Borylated Cymantrenes and Tromancenium Salts with Unusual Reactivity

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ABSTRACT: In continuation of our study of the chemistry of cationic (cycloheptatrienyl)-(cyclopentadienyl)manganese(I) sandwich complexes, so-called “tromancenium” salts, we report here on their boron-substituted derivatives focusing on useful boron-mediated synthetic applications. Transmetalation of lithiated tricarbonyl(cyclopentadienyl)manganese (“cymantrene”) with boric or diboronic esters affords monoborylated cymantrenes that are converted by advanced high-power LED photosynthesis followed by oxidation with tritylium to their 8-boron-substituted tromancenium complexes. These new functionalized tromancenium salts are fully characterized by $^1$H/$^11$B/$^13$C/$^19$F/$^{55}$Mn NMR, IR, UV–vis, HRMS spectroscopy, single-crystal structure analysis (XRD) and cyclic voltammetry (CV). IR spectra were thoroughly analyzed by density functional theory (DFT) on the harmonic approximation in qualitative agreement of calculated vibrations with experimental values. Uncommon chemical reactivity of these borylated tromancenium salts is observed, due to the strongly electron-withdrawing cationic tromancenium moiety. No Suzuki-type cross-coupling reactions proved so far achievable, but unusual copper-promoted amination with sodium azide under microwave irradiation is possible. Diazoniation of aminotromancenium affords an extremely reactive dicationic tromanceniumdiazonium salt, which is too labile for standard Sandmeyer reactions, in contrast to analogous chemistry of cobaltocenium salts. Overall, borylated tromancenium salts display unexpected and intriguing chemical properties with the potential for novel synthetic applications in future work.

INTRODUCTION

Cationic $\eta^7$-cycloheptatrienyl $\eta^5$-cyclopentadienyl manganese sandwich complexes, commonly called “tromancenium”, are an interesting and neglected class of 18-valence-electron, air-stable, polar metallocenes that have only recently been fully characterized, enabled by an innovative photochemical synthetic approach using advanced high-power LED light sources.1 Electronically, these tromancenium salts may be viewed as typical heteroleptic metallocenes containing manganese in the oxidation state +1 coordinated to $6\pi$-Hückel-aromatic cyclopentadienide $\text{C}_5\text{H}_5^-$ and tropylium $\text{C}_7\text{H}_7^+$ ligands.

In this contribution, we aim to develop this chemistry further with a focus on their boron-substituted functionalized derivatives with potentially widespread useful applications in synthesis, thereby allowing expansion of the chemical space of tromancenium complexes. Due to the air-stability and ionicity of tromancenium salts, they are also soluble in water, a desirable feature for potential applications in green chemistry or medicinal chemistry. Tromancenium salts in general display quasi-reversible one-electron oxidation and reduction,2 a desirable feature for potential applications in electrochemistry, redox sensing, and redox catalysis. Given these advantageous properties, we believe it is worthy to develop this chemistry further.

RESULTS AND DISCUSSION

Synthesis and Reactivity. In our previous paper on tromancenium chemistry,1 we have seen that the most convenient way to functionalize tromancenium salts consists of the introduction of the functional group (FG) at an early stage of the synthetic sequence at the Cp ring of cymantrene, (CO)$_3$MnCp, the key starting material for this chemistry. Subsequent photochemical substitution of all three CO ligands with cycloheptatriene under blue light irradiation (450 nm) with high-intensity LED light sources (370 W) affords air-sensitive ($\eta^8$-C$_7$H$_7$)($\eta^5$-C$_5$H$_5$-FG)Mn intermediates that are oxidized with tritium salts by the removal of a hydride from the $\eta^6$-C$_7$H$_7$ ligand to yield the targeted air-stable tromancenium salts. Following this route, 8-substituted tromancenium complexes were readily accessible. Because derivatization of cymantrene by standard organometallic chemistry is very well developed,2 either by metalation and nucleophilic substitution with electrophiles or by electrophilic aromatic substitution, a wide range of functional groups is in principle possible.

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However, the following photochemical substitution of the CO ligands by cycloheptatriene is the critical step in this synthetic protocol—not all functional groups are compatible as we will see in the following (Scheme 1).

Metalation of cymantrene (1) by n-butyl lithium under standard conditions (THF, −78 °C) followed by reaction with trimethylborate and aqueous workup afforded cymantrenyl boronic acid (2) in a satisfying yield of 87% as yellow air-stable compound with spectroscopic properties fully in line with its structure (vide infra). Interestingly, crystallization of 2 aiming at growing suitable single crystals for XRD analysis revealed that condensation to its cyclic anhydride [(CO)₃Mn-(C₅H₄)B₃O₃ (3) had occurred. We note that 2 has been already synthesized about 50 years ago by Nesmeyanov³ and characterized by proton NMR,⁴ but no further information is available in the literature.

In general, organic boron derivatives of the type boronic acid RB(OH)₂, boronic ester RB(OR')₂ and trifluoridoborate RBF₃⁻ are very useful synthons for carbon–carbon and carbon–nitrogen Suzuki cross-coupling reactions; therefore 2 was converted with KHBF₄ to its trifluoridoborate 4 in 60% yield and with pinacol to its ester 5 in 86% yield. We note that 5 has been prepared before by an iridium-catalyzed C=H activation and borylation of cymantrene,⁵ but our route is simpler and avoids costly iridium. Having these three boronic derivatives in hand, we next tested their compatibility with the rather harsh photochemical reaction conditions¹ (450 nm, 370 W) of the substitution of their CO ligands with cycloheptatriene. As we suspected from our earlier experience with other substituted cymantrenes,¹ protic or highly polar substituents should be avoided because of either complete photochemical degradation or a rather poor isolated yield after workup. This proved to be the case also with 2 and 4 as substrates and no productive outcome of the reaction was observed. Contrary, pinacol ester 5 afforded the desired tromanceniumylboronic acid pinacol esters 6 and 8.

Interestingly, tromanceniumylboronic ester (6) containing hexafluoridophosphate as counterion proved unstable in solution and reacted within 18 h to mesoionic tromanceniumyltrifluoridoborate (7), indicating high thermodynamic stability of this red zwitterion. Mechanistically, we assume that this unusual fluoride abstraction from an otherwise "inert" PF₆⁻ anion is driven by the formation of strong boron–fluoride bonds, facilitated by the electron-deficient 6-valence-electron boron, and by the high oxophilicity of phosphorus under formation of a five-coordinated heteroleptic pinacolato/trifluorido anion [(C₆H₁₂O₂)PF₃]⁻. From an organometallic chemist's viewpoint, 7 is an interesting zwitterionic species containing an interesting novel metallocarbene ligand. In analogy to "cobaltocenylidene" gold complex⁶ [(C₅H₅)Co-(C₅H₄)Au(CN)₃], 7 may be viewed as a BF₃ complex of the analogous, mesoionic metallocenocarbene "tromancenylidene" C with a similar electronic structure (Scheme 2). With this analogy in mind, we attempted a carbene transfer reaction of 7...
with AgF, aiming at a [(tromancenylidene)Ag]BF₄ complex that would be a very useful synthon for other tromancenylidene metal complexes, similarly as silver NHC complexes that are preferred carbene precursors for other NHC metal complexes. Unfortunately, no such reactivity proved possible, even under forcing microwave irradiation, indicating very strong tromancenylidene-boron bonding. Similar earlier attempts by Arduengo to transfer an imidazolylidene from an NHC-BF₄ adduct to mercury by reaction with HgF₂ were also met with failure.

To finally get access to tromanceniumyl pinacol boronic ester (8), we therefore had to exchange the noninnocent hexafluoridophosphate by a more suitable stable anion. This is most easily accomplished using tritylium triflate instead of tritylium hexafluorophosphate in the hydride removal/oxidation step after photolysis of 5 with cycloheptatriene. In this manner, 8 was synthesized in a satisfying yield of 80%. Subsequent mild hydrolysis with aqueous sodium bicarbonate afforded the parent tromanceniumylboronic acid triflate (9) also in 80% yield as an air-stable, purple salt that crystallizes (vide infra) without condensation to its anhydride, in contrast to cymantrenylboronic acid (2) (vide supra).

With three new tromanceniumylboronic derivatives 7, 8, and 9 in hand, it was obviously of interest to use them in Suzuki–Miyaura cross-coupling reactions to expand the chemical space of tromancenium salts. Toward this goal, we performed Suzuki–Miyaura reactions with bromobenzene as electrophilic test substrate, employing various standard Pd, Ni, or Cu catalysts under a variety of experimental conditions, including also dual photoredox catalysis. Unfortunately, in no case successful cross-coupling under formation of 8-phenyltromancenium triflate was observed, in part explainable by the strongly electron-withdrawing and deactivating cationic tromancenium moiety. Another useful reaction of boronic derivatives is the copper-catalyzed Chan–Evans–Lam amination of boronic acids or esters to primary, secondary, or tertiary aryl amines. Synthetically, primary aryl amines are clearly the most valuable compounds for further N-functionalization; therefore we focused our efforts toward 8-aminotromancenium triflate (10) as target. We have synthesized 8-aminotromancenium hexafluoridophosphate before by direct photochemical synthesis starting from amino cymantrene, but due to the photolabile amino substituent the isolated yield was less than 10%, thereby preventing further study of its reactivity. Applying standard Chan–Evans–Lam reaction conditions on boronic derivatives 7, 8, and 9 proved unfortunately unsuccessful, but interestingly, reaction of pinacol ester 8 with sodium azide under microwave irradiation gave 8-aminotromancenium triflate (10) in a satisfying yield of 72%. The mechanism of this unusual reaction is unclear at the moment, but besides carbon–nitrogen coupling a reduction of azide to amino has to occur, most likely by the protic solvent ethanol.

Having now aminotromancenium 10 available in sufficient quantity, we studied next its diazoniation to dicaticonic tromanceniumdiazonium salt (11), based on our experience with nucleophilic or radical substitution reactions of cobaltoceniumdiazonium bis(hexafluoridophosphate). Conversion of aminotromancenium triflate (10) with sodium nitrite in aqueous hydrochloric acid or with aqueous hexafluorophosphoric acid afforded extremely reactive diazonium species. All our attempts to characterize or isolate this compound by precipitation as its bis(hexafluoridophosphate) salt met without success, in contrast to its cobaltocenium analogue. Furthermore, attempts to react tromanceniumdiazonium in situ with azide and iodide as the most reactive nucleophiles in dediazination reactions did neither afford azidotromancenium nor iodotromancenium. Instead, only chlorotromancenium triflate (12) in admixture with parent unsubstituted tromancenium was obtained from 11 in <50% yield, obviously formed by reaction with the chloride counteranion. With tromanceniumdiazonium bis(hexafluoridophosphate) generated in situ by NaNO₂/HPF₆ followed by reaction with NaN₃ or KI, only complete degradation to unsubstituted tromancenium was observed. This is in stark contrast to common organic aryldiazonium chemistry where dediazination by the poor nucleophile chloride is only possible under copper-catalyzed Sandmeyer conditions, but not without copper catalysts. Overall,

Scheme 2. Comparison of Polar Resonance Structures of N-Heterocyclic Carbenes (A), Cobaltocenylidene (B), and Tromancenylidene (C)

Figure 1. Molecular structure of cymantrene derivatives 3, 4, and 5. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): 3: Mn1–C5(avg) = 2.142, Mn2–C1(avg) = 2.140, Mn3–C5(avg) = 2.141, C1–B1 = 1.545(2), C6–B2 = 1.537(3), C11–B3 = 1.532(3), B1–O1 = 1.376(2), B1–O3 = 1.374(2), B2–O1 = 1.384(2), B2–O2 = 1.374(2), B3–O2 = 1.379(2), B3–O3 = 1.379(2), 4: Mn1–C5(avg) = 2.147, C5–B1 = 1.394(2), B1–F1 = 1.413(2), B1–F2 = 1.411(2), B1–F3 = 1.429(2), 5: Mn–C5(avg) = 2.143, C1–B1 = 1.547(2), B1–O1 = 1.368(2), B1–O2 = 1.364(2).
tromanceniumdiazonium salts are very labile species exhibiting surprising chemoselectivity, in contrast to cobaltoceniumdiazonium salts that have more common and synthetically more useful reactivity in nucleophilic or radical substitution reactions.

Structural, Spectroscopic, and Electrochemical Properties. Single crystal analyses are available for cymantrene derivatives 3, 4, 5 (Figure 1) and for tromancenium salts 7, 8, 9, and 12 (Figure 2). The solid-state structure of an aminotromancenium 10 containing hexafluorodiphosphate as counterion is already included in our previous paper.1 In general, the molecular structures of these new cymantrenes and tromancenium salts prove unambiguously their chemical identity, displaying regular half-sandwich (Cht) rings, thereby the larger 7-membered Cht es, 8a,b indicating at first sight a comparable donor strength of their manganese−carbon bond distances (Mn−C averaged = 2.12 Å) to carbons of the cyclopentadienyl (Cp) and cycloheptatrienyl (Cht) rings, thereby the larger 7-membered Cht ligand is pulled closer to the central manganese atom with corresponding shorter Mn−Cht centroid distances (approximately 1.3 Å) in comparison to those of the smaller S-membered Cp ligand (approximately 1.7 Å). Similar structural properties have been reported for Cht/Cp sandwich metal complexes of early transition metals.16 The C(8)−B(1) bond distance of tromanceniumyltrifluoroborate ("tromancenylidene"-BF₃, ad- duct) (7) is 1.619(11) Å (Figure 2), very similar to carbene carbon−boron bond lengths of imidazolylidene-BF₃ complexes,8a,b indicating at first sight a comparable donor strength of tromancenylidene C and standard Arduengo carbenes A (Scheme 2).

High-resolution mass spectra show the monoisotopic most abundant signals of the molecular ions (2, 4, 5) or of the cations (7, 8, 9, 12) in excellent agreement with theoretical values (see Supporting Information). UV−vis spectra of yellow cymantrene derivatives 2, 4, and 5 are rather simple, but those of tromancenium salts 7, 8, 9, and 12 display a broad charge-transfer absorption at 550−580 nm, in line with their red color. IR spectroscopy of cymantrenes 2, 4, and 5 as well as those of tromancenium salts 7, 8, 9, and 12 were measured in the ATR mode and fully analyzed by DFT calculations in the gas phase approximating vibration modes as harmonic oscillations (see Supporting Information). This allowed a detailed assignment of all relevant absorptions, a representative example of calculated IR bands are in good qualitative agreement, whereas the relative intensities are not so well reproduced, explainable by the ATR-measurement of the experimental data in the bulk phase and by the DFT calculation in the gas phase. In general, C−C vibrations of the cyclopentadienyl/cycloheptatrienyl ligands and of the pinacol ester show higher intensities in the bulk compared to the gas phase.

Multinuclear NMR spectroscopic characterization includes ¹H, ¹³C, ¹⁹F and most notably also ¹¹B NMR data (compare Supporting Information). All these new cymantrenes and tromancenium complexes contain monosubstituted Cp ligands with corresponding simple signal patterns in their ¹H NMR spectra of the unsubstituted cycloheptatrienyl ligand of tromancenium salts 7, 8, 9, and 12 are observed in a narrow range of 6.7 to 6.92 ppm (¹H) and 97.1 to 99.2 ppm (¹³C), respectively. ¹H/¹³C chemical shifts of neutral cymantrene derivatives 2, 4, and 5 are at higher field in comparison to those of cationic tromancenium complexes 7, 8, 9, and 12, as expected. ¹¹B NMR spectra of 2, 4, 5, 7, 8 show quadrupolar-broadened signals from −16 to +30 ppm with the most shielded chemical shifts observed for BF₃ derivatives (4, δ (¹¹B) = −7 ppm; 7, δ (¹¹B) = −15.7 ppm) that also resolve quartets due to
The 13C chemical shift of the quaternary ipso-carbon of tromancenylidene-BF3 adduct 7 has been observed at 157 ppm in comparison to those of tromancenium cymantrenyltri quartets in a 1:1:1:1 signal intensity ratio in their 19F spectra, due to the 1/2 nuclear spin of 11B.

Of special interest is the 13C chemical shift of the quaternary ipso-carbon of tromancenylidene-BF3 adduct 7 to evaluate the donor character of this new metallocenocarbene C (Scheme 2) in comparison to standard N-heterocyclic carbenes A (Scheme 2). This is a challenging task, because the expected signal intensity will be extremely low due to splitting into a 16-line multiplet (quartet (J(13C−11B)[I = 3/2]) × quartet (J(13C−19F)) in 80% relative intensity (natural abundance of 11B = 80.1%), overlaid (if resolved at all) on a 28-line multiplet (septet (J(13C−10B)[I = 3]) × quartet (J(13C−19F)) in 20% relative intensity (natural abundance of 10B = 19.9%).

Under standard 13C NMR measurement conditions, such a high-multiplicity signal is obviously very difficult to detect. However, for highly concentrated solutions8b or with 19F−13C decoupling8 the carbene centers of two NHC-BF3 adducts have been observed in the range of 157−163 ppm. In our case, a (19F/13C)-HSQC NMR of a saturated solution of 7 in DMSO-d6 on a 700 MHz NMR spectrometer gave a distinctive elongated cross-peak (Figure 4) with an appearance explainable as an unresolved quartet due to J(13C−11B) coupling. Its 13C chemical shift of 96.8 ppm is extremely shielded by 65 ppm in comparison to carbene signals of NHC-BF3 adducts (157−163 ppm).8,9b By incidence, the signals of the ipso-carbon (96.8 ppm) and cycloheptatrienyl-carbons (singlet, 95.8 ppm) of 7 are close in value, but clearly no coupling between the BF3 group and the remote cycloheptatrienyl ligand is possible or evident. For comparison of tromancenylidene C (Figure 2) with metallocenocarbene B (Figure 2), the ipso-carbon of cobaltocenylidene-Au(CN)3 has been observed at 113.6 ppm.9b Hence we may conclude that tromancenylidene C is an extraordinarily electron-rich carbene, probably even more nucleophilic than cobaltocenylidene B with a calculated Tolman electronic parameter (TEP) of 2037.1 cm⁻¹.6

55Mn NMR spectroscopy (natural abundance: 100%, receptivity relative to 1H: 0.179, I = 5/2, Q = 0.40 × 10⁻¹⁸ m²) is in general very rarely applicable in molecular chemistry, mainly due the high nuclear electric quadrupole moment Q preventing observation of signals for nonsymmetric diamagnetic compounds. However, manganese carbonyl derivatives and tromancenium salts have a distorted but sufficiently symmetric pseudo-octahedral ligand sphere at the manganese center that allows detection of signals with peak widths at half-height (h1/2) in the kHz range.1,17 55Mn NMR spectra of the new cymantrenes 2, 4, and 5 and tromancenium salts 7, 8, 9, and 12 (Figure 5, Table 1, for spectra see Supporting Information) show broad signals with larger peak widths h1/2 for the “less” symmetric cymantrene derivatives in comparison to those of tromancenium complexes with higher local symmetry at the manganese center. Evidently, manganese complexes of similar structure give rise to 55Mn chemical shifts in a narrow range (approximately 300 ppm for cymantrenes and also for tromancenium salts) but in well-separated spectral domains [Δ(δ55Mn cymantrenes) = 2000 ppm]. As we have observed earlier and as it is common in transition metal NMR spectroscopy, there is no simple correlation of chemical shifts with Hammett substituent parameters within a subclass of compounds. However, the value of 161.6 ppm for tromanceniumyltrifluoridoborate (7) is quite low, indicating an unusual electronic structure at

![Figure 4](image-url)  (19F/13C)-HSQC NMR spectrum of tromancenylidene-BF3 adduct 7 in saturated DMSO-d6 solution.

![Figure 5](image-url)  Comparison of 55Mn NMR chemical shifts (δ) and peak widths at half height (h1/2) of tromanceniumyltrifluoridoborate (7) (left) and potassium cymantrenyltrifluoridoborate (4) (right).
tromancenium complexes in our previous paper. In general, 
Supporting Information) and comparable to those of other 
tromancenium salts were more or less similar (Table 1, 
9) as solvent using 0.15 M NBu₄PF₆ as the supporting electrolyte. 
9 electron donating or electron withdrawing substituents, 
anodic side with Mn(I)/Mn(II) redox couples dependent on 
chemical partially reversible oxidation processes at mild 
potential were observed, corresponding to the Mn(I)/Mn(II) 
chemically irreversible reductions that are di 
representative cyclovoltammogram of tromanceniumyltri 
Table 2 summarizes the results and Figure 6 shows a 
unusual tromancenylidene-BF₃ complex (vide supra).

Table 1. 55Mn Chemical Shifts of Cymantrene Derivatives 
and of Tromencenium Salts

| compound formula (number) | Cp substituent | δ(55Mn) | h₁/₂ | reference |
|--------------------------|---------------|---------|------|-----------|
| (CO)₃MnC₅H₅ | H | -2225 | 9.03 | 17a, 17c |
| (CO)₃MnC₅H₅B(OH)₂ | B(OH)₂ | -2140 | 13.27 | this work |
| K[(CO)₃MnC₅H₅BF₃] | BF₃⁻ | -2311 | 9.12 | this work |
| (CO)₃MnC₅H₅Bpin | pin⁻ | -2138 | 7.76 | this work |
| [(C₇H₇)Mn(C₅H₅)]PF₆ | H⁺ | +271 | 1.20 | 1 |
| [(C₇H₇)Mn(C₅H₄Cl)]PF₆ | Br | +368 | 1.95 | 1 |
| [(C₇H₇)Mn(C₅H₄B(OH)₂)]PF₆ | pin⁻ | +162 | 2.89 | this work |
| [(C₇H₇)Mn(C₅H₄CH₃)]PF₆ | CH₃ | +257 | 1.75 | 1 |
| [(C₇H₇)Mn(C₅H₄NH₂)]PF₆ | NH₂ | +238 | 3.60 | 1 |
| [(C₇H₇)Mn(C₅H₄Br)]PF₆ | Br | +368 | 1.95 | 1 |
| [(C₇H₇)Mn(C₅H₄C(O)CH₃)]PF₆ | C(O)CH₃ | +538 | 1.85 | 1 |
| [(C₇H₇)Mn(C₅H₄BF₃)(C₇H₇)] | BF₃⁻ | +162 | 2.89 | this work |
| [(C₇H₇)Mn(C₅H₄Bpin)]OTf | pin⁻ | +415 | 2.92 | this work |
| [(C₇H₇)Mn(C₅H₄B(OH)₂)]OTf | B(OH)₂ | +367 | 3.80 | this work |
| [(C₇H₇)Mn(C₅H₄CH₃)]OTf | CH₃ | +369 | 1.55 | this work |

“Referenced versus saturated KMnO₄/D₂O solution (ppm). Peak width at half-height (kHz). “pin = pinacolate. “Aminotromencenium (10) with PF₆⁻ counterion.

manganese, correlating in part with its description as an 
unusual tromancenylenediene-BF₃ complex (vide supra).

Electrochemical characterization of tromencenium salts 7, 8, 
9, and 12 was performed by cyclovoltammetry in acetonitrile 
as solvent using 0.15 M NBu₄PF₆ as the supporting electrolyte. 
Table 2 summarizes the results and Figure 6 shows a 
representative cyclovoltammogram of tromenceniumyltrifluoridoborate (7). Cyclic voltammetric responses for these 
tromencenium salts were more or less similar (Table 1, 
Supporting Information) and comparable to those of other 
tromencenium complexes in our previous paper. In general, 
chemically partially reversible oxidation processes at mild 
potential were observed, corresponding to the Mn(I)/Mn(II) 
couple. On the cathodic side, chemically irreversible reductions 
that are difficult to assign are evident. Overall, redox chemistry 
of tromencenium salts is more or less well behaved on the 
anodic side with Mn(I)/Mn(II) redox couples dependent on 
electron donating or electron withdrawing substituents,

Figure 6. Cyclic voltammogram of tromenceniumyltrifluoridoborate (7) in CH₃CN (0.15 M NBu₄PF₆) on a glassy carbon working electrode at sweep rates of 0.1 (solid line) and 0.5 V s⁻¹ (dotted line).

whereas reductions give rise to chemical follow-up products of 
unknown structure.

SUMMARY

Cymantrenylboronic acid, (CO)₃Mn(C₅H₄B(OH)₂), was 
conveniently synthesized by lithiation of cymantrene followed 
by reaction with trimethylborate and hydrolysis. Reaction with 
KHF₂ gave the trifluoridoborate derivative and transester-
ification with pinacol afforded cymantrenylboronic acid pinacol 
ester. These three new borylated cymantrenes might become 
valuable synthons for Suzuki-type carbon—carbon cross-
coupling reactions. Photochemical displacement of all three 
carbonyl ligands using high-intensity blue light in a LED 
photoreactor followed by hydride removal/oxidation with 
trityl hexafluoridophosphate or triflate enabled access to 
new cationic cycloheptatrienyl cyclopentadienyl manganese 
tritylium hexafluoropropionate salt is 

Table 2. Redox Potentials of Tromencenium Salts 7, 8, 9, 
and 12

| compound # | Eₘₚ | Eₘₚ+1 | Eₘₚ+3 |
|------------|-----|-------|-------|
| 7 | +0.56 | -1.96 | -2.48 |
| 8 | +0.83 | -1.55 | -2.46 |
| 9 | +0.81 | -1.58 | |
| 12 | +0.01 | -1.40 | |

“Potentials are given in volts, calibrated against the ferrocene/ 
ferrocenium redox couple. Measurements were conducted in 0.15 M 
NBu₄PF₆ in acetonitrile at sweep rates of 0.1 V s⁻¹. “Half-wave 
potential of a chemically quasi-reversible process. “Peak potential of a 
chemically irreversible process. 

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proved possible, as well as complete assignment of IR vibrations by DFT calculations.

In summary, tromancenium complexes containing functionalized boron substituents were synthesized from their cymantrene precursors and showed uncommon reactivities, due their cationic, strongly electron-withdrawing and deactivating tromancenium moiety. Further studies are under way to exploit this chemistry toward new synthetic targets and potential catalytic or bioorganometallic applications.

**EXPERIMENTAL SECTION**

**General Procedures.** Standard methods and procedures of organometallic synthesis were performed. Starting chemicals were obtained commercially and used as received, except for CpMn(CO)3 (cymantrene) (1), which was purified by chromatography as described recently. Trityltriﬂum triﬂate was synthesized as published.1

1H, 19F NMR spectra (Bruker Ascent 400 NMR spectrometer), 13B, 19F, 55Mn NMR spectra (Bruker Avance DPX300 NMR spectrometer), and 1H/13C-HSQC-NMR spectra (700 MHz Bruker Avance 4 Neo spectrometer) were recorded at ambient temperature. Signals were referenced internally against 1H/13C residual solvent peaks or externally: 11B, B(OCH3)3 neat (Bruker Avance DPX300 NMR spectrometer) for comparison of data to the IUPAC standard BF3−(C2H5)2, 11B, 19F NMR spectra (Bruker Ascent 400 NMR spectrometer),11B, 13C−(C2/C5 of Cp), 94.2 (ipso-carbon), 225.7 (carbonyl-carbon).55Mn NMR (74 MHz, CD3CN, ppm) δ = −2140. 1B NMR (96 MHz, CD2CN, ppm) δ = 10.2. IR (ATR, cm−1) 3115 (ν(C≡H)), 2011, 1901, 1881, 1860 (ν(C≡C)), 1414 (ν(C−F)), 1377, 1351, 1260 (ν(C−F)), 1318 (δ(C−F)), 744, 734 (δ(C−F)), 661 (δ(C−F)), 622 (δ(C−F)), 529 (ν(C−F)), 485 (δ(C−F)). HRMS (ESI neg, m/z) 246.9614 ([M − H]+), calc. for C9H10O3MnB: 246.9616. UV−vis (CH3CN, [nm]) λmax = 323 nm. Single crystals were obtained from acetone at room temperature whereby condensation led to cymantrenylboronic acid anhydride (3).

Potassium cymantrenyltriﬂum borate (4). A yellow round-bottom flask was charged with 0.0305 g (p. 1.0 equiv) of cymantrenylboronic acid (2), 10 mL of acetone−water (1:1) and potassium hydrogen difluoride (0.022 g, 0.64 equiv). The solution was stirred overnight, then solvents were removed in vacuo, and the product was extracted with acetone and ﬁltered off. Removal of acetone resulted in 60% yield (0.0227 g, 0.0732 mmol). 4 is soluble in acetonitrile, acetone, and water. mp 319.7 °C dec. 1H NMR (400 MHz, CD2CN, ppm) δ = 4.69 (s, 4H, C1), 4.73 (s, 4H, C3/C4 of Cp), 8.00 (s, 2H, OH). 13C NMR (75 MHz, CD2CN, ppm) δ = 226.0 (carbonyl-carbon), 201.1 (C5 of Cp), 118.9 (C2 of Cp), 92.2 (C2/C5 of Cp), 122.66 (C2/C5 of Cp), 78.92 (C5α, C5β), 68.92 (C4α, C4β), 68.82 (C3α, C3β). 

**Density Functional Theory Calculations.** The calculated infrared spectra are for single molecules in vacuo. The calculations rely on the harmonic approximation, where the overall molecular vibration is simpliﬁed as uncoupled vibrational modes each described by a parabolic function. This model generally overestimates vibrational frequencies compared to experiment, which is why a scaling factor was introduced for each computed spectrum separately to better ﬁt the experimental spectra. The scaling factors (αs) are given in the ﬁgures of the IR spectra. For the molecules 2, 4, 5, 7, 8, 9, and 12, the harmonic frequencies have been computed with the Gaussian16 software package,19 where the Hessian is constructed by numerical second derivatives of the electronic energy with respect to Cartesian displacements. The electronic energy has been computed with density functional theory, using the B3LYP functional and the 6-311G(d,p) basis set. Counterions have not been considered explicitly. The triﬂate ion was computed separately to assign its characteristic bands in the spectra of 8, 9, and 12.
acetone, acetonitrile, and dimethyl sulfoxide. mp 139.3 °C. The compound was separated by back-weighing. The mixture was stirred for 1 h under exclusion of light. Dichloromethane was concentrated in vacuo. After precipitation with diethyl ether, the air-stable product was filtered off and washed three times with 20 mL portions of diethyl ether. The product was dissolved with acetonitrile from the folded filter and the solvent was removed in vacuo affording 7 as red solid in 43% yield (0.183 g, 0.66 mmol). An overall quantum yield of 5.97% was calculated.

8-Tromanceniumylboronic acid pinacol ester triflate (8). A Schlenk flask, equipped with a cooling finger and a bubbler, was charged with 0.250 g of cymanternylboronic acid pinacol ester (8) (0.758 mmol, 1.00 equiv), 104 μL of 1,3,5-cycloheptatriene (0.997 mmol, 1.32 equiv), and 30 mL of dry heptane. The apparatus was then irradiated with blue light (450 nm) and 370 W for 33 min until no further carbon monoxide exclusion was observed. Note: A successful reaction is indicated by a color change from yellow to red-orange. Heptane was removed in vacuo. The intermediate highly air-sensitive complex was dissolved in 40 mL of dichloromethane (abs) and cooled to 0 °C. Trityltrim (0.500 g, 1.274 mmol, 1.68 equiv) was charged with 0.090 g of purple 8-Tromanceniumylboronic acid pinacol ester (8), 64.8 mg of 8-Tromanceniumylboronic acid pinacol ester (8), 64.8 mg of 8-Tromanceniumylboronic acid pinacol ester (8), 86.6 mg of sodium azide (1.33 mmol, 10 equiv), and 30 mL of dry ethanol. The mixture was saturated with argon and stirred for 30 min until almost everything was dissolved whereby a color darkening from orange to dark brown was observed. The reaction mixture was then irradiated in a microwave synthesis reactor with 600 W for 10 min at 105 °C (the ramp time is 2 min). The reaction mixture was allowed to cool to room temperature before the vessel was opened and then decanted into a round-bottom flask in order to remove the solvent in vacuo. The product was extracted with ethyl acetate and filtered off. Ethyl acetate was removed in vacuo and the residue was washed three times with 5 mL portions of diethyl ether, which were removed by pipet affording 9 as pink solid in 74.2% yield (0.133 mmol, 1 equiv). 6.6 mg of sodium azide (1.33 mmol, 10 equiv), 26.6 mg of copper(II) acetate monohydrate and 30 mL of dry ethanol. The mixture was saturated with argon and stirred for 30 min until almost everything was dissolved whereby a color darkening from orange to dark brown was observed. The reaction mixture was stirred for 1 h under exclusion of light. Dichloromethane was concentrated in vacuo. After precipitation with diethyl ether, the air-stable product was filtered off and washed three times with 10 mL portions of diethyl ether. The product was dissolved with acetonitrile from the folded filter and the solvent was removed in vacuo affording 8 as purple solid in 79.5% yield (0.293 g, 1.32 mmol). An overall quantum yield of 1.36% was calculated. Compound 8 is air-stable and soluble in acetonitrile, acetone, and dimethyl sulfoxide.

8-Tromanceniumylboronic acid pinacol ester triflate (9). A round-bottom flask was charged with 0.090 g of purple 8-Tromanceniumylboronic acid pinacol ester (8) (0.185 mmol, 1 equiv), 10 mL of THF—water (9:1) and 362 μL of a saturated sodium carbonate solution. The mixture was stirred for 30 min at room temperature, while a pink intermediate precipitated. The precipitation was completed by adding 20 mL of diethyl ether to the mixture. The solvents were removed with a pipet and the residue was dissolved in 10 mL of water and washed three times with 20 mL portions of diethyl ether in a separating funnel in order to remove pinacol remains completely. The organic layer was discarded and the aqueous phase was acidified with 139 μL (9 equiv) of HCl (37%) until the pH value was approximately 1. A color change from pink to yellow was observed. Water was removed in vacuo and the product was dissolved in acetonitrile and filtered off to remove sodium chloride. The solvent was removed in vacuo affording 9 as purple resin in 79% yield (0.059 g, 0.146 mmol). Compound 9 is air-stable and soluble in acetonitrile, acetone, and dimethyl sulfoxide.

mp 76.2 °C. 1H NMR (400 MHz, CD3CN, ppm) δ = 4.89 (s, 4H, C8–12 of Cp), 6.40 (s, 2H, OFH), 6.81 (s, 7H, C1–7 of Cp). 13C NMR (75 MHz, CD3CN, ppm) δ = 81.8 (C10/C11 of Cp), 83.3 (C9/C12 of Cp), 97.1 (C1–7 of Cp) not observed. 19F NMR (74 MHz, CD3CN, ppm) δ = 162. 15N NMR (74 MHz, CD3CN, ppm) δ = −15.8 (q, J = 46.6 Hz). IR (ATR, cm−1) 3110, 3075, 1746, 1466, 1238 (C=C), 1388 (ν(Co)), 850, 853 (C=O), 830 (δ(δ)), 789, 720, 706 (δ(δ)), 575, 510 (δ(δ)), 449, 411 (δ(δ)). HRMS (ESI pos, m/z) 255.0381 [M + OTf]+. UV–vis (CH3CN, nm) λmax = 283 nm, λmax = 549 nm. Single crystals of 9 were obtained from a mixture of acetone and diethyl ether at 4 °C by diffusion crystallization.

8-Aminotromanceniumylboronic acid triflate (10). A Teflon microwave vessel was charged with 64.8 mg of 8-Tromanceniumylboronic acid pinacol ester (8) (0.133 mmol, 1 equiv), 86.6 mg of sodium azide (1.33 mmol, 10 equiv), and 6.6 mg of copper(II) acetate monohydrate and 30 mL of dry ethanol. The mixture was saturated with argon and stirred for 30 min until almost everything was dissolved whereby a color darkening from orange to dark brown was observed. The reaction mixture was then irradiated in a microwave synthesis reactor with 600 W for 10 min at 105 °C (the ramp time is 2 min). The reaction mixture was allowed to cool to room temperature before the vessel was opened and then decanted into a round-bottom flask in order to remove the solvent in vacuo. The product was extracted with ethyl acetate and filtered off. Ethyl acetate was removed in vacuo and the residue was washed three times with 5 mL portions of diethyl ether, which were removed by pipet affording 10 as pink solid in 72.4% yield (36.2 mg, 0.096 mmol). Spectroscopic data (see Supporting Information) concur with recently published data.1

8-Chlorotromancenium trifluoromethanesulfonate (11). A 10 mL round-bottom flask was charged with 20 mg of 8-aminotromanceniumylboronic acid triflate (10) (0.082 mmol, 1 equiv) and dissolved in 4 mL of HCl (37%). The solution was cooled to −40 °C before an aqueous solution of sodium nitrite (11,33 mg, 0.165 mmol, 2 equiv) was added. An initial color change from pink to yellow was observed. The reaction was stirred for 10 min at −40 °C and then allowed to warm to room temperature, whereby a further color change from yellow to pink as well as gas evolution was observed. The hydrochloric acid was removed in vacuo and the residue was washed three times with 5 mL portions of diethyl ether. The product was dissolved in acetonitrile and filtered off through a paper filter. The solvent was removed in vacuo affording 12 in 43.2% yield (0.014 g, 0.035 mmol). mp 83.3 °C. 1H NMR (400 MHz, CD3CN, ppm) δ = 4.73 (unresolved pseudo-t, 2H, C8–12 of Cp), 5.06 (unresolved pseudo-t, 2H, C9/C12 of Cp), 6.92 (s, 7H, C1–7 of Cp). 13C NMR (75 MHz, CD3CN, ppm) δ = 76.1 (C10/C11 of Cp), 78.8 (C9/C12 of Cp), 99.2 (C1–7 of Cp). 55N NMR (74 MHz, CD3CN, ppm) δ = 567. IR (ATR, cm−1) 3106, 3075 (ν(C=C)), 3036 (ν(C=CH)), 1561, 1481 (ν(C=CC)); 1449 (δ(δ)), 1432, 1402, 1371 (ν(C=C)), 1342, 1371, 1165 (ν(C=C)), 1022 (δ(δ)), 906 (δ(δ)), 884 (δ(δ)), 832 (δ(δ)), 514 (δ(δ)), 496, 480, 449, 422 (δ(δ)). HRMS (ESI pos, m/z) 244.9917 [M − OTf]+. UV–vis (CH3CN, nm) λmax = 279 nm, λmax = 576 nm. Single crystals of 8 were obtained from a mixture of acetonitrile and diethyl ether at room temperature by diffusion crystallization.
244.9924. UV–vis (CH₂CN, [nm]) λ_max = 379 nm, λ_max = 548 nm. Single crystals of 12 were obtained from a mixture of acetonitrile and diethyl ether at 4 °C by diffusion crystallization.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge via https://pubs.acs.org/doi/10.1021/acs.organomet.2c00179.

Accession Codes
CCDC 2159454–2159460 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES

(1) Basse, R.; Vanicek, S.; Hofer, T.; Kopacka, H.; Wurst, K.; Muller, T.; Schwartz, H. A.; Othlof, S.; Casper, L. A.; Nau, M.; Winters, R. F.; Podewitz, M.; Bildstein, B. Cationic Cycloheptatrienyl Cyclopentadienyl Manganese Sandwich Complexes: Tromancenium Explored with High-Power LED Photosynthesis. Organometallics 2021, 40, 2736–2749.

(2) Ginzburg, A. G. The chemistry of cyantrane. Russ. Chem. Rev. 2009, 78, 195–210.

(3) Nemesyanov, A. N.; Sazanova, V. A.; Sedova, N. N. Reactions of cyclopentadienylmanganesetrifluoroboryl acid with copper salts. Doklady Akademii Nauk SSSR 1970, 194, 825–826.

(4) Fedin, E. I.; Petrovskii, V. P.; Fedorov, L. A.; Makarov, Yu. V.; Kolobova, N. E.; Anisimov, K. N. Comparison of PMR of monosubstituted cyclopentadienylmanganese and cyclopentadienylhydride derivatizes. Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya 1973, 2143.

(5) Datta, A.; Köllhofer, A.; Plenio, H. Ir-catalyzed C=H activation in the synthesis of borylated ferrocenes and half sandwich compounds. Chem. Commun. 2004, 1508–1509.

(6) Vanicek, S.; Podewitz, M.; Hassencruck, C.; Pittmacher, M.; Kopacka, H.; Wurst, K.; Müller, T.; Liedl, K. R.; Winter, R. F.; Bildstein, B. Cobaltocenylidene: A Mesoionic Metalloco Carbene, Stabilized in a Gold(II) Complex. Chem. Eur. J. 2018, 24, 3165–3169.

(7) Selected books: (a) N-Heterocyclic Carbene in Transition Metal Catalysis and Organocatalysis; Cazin, C. S. J. C.; Springer: London, 2011. (b) N-Heterocyclic Carbenes in Synthesis; Nolan, S. P.; Wiley-VCH: Weinheim, 2006. (c) Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents; Bertrand, G.; Marcel Dekker Inc.: New York, 2002. (d) Functionalised N-Heterocyclic Carbenes Complexes; Kuhl, O.; John Wiley & Sons Ltd.: Chichester, United Kingdom, 2010. (e) N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, 2nd ed.; Díez-Gonzalez, S.; RSC Publishing: London, 2017.

(8) (a) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Schmutzler, R. Carbone Complexes of Pnicogten Pentfluorides and Boron Trifluoride. Monats. Chem. 2000, 131, 251–265. (b) Tian, C.; Nie, W.; Borzov, M. V.; Su, P. High-Yield Thermolytic Conversion of Iridiaodium Salts into Arduengo Carbone Adducts with BF₃ and PF₅. Organometallics 2012, 31, 1751–1760. (c) Kuhn, N.; Henkel, G.; Kratz, T.; Kreutzberg, J.; Boese, R.; Maulitz, H. Stabile Carben-Borane. Chem. Ber. 1993, 126, 2041–2045.

(9) Hinz, A.; Labbow, R.; Reiß, F.; Schulz, A.; Sievert, K.; Villinger, A. Synthesis and structure of tritellium salts. Struct. Chem. 2015, 26, 1641–1650.

(10) Selected references: (a) Suzuki, A. Carbon–carbon bonding made easy. Chem. Commun. 2005, 4759–4763. (b) Han, F.-S. Transition-metal-catalyzed Suzuki-Miyaura cross-coupling reactions: a remarkable advance from palladium to nickel catalysts. Chem. Soc. Rev. 2013, 42, 5270–5298. (c) Bullfield, D.; Huber, S. M. Synthesis of Polyfluorinated Biphenyls; Pushing the Boundaries of Suzuki-Miyaura Cross Coupling with Electronic-Poor Substrates. J. Org. Chem. 2017, 82, 13188–13023. (d) El-Maiss, J.; El Dine, T. M.; Lu, C.-S.; Karamé, I.; Kanj, A.; Polychronopoulou, K.; Shaya, J. Recent Advances in Metal-Catalyzed Alkyl-–Boron (C(sp³)–C(sp³)) Suzuki-Miyaura Cross-Couplings. Catalysis 2020, 10, 296.

(11) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Dual Catalysis Strategies in Photochemical Synthesis. Chem. Rev. 2016, 116, 10035–10074.
(12) Selected references: (a) Rao, H.; Fu, H.; Jiang, Y.; Zhao, Y. Easy Copper-Catalyzed Synthesis of Primary Amines by Coupling Aromatic Boronic Acids with Aqueous Temperature. Angew. Chem., Int. Ed. 2009, 48, 1114–1116. (b) Vantourout, J. C.; Law, R. P.; Isidro-Llobet, A.; Atkinson, S. J.; Watson, A. J. B. Chan—Evans–Lam Amination of Boronic Acid Pinacol (BPin) Esters: Overcoming the Aryl Amine Problem. J. Org. Chem. 2016, 81, 3942–3950. (c) Zhang, M.; Xu, Z.; Shi, D. Cu(I)—N-heterocyclic carbene-catalyzed base formation of arylboronic acids with amines and azoles. Tetrahedron 2021, 79, 131861.

(13) Vaincek, S.; Kopacka, H.; Wurst, K.; Muller, T.; Hassenriick, C.; Winter, R. P.; Bildstein, B. Nonfunctionalized Cobaltocene Compounds by Dediation Reactions of Cobaltoceniumdiazonium Bis(hexafluoro phosphate). Organometallics 2016, 35, 2101–2109.

(14) (a) Galli, C. Radical Reactions of Arenediazonium Ions: An Easy Entry into the Chemistry of the Aryl Radical. Chem. Rev. 1988, 88, 765–792. (b) The Chemistry of Diazonium and Diao Groups; Patai, S., Ed.; John Wiley & Sons: Chichester, U.K., 1978; Parts 1 and 2.

(15) Braunshweig, H.; Bera, H.; Stellweg, S.; Schwarz, S.; Hemberger, Y.; Radacki, K. [(Br2Bn-C5H5)]Mn(CO)3 – A versatile Precursor for Boron-based Ligands. Z. Allg. Anorg. Chem. 2007, 633, 2314–2320.

(16) (a) Zeinstra, J. D.; De Boer, J. L. Structure of cyclopentadienylcycloheptatrienyl-titanium. J. Organomet. Chem. 1973, 54, 207–211. (b) Lysenko, K. A.; Antipin, M. Yu; Ketsk, S. Yu. Electron density distribution in vanadocene (η-C5H5)2V and mixed metalocenes (η-C5H5)M(η-C5H5) (M = Ti, V, or Cr) and (η-C5H5)(η-C5H5)Ti(CO)3. Effect of the nature of the cyclic ligand on the character of the M–(π-ligand) bond. Russ. Chem. Bull., Int. Ed. 2001, 50, 130–141. (c) Mohapatra, S. K.; Bueschel, S.; Daniluc, C.; Jones, P. G.; Tamm, M. Selective Lithiation and Phosphane-Functionalization of [(η5-C5H5)2Ti(η5-C5H5)2] (Troticene) and Its Use for the Preparation of Early-Late-Heterobimetallic Complexes. J. Am. Chem. Soc. 2009, 131, 17014–17023. (d) Niinisto, J.; Hatanpaa, T.; Karinemi, M.; Mantymaki, M.; Costelle, L.; Mizobata, K.; Kuuki, K.; Ritala, M.; Leskela, M. Cycloheptatrienyl Cyclopentadienyl Heteroleptic Precursors for Atomic Layer Deposition of Group 4 Oxide Thin Films. Chem. Mater. 2012, 24, 2002–2008. (e) Kuete, A. C.; Sameni, S.; Freytag, M.; Jones, P. G.; Tamm, M. Phosphane-Functionalized Cycloheptatrienyl–Cyclopentadienyl Titanium Sandwich Complexes: Phosphorus Ligands with an Integrated Reducing Agent for Palladium(0) Catalyst Generation. Angew. Chem., Int. Ed. 2013, 52, 8638–8642. (f) Green, J. C.; Green, M. L. H.; Kaltsoyannis, N.; Mountford, P.; Scott, P.; Simpson, S. J. Synthesis and Electronic and Molecular Structures of η-Cycloheptatrienyl η-Cyclopentadienyl Derivatives of Vanadium, Niobium, and Tantalum: Photoelectron Spectroscopic, Electrochemical, and X-ray Crystallographic Study. Organometallics 1992, 11, 3353–3361. (g) Elschendorf, C.; Schiemann, O.; Burghaus, O.; Harms, K. Exchange Interaction Mediated by O–H–H Bonding. Synthesis, Structure, and EPR Study of the Paramagnetic Organometallic Carboxylic Acid (η-C5H5)2V(η2-C5H5COOH). J. Am. Chem. Soc. 1997, 119, 7452–7457. (h) Elschendorf, C.; Plackmeyer, J.; Nowotny, M.; Harms, K.; Peiber, J.; Burghaus, O. Di[5-[(trivacenylethene), Di[(5-trivacenyl)-butydinye, and Di-1,4-((5-trivacenylethylene)benzene: Electromagnetic and Magnetocumunication Mediated by –CC––, –CC– and –CC–H–CC– Spacers. Inorg. Chem. 2005, 44, 955–963.

(17) (a) Calderazzo, F.; Lucken, E. A. C.; Williams, D. F. The 51Mn Nuclear Magnetic Resonance Spectra of Alkyl- and Acan-manganese-pentacarbonyls and Related Compounds. J. Chem. Soc. (A) 1967, 154–158. (b) Wrackmeyer, B.; Hofmann, T.; Herberhold, M. Characterization of manganic sandwich complexes by 51Mn NMR spectroscopy. J. Organomet. Chem. 1995, 486, 255–258. (c) Arsenault, C.; Bougeard, P.; Sayer, B. G.; Yeroushalmi, S.; McGlinchey, M. J. [n(C5H5)2]2V(η2-C5H5COOH) at 150 K. Inorg. Chem. 2004, 43, 4762–4766.