1c and B₂pin₂. When the experiment was performed with a concentration of Mn₂(CO)₁₀ used in the previous experiments, but the ratio of reagents used in Table 1, then [Mn(CO)₃(NCMe)₃]⁺ was the dominant product formed from [Mn(CO)₅][•] (Figure 3a). A related experiment performed at the same concentration as the synthetic chemistry showed more complicated behavior (Figure 3b) with evidence for the formation of both [Mn(CO)₃(NCMe)₃]⁺ and [Mn(CO)₅(NCMe)]⁺. While an additional unassigned band at 2071 cm⁻¹ was also present in this experiment, these results support the conclusion that photochemically generated [Mn(CO)₅][•] may either act as reducing agent directly or, following solvent substitution, through [Mn(CO)₃(NCMe)₃][•]. It is likely that subsequent to initiation, the reaction proceeds through a chain propagation process whereby trapping of the aryl radical results in the formation of a borvl radical anion that can reduce another molecule of aryl diazonium 1.^[15] Of note, even though the reaction is thought to proceed through a chain propagation process, constant irradiation is required due to the facile recombination of [Mn(CO)₅]• to regenerate Mn₂(CO)₁₀.

FT-IR analysis of a reaction mixture performed using the conditions in Table 1, entry 1, demonstrated that $[Mn(CO)_5(NCMe)]^+$ was the dominant metal carbonyl-containing species at the end of the reaction (see Supporting Information). This is consistent with the primary activation pathway involving reduction of **1c** by $[Mn(CO)_5]^{\bullet}$ and provides an important link between the data obtained by TR^MPS and the synthetic chemistry.



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Figure 3 TR^MPS-IR data for the reaction between $Mn_2(CO)_{10}$ and PhN_2BF_4 1c and B_2pin_2 (a) $Mn_2(CO)_{10}$ (0.1 equiv. 0.70 mmol dm⁻³), and B_2pin_2 (3 equiv., 21.1 mmol dm⁻³) (b) $Mn_2(CO)_{10}$ (0.04 equiv., 2.29 mmol dm⁻³) PhN_2BF_4 1c (1.7 equiv., 90.6 mmol dm⁻³) and B_2pin_2 (3 equiv., 156.9 mmol dm⁻³) in MeCN (10 mL).

Conclusion

In this paper we have innovated a robust borylation reaction for aryl/heteroaryl diazonium salts involving Mn₂(CO)₁₀ as an initiator. The reaction proved the ideal manifold for state-of-the-art mechanistic work, through a study on the behavior of the Mn^Icarbonyl species utilizing time-resolved multiple probe spectroscopy (TR^MPS-IR). This enabled the transient species pertinent to the chemistry and their fates to be mapped out. Our findings indicate that Mn radical species of the type, [Mn(CO)₅]• are formed, which is then susceptible to oxidation at the Mn centre (Figure 4). A clean reaction is seen upon treatment of [Mn(CO)₅]• with high concentrations of PhN_2BF_4 1c to give $[Mn(CO)_5(S)]^+$ species, where $S = CH_3CN$ (we expect polar aprotic solvents to behave similarly). At lower concentrations of PhN₂BF₄ 1c [Mn(CO)₃(S)₃]⁺ is generated through oxidation of 19-electron [Mn(CO)₃(S)₃]. In both cases, reduction of the 1c will result in the generation of aryl radicals which then react with $B_2 pin_2$ to give **2c**. We presume that this results in the concomitant generation of boron-based radicals which propagate the reaction, highlighting the role of the Mn-carbonyl complex as a photo-initiator. In the presence of the $B_2 pin_2$ we also see that $[Mn(CO)_3(S)_3]^+$ is formed,

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indicating that the boronate may also be reduced. While $[Mn(CO)_5(S)]^+$ and $[Mn(CO)_3(S)_3]^+$ are both cationic Mn¹ species, the electron-deficiency of the former at Mn will be significant and potentially important when considering downstream reaction chemistries.

Given the promise of light-induced activation of Mn₂(CO)₁₀ in synthetic chemistry,^[77] our results taken together are important in proposing future mechanistic schemes and taking advantage of the unique reactivity of Mn-carbonyl species. As with C-H bond activation-functionalization catalytic chemistries, the TR^MPS-IR approach has proven valuable, as an important mechanistic tool, in mapping out the reactive species that develop from metal carbonyl complexes such as Mn₂(CO)₁₀ and determining their roles in synthetic chemistry.



Figure 4. Light activation of Mn₂(CO)₁₀ at 400 nm: impact of reaction components on the formation of cationic Mn¹-carbonyl species generated under working reaction conditions.

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Keywords: Manganese · Photocatalysis · Mechanism · Radicals • Spectroscopy

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Mn-mediated borylation of aryl/heteroaryl diazonium salts emerges as a general and versatile synthetic methodology for the synthesis of aryl/heteroaryl boronate esters. The Mn¹-carbonyl species generated under the reaction conditions has been revealed by time-resolved multiple probe spectroscopy (TR^MPS-IR).

Institute and/or researcher Twitter usernames: @Ian_Fairlamb @ChemistryatYork @legosnail1