

Syntheses and structures of missing links among polybromocyclopentadienyl rhenium and manganese tricarbonyl complexes

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Abstract

Reactions of diazocyclopentadiene and NBS at appropriate stoichiometries give 2,5-dibromodiazocyclopentadiene and 2,3,5-tribromodiazocyclopentadiene in 40% and 30% yields, respectively, after chromatography. These react with $\text{BrRe}(\text{CO})_5$ or $\text{BrMn}(\text{CO})_5$ (80 °C, $\text{CF}_3\text{C}_6\text{H}_5$) to give $(\eta^5\text{-}1,2,3\text{-C}_5\text{H}_2\text{Br}_3)\text{M}(\text{CO})_3$ (**3**; M = **a**, Re; **b**, Mn) and $(\eta^5\text{-C}_5\text{HBr}_4)\text{M}(\text{CO})_3$ (**4a,b**) in 75–85% yields. In the case of **4a**, the intermediate η^1 -cyclopentadienyl complex $(\eta^1\text{-C}_5\text{HBr}_4)\text{Re}(\text{CO})_5$ (**4'a**) can be isolated (44%). An isomer of **3b**, $(\eta^5\text{-}1,2,4\text{-C}_5\text{H}_2\text{Br}_3)\text{Mn}(\text{CO})_3$, is accessed by desilylating previously reported $(\eta^5\text{-}1,2,4\text{-C}_5(\text{SiMe}_3)_2\text{Br}_3)\text{Mn}(\text{CO})_3$ with CsF/MeOH (85%). The reaction of tetrabromodiazocyclopentadiene and $\text{BrRe}(\text{CO})_5$ at 80 °C in $\text{CF}_3\text{C}_6\text{H}_5$ gives the η^1 -cyclopentadienyl complex $(\eta^1\text{-C}_5\text{Br}_5)\text{Re}(\text{CO})_5$ (**5'a**, 74%) which cannot be induced to decarbonylate to $(\eta^5\text{-C}_5\text{Br}_5)\text{Re}(\text{CO})_3$ (**5a**) under a variety of conditions. However, **5a** can be isolated (45%) when a similar reaction is conducted at 120 °C. The IR properties of the preceding complexes are compared, and the crystal structures of **3a**, **3b**, **5a**, and **5'a** are determined and analyzed.

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Keywords: Rhenium; Manganese; Diazo compounds; NBS; Cyclopentadienyl complexes

1. Introduction

A cyclopentadienyl moiety can be found in nearly 80% of all organometallic compounds [1], and there is ongoing interest in the preparation of new derivatives with unusual functionality and/or substitution patterns [2]. Towards this end, polyhalocyclopentadienyl complexes, a variety of which have been described in the literature [3], represent particularly versatile building blocks [4]. For example, the manganese η^5 -pentaiodocyclopentadienyl complex $(\eta^5\text{-C}_5\text{I}_5)\text{Mn}(\text{CO})_3$ has been used as a springboard to pentaalkynylcyclopentadienyl

complexes [4c,4d] that have been incorporated into various organometallic arrays.

We were attracted to similar polyhalogenated manganese and rhenium complexes as possible precursors to “heavy” fluoros cyclopentadienyl species [5]. Since cyclopentadienyl ligands are easily detached from manganese tricarbonyl fragments [6], large families of metal derivatives might be accessed. However, rhenium tricarbonyl complexes are often more robust and better suited to exploratory chemistry. In any event, scout reactions with $(\eta^5\text{-C}_5\text{I}_5)\text{Mn}(\text{CO})_3$ and fluoros organozinc reagents gave disappointing results, and there are other drawbacks of this route as detailed elsewhere [7]. Since brominated pyridines had proven effective for such coupling reactions [8], a series of manganese and rhenium tri-, tetra-, and pentabromocyclopentadienyl complexes was sought.

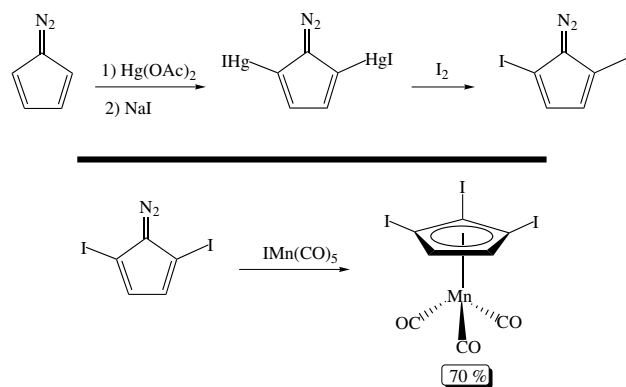
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An efficient synthesis of one such complex was already known. As shown in Scheme 1 (top), the reaction of $\text{BrMn}(\text{CO})_5$ and tetrabromodiazocyclopentadiene gives an η^1 -pentabromocyclopentadienyl pentacarbonyl complex, which upon heating decarbonylates to the η^5 -pentabromocyclopentadienyl tricarbonyl complex ($\eta^5\text{-C}_5\text{Br}_5$) $\text{Mn}(\text{CO})_3$ (**5b**) [9]. The η^5 -pentachlorocyclopentadienyl complex can be prepared similarly [10], but rhenium analogs have remained unknown. It is instructive to contrast this sequence with the reaction of $\text{BrMn}(\text{CO})_5$ and diazocyclopentadiene (Scheme 1, middle) [11,12]. In this case, the η^5 -bromocyclopentadienyl tricarbonyl complex ($\eta^5\text{-C}_5\text{H}_4\text{Br}$) $\text{Mn}(\text{CO})_3$ is obtained directly at room temperature. The higher temperature required for **5b** presumably reflects the diminished nucleophilicity of the pentabrominated η^1 ligand.

A “combinatorial” synthesis of all possible bromocyclopentadienyl manganese complexes ($\eta^5\text{-C}_5\text{H}_{5-n}\text{Br}_n$) $\text{Mn}(\text{CO})_3$ has also been reported [13]. As shown in Scheme 1 (bottom) this involves the reaction of the 1,2- and 1,3-dimercurated complexes ($\eta^5\text{-C}_5\text{H}_3(\text{HgBr})_2$) $\text{Mn}(\text{CO})_3$ with CuBr_2 . However, the fractions of individual products range from 4% to 26%, and preparative GC is required for separation.

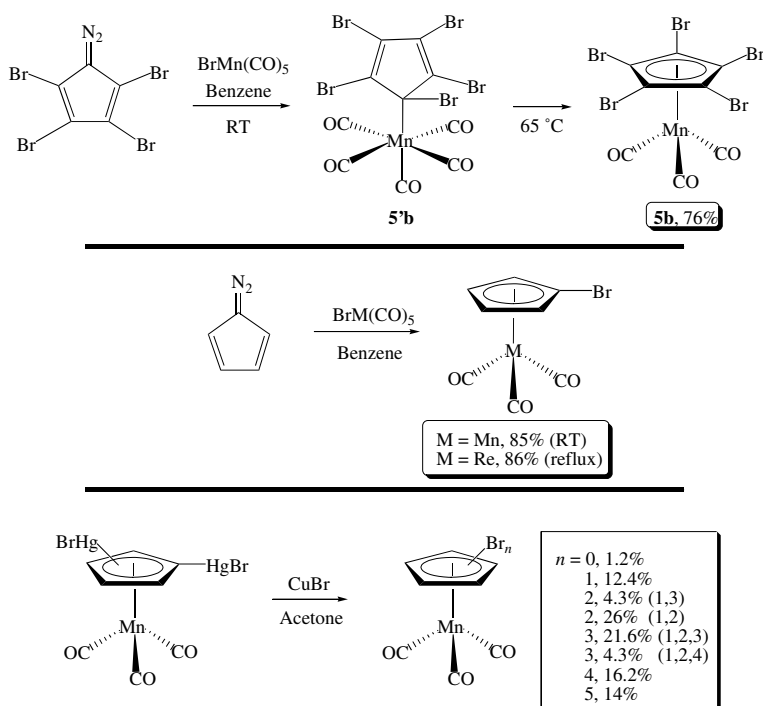
Hence, our attention was drawn to the synthesis of the manganese η^5 -triiodocyclopentadienyl complex ($\eta^5\text{-1,2,3-C}_5\text{H}_2\text{I}_3$) $\text{Mn}(\text{CO})_3$ shown in Scheme 2. This sequence starts with diazocyclopentadiene [14], which undergoes electrophilic substitution preferentially at the 2- and 5-positions [15]. However, rather than an initial mercuriation as in Scheme 2, we sought to examine



Scheme 2. Synthesis of a manganese η^5 -1,2,3-triiodocyclopentadienyl complex.

bromination. The reaction of diazocyclopentadiene and four equivalents of *N*-bromosuccinimide (NBS) in acetonitrile yields tetrabromodiazocyclopentadiene [9,15]. The unaddressed question was whether or not smaller quantities of NBS would afford selective brominations.

In this paper, we describe the successful realization of such brominations, and their use in syntheses of manganese and rhenium η^5 -tri- and tetrabromocyclopentadienyl complexes. We also report that under appropriate conditions, rhenium η^1 - and η^5 -polybromocyclopentadienyl complexes can be accessed similarly to the manganese analogs in Scheme 1. Both binding modes (and two η^5 -tribromocyclopentadienyl species) are crystallographically characterized, enabling the first detailed structural comparison of formally analogous η^1 - and η^5 -cyclopentadienyl compounds.



Scheme 1. Earlier syntheses of manganese and rhenium bromo- and polybromocyclopentadienyl complexes.

2. Results

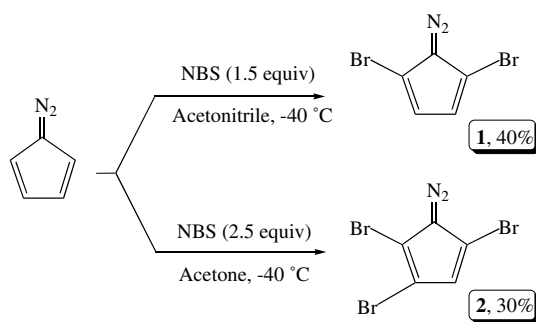
2.1. Tri- and tetrabromocyclopentadienyl complexes

As shown in Scheme 3, diazocyclopentadiene and 1.5 equivalents of NBS were combined in acetonitrile at -40 °C. Column chromatography gave 2,5-dibromodiazocyclopentadiene (**1**) in 40% yield. When an analogous reaction was conducted with 2.5 equivalents of NBS in acetone, 2,3,5-tribromodiazocyclopentadiene (**2**) was isolated in 30% yield. Both procedures gave mixtures of **1** and **2**, with the less polar **1** eluting first. Intermediate fractions contained both compounds, resulting in some yield loss. However, the substoichiometric quantities of NBS employed represent optimized conditions. When 3.0 equivalents of NBS were used, tetrabromodiazocyclopentadiene [9] was isolated in 53% yield.

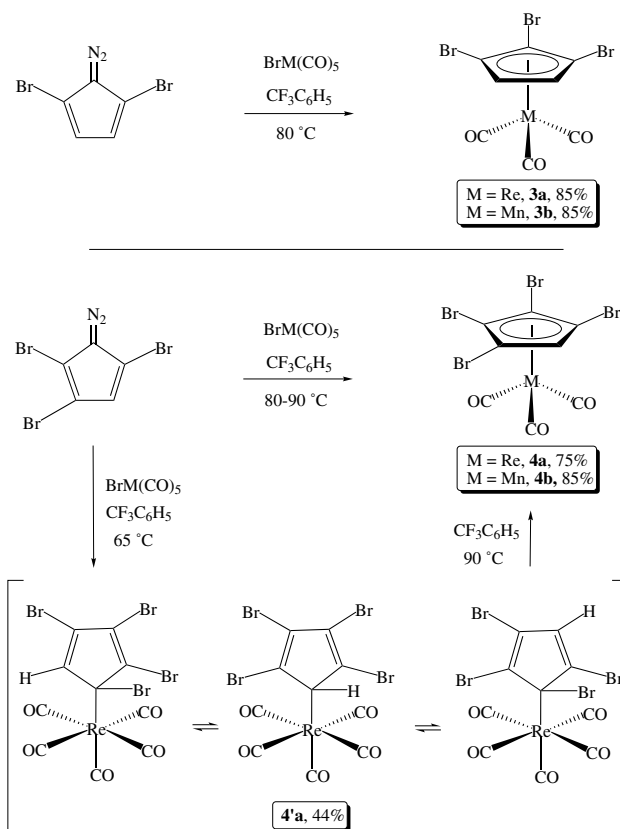
Compounds **1** and **2** were orange liquids at room temperature, with the latter somewhat darker. They showed substantial decomposition when kept for 10 h at room temperature, but could be stored for several months at -20 °C. They also exhibited some light (but not air) sensitivity. Their ^1H and ^{13}C NMR properties were routine (Section 4), and IR spectra showed intense bands characteristic of diazo groups ($2092/2096\text{ cm}^{-1}$).

As shown in Scheme 4 (top), $\text{BrRe}(\text{CO})_5$ or $\text{BrMn}(\text{CO})_5$ and **1** were reacted at 80 °C in $\text{CF}_3\text{C}_6\text{H}_5$, an increasingly popular solvent [16]. Workups gave the rhenium and manganese η^5 -tribromocyclopentadienyl complexes (η^5 -1,2,3- $\text{C}_5\text{H}_2\text{Br}_3$) $\text{M}(\text{CO})_3$ ($\text{M} = \text{Re}$, **3a**; Mn , **3b**) in 85% yields after recrystallization. Although the latter is technically not a new compound (see Scheme 1, bottom), only fragmentary data had been reported [13]. Thus, both were characterized by: (a) microanalysis, (b) IR and NMR (^1H , ^{13}C) spectroscopy, and (c) mass spectrometry, as summarized in Section 4. IR data are collected in Table 1, together with values obtained under identical conditions for previously reported compounds. The mass spectra showed molecular ions for all complexes.

Both **3a** and **3b** were air stable, but the latter discolored with extended exposure to light. The crystal struc-



Scheme 3. Syntheses of 2,5-dibromo- and 2,3,5-tribromodiazocyclopentadienes.



Scheme 4. Syntheses of rhenium and manganese η^5 -1,2,3-tribromo- and tetrabromocyclopentadienyl complexes.

tures were determined as summarized in Table 2 and Section 4. The molecular structures are illustrated in Fig. 1. With **3a**, two independent molecules were found in the unit cell. However, the structures were essentially identical. Key metrical parameters are summarized in Table 3, and selected features are analyzed below.

As shown in Scheme 4 (bottom), similar reactions of $\text{BrRe}(\text{CO})_5$ or $\text{BrMn}(\text{CO})_5$ with **2** gave the rhenium and manganese η^5 -tetrabromocyclopentadienyl complexes (η^5 - C_5HBr_4) $\text{M}(\text{CO})_3$ ($\text{M} = \text{Re}$, **4a**; Mn , **4b**) in 75–85%

Table 1
IR ν_{CO} values of rhenium and manganese η^5 -cyclopentadienyl complexes

Complex	IR ν_{CO} ($\text{CF}_3\text{C}_6\text{H}_5$, cm^{-1})
5a (η^5 - C_5Br_5) $\text{Re}(\text{CO})_3$	2046/1965
4a (η^5 - C_5HBr_4) $\text{Re}(\text{CO})_3$	2042/1961
3a (η^5 -1,2,3- $\text{C}_5\text{H}_2\text{Br}_3$) $\text{Re}(\text{CO})_3$	2038/1953
(η^5 - $\text{C}_5\text{H}_4\text{Br}$) $\text{Re}(\text{CO})_3$	2030/1934
(η^5 - C_5H_5) $\text{Re}(\text{CO})_3$	2026/1926
5b (η^5 - C_5Br_5) $\text{Mn}(\text{CO})_3$	2045/1976
4b (η^5 - C_5HBr_4) $\text{Mn}(\text{CO})_3$	2042/1972
3b (η^5 -1,2,3- $\text{C}_5\text{H}_2\text{Br}_3$) $\text{Mn}(\text{CO})_3$	2038/1961
3c (η^5 -1,2,4- $\text{C}_5\text{H}_2\text{Br}_3$) $\text{Mn}(\text{CO})_3$	2042/1965
(η^5 - $\text{C}_5\text{H}_4\text{Br}$) $\text{Mn}(\text{CO})_3$	2034/1949
(η^5 - C_5H_5) $\text{Mn}(\text{CO})_3$	2023/1923

Table 2
General crystallographic data^a

Complex	3a	3b	5'a	5a
Formula	C ₈ H ₂ Br ₃ O ₃ Re	C ₈ H ₂ Br ₃ O ₃ Mn	C ₁₀ Br ₅ O ₅ Re	C ₈ Br ₅ O ₃ Re
Formula weight	572.03	440.77	785.85	729.83
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	7.00820(10)	13.4016(4)	13.7080(3)	7.6130(2)
<i>b</i> (Å)	13.4855(2)	6.9157(2)	9.0230(2)	8.9700(3)
<i>c</i> (Å)	13.7155(3)	13.3248(5)	16.2940(3)	10.2020(3)
α (°)	111.6520(10)	90	90	85.9380(16)
β (°)	96.0010(10)	114.645(2)	125.4650(13)	80.2090(17)
γ (°)	101.0160(10)	90	90	83.6970(18)
<i>V</i> (Å ³)	1160.61(3)	1122.47(6)	1641.45(6)	681.41(4)
<i>Z</i>	4	4	4	2
ρ_{calc} (Mg/m ³)	3.274	2.608	3.180	3.557
Absorption coefficient (mm ⁻¹)	20.779	11.835	19.587	23.566
<i>F</i> (000)	1016	816	1400	644
Crystal size (mm ³)	0.30 × 0.20 × 0.20	0.10 × 0.05 × 0.05	0.30 × 0.20 × 0.20	0.20 × 0.15 × 0.10
θ limit (°)	2.76–27.49	1.67–27.45	2.50–27.52	2.03–27.53
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	–17, 17; –9, –9; –17, 17	–17, 17; –8, 8; –17, 17	–17, 17; –11, 11; –21, 21	–9, 9; –11, 11; –13, 13
Reflections collected	9870	4218	7127	5907
Independent reflections	5244	2558	3754	3122
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	4173	1763	3441	2833
Data/restraints/parameters	5244/0/271	2558/0/144	3754/0/191	3122/0/154
Goodness-of-fit on <i>F</i> ²	1.009	1.058	1.033	1.088
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0473, <i>wR</i> ₂ = 0.1131	<i>R</i> ₁ = 0.0356, <i>wR</i> ₂ = 0.0750	<i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0791	<i>R</i> ₁ = 0.0287, <i>wR</i> ₂ = 0.0737
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0642, <i>wR</i> ₂ = 0.1218	<i>R</i> ₁ = 0.0724, <i>wR</i> ₂ = 0.1074	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0810	<i>R</i> ₁ = 0.0329, <i>wR</i> ₂ = 0.0755
Largest difference in peak/hole (e Å ⁻³)	2.614/–4.832	0.703/–1.188	2.614/–4.832	0.703/–1.188

^a Data common to all structures: Diffractometer, Nonius KappaCCD; temperature (K), 173(2); wavelength (Å), 0.71073.

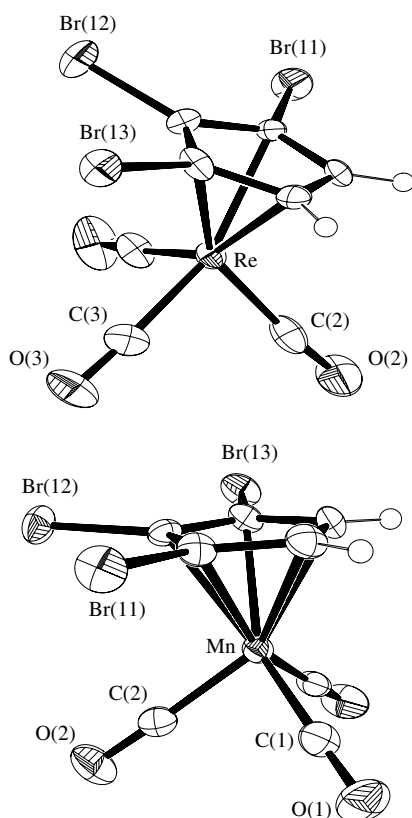
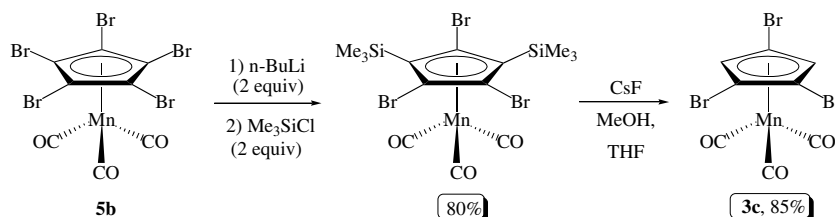


Fig. 1. Molecular structures of **3a** (top) and **3b** (bottom).

yields. These were characterized analogously to **3a** and **3b**. When the reactions of BrRe(CO)₅ with **1** and **2** were monitored by in situ IR spectroscopy, intermediates were detected (**3'a**, **4'a**) with ν_{CO} patterns consistent with

Table 3
Selected bond lengths (Å) and angles (°) for **3a** and **3b**

	3a (molecule 1)	3a (molecule 2)	3b
M(1)–centroid	1.969	1.969	1.766
M(1)–C(11)	2.312(8)	2.301(8)	2.136(6)
M(1)–C(12)	2.312(9)	2.316(9)	2.149(5)
M(1)–C(13)	2.275(8)	2.307(9)	2.138(5)
M(1)–C(14)	2.315(8)	2.312(9)	2.130(6)
M(1)–C(15)	2.304(8)	2.320(8)	2.138(6)
C(11)–Br(11)	1.875(8)	1.875(8)	1.875(8)
C(12)–Br(12)	1.858(9)	1.863(9)	1.858(9)
C(13)–Br(13)	1.879(9)	1.879(9)	1.879(9)
M(1)–C(1)	1.923(10)	1.929(9)	1.804(7)
M(1)–C(2)	1.923(10)	1.901(11)	1.802(7)
M(1)–C(3)	1.924(12)	1.919(9)	1.794(6)
C(1)–O(1)	1.134(12)	1.132(11)	1.143(7)
C(2)–O(2)	1.137(12)	1.137(12)	1.141(7)
C(3)–O(3)	1.139(13)	1.139(11)	1.141(7)
C1–M(1)–C2	89.2(4)	90.8(4)	92.1(3)
C1–M(1)–C3	91.5(4)	91.0(4)	91.0(3)
C2–M(1)–C3	89.6(4)	89.0(4)	92.1(3)

Scheme 5. Synthesis of a manganese η^5 -1,2,4-tribromocyclopentadienyl complex.

octahedral pentacarbonyl complexes (**3'a**, 2142 w, 2092 w, 2034 s, 1999 s; **4'a**, 2142 w, 2077 w, 2038 s, 2003 s). The latter was longer lived, and workup of a preparative reaction conducted at 65 °C gave **4'a** in 44% yield.

A variety of data established that **4'a** was the η^1 -tetrabromocyclopentadienyl complex (η^1 -C₅HBr₄)Re(CO)₅, possible isomers of which are depicted in Scheme 4 (bottom) [17]. First, a mass spectrum showed an intense molecular ion, and a correct carbon analysis was obtained. Second, the ¹H NMR spectrum exhibited a broad peak at room temperature (4.86 ppm), but three signals at -75 °C (6.92, 6.41 4.70 ppm, 1:3:96, THF-d₈), one of which was much more intense. This is consistent with the rapid equilibration of the isomers shown in Scheme 1 via sigmatropic shifts – a well-established phenomenon [18]. Third, a low temperature ¹³C NMR spectrum exhibited three signals for the η^1 -cyclopentadienyl ligand (131.75, 109.73, 49.45 ppm; 2:2:1, -100 °C, THF-d₈), and two for the carbonyl ligands (4:1). This suggests that the middle isomer in Scheme 4 dominates, as the others would give five cyclopentadienyl signals. Fourth, when a CF₃C₆H₅ solution of **4'a** was heated at 90 °C, **4a** was obtained in quantitative spectroscopic and 95% isolated yield.

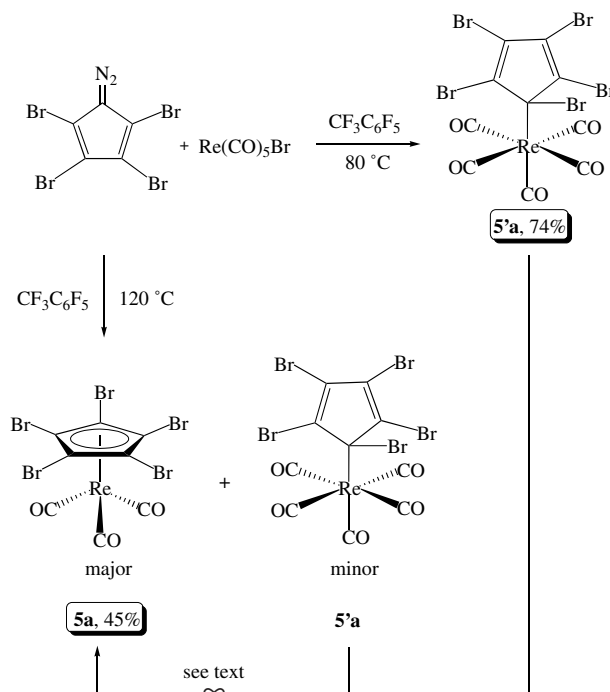
Since there is no obvious way to synthesize 2,4-dibromodiazocyclopentadiene via the methodology described above, the analogous η^5 -1,2,4-tribromocyclopentadienyl complexes cannot be accessed. However, as shown in Scheme 5, the reductive lithiation and trimethylsilylation of the manganese η^5 -pentabromocyclopentadienyl complex **5b** has been previously reported [19]. We repeated this sequence, and treated the bis(trimethylsilyl)-1,2,4-tribromocyclopentadienyl species with CsF in MeOH/THF. Workup gave the target complex (η^5 -1,2,4-C₅H₂Br₃)Mn(CO)₃ (**3c**) in 85% yield, which was characterized analogously to the other compounds described above.

2.2. Pentabromocyclopentadienyl complexes

Attention was next turned to the unknown η^5 -pentabromocyclopentadienyl complex (η^5 -C₅Br₅)Re(CO)₃ (**5a**). As shown in Scheme 6, BrRe(CO)₅ and tetrabromodiazocyclopentadiene were reacted in CF₃C₆H₅ at 80 °C. However, workup gave the η^1 -cyclopentadienyl complex (η^1 -C₅Br₅)Re(CO)₅ (**5'a**) in 74% yield. The

structure was evidenced by: (a) an intense molecular ion in the mass spectrum, (b) a correct carbon analysis, (c) an IR ν_{CO} pattern appropriate for an octahedral pentacarbonyl complex, and (d) low temperature ¹³C NMR spectra that showed three signals for the η^1 -cyclopentadienyl ligand (2:2:1; 140.5, 113.5, 49.0 ppm, THF-d₈) and two for the carbonyl ligands (4:1). In order to confirm this assignment, and support those for **3'a** and **4'a** above, a crystal structure was determined (see below).

Complex **5'a** was air stable and could be stored indefinitely at room temperature. It decomposed at 165–167 °C with effervescence. An IR spectrum of the resulting black solid showed numerous ν_{CO} bands, but none with properties appropriate for **5a** (see below). Mass spectra of the solid also gave no evidence for **5a**. DSC [20] analyses showed only a single transition in the range from 25 to 300 °C (exothermic decomposition, T_e 167.9 °C). TGA measurements indicated the onset of mass loss at 160 °C. When CF₃C₆H₅ solutions of **5'a** were heated to 80–100 °C, no reactions were observed. When

Scheme 6. Syntheses of rhenium η^1 - and η^5 -pentabromocyclopentadienyl complexes.

solutions were heated to 120 °C, traces of **5a** could be detected by mass spectrometry, but nearly all of the **5'a** could be recovered. Further increases in temperature only gave general decomposition.

In contrast to the cases with **5'b** and **5b** in Scheme 1, **4'a** and **4a** in Scheme 4, and related complexes discussed below, there is an appreciable kinetic barrier for the conversion of **5'a** to **5a**. A logical initial step would be the loss of CO. The photolysis of (η^1 -C₅H₅)Re(CO)₅ at 22 °C gives (in addition to homolytic cleavage of the cyclopentadienyl ligand) CO loss, with the subsequent formation of (η^5 -C₅H₅)Re(CO)₃ [21]. However, irradiation of THF solutions of **5'a** gave, under all conditions investigated, no trace of **5a**. Rather, **5'a** was recovered in high yields. Palladium oxide has been observed to catalyze substitution reactions of metal carbonyl complexes [22]. However, no reaction occurred when a CF₃C₆F₅ solution of **5'a** was heated at 80 °C in the presence of palladium oxide.

Out of desperation, a reaction of BrRe(CO)₅ and tetrabromodiazocyclopentadiene in CF₃C₆H₅ was conducted at 120 °C, as shown in Scheme 6. To our surprise, **5a** could now be isolated in 45% yield, which was sufficient for our preparative purposes [5]. Small quantities of **5'a** formed concurrently. In situ IR monitoring experiments confirmed that only minor amounts of **5'a** are generated at 120 °C, and that at most only traces of **5a** form at 80 °C. Possible rationales for this

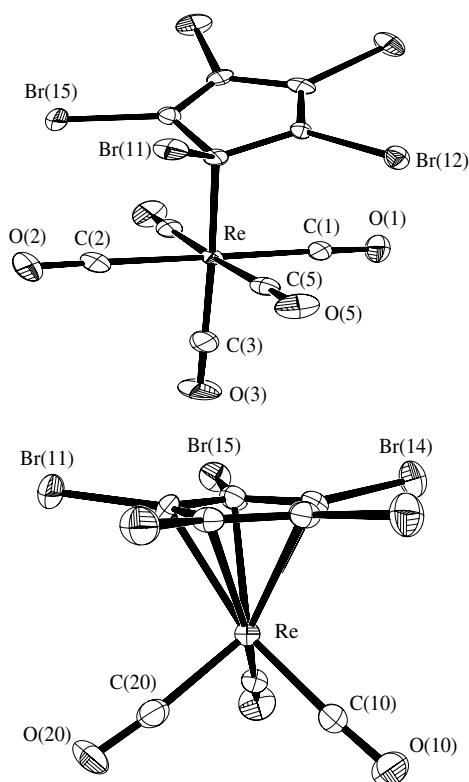


Fig. 2. Molecular structures of **5'a** (top) and **5a** (bottom).

Table 4

Selected bond lengths (Å) and angles (°) for **5'a** and **5a**

5'a		5a	
Re(1)–C(11)	2.298(4)	Re(1)–centroid	1.968
Re(1)–C(1)	1.993(5)	Re(1)–C(11)	2.319(5)
Re(1)–C(2)	2.018(5)	Re(1)–C(12)	2.301(5)
Re(1)–C(3)	1.972(5)	Re(1)–C(13)	2.316(5)
Re(1)–C(4)	1.994(5)	Re(1)–C(14)	2.316(5)
Re(1)–C(5)	2.031(5)	Re(1)–C(15)	2.315(5)
O(1)–C(1)	1.130(6)	Re(1)–C(10)	1.911(5)
O(2)–C(2)	1.128(6)	Re(1)–C(20)	1.926(6)
O(3)–C(3)	1.129(7)	Re(1)–C(30)	1.931(6)
C(4)–O(4)	1.139(6)		
O(5)–C(5)	1.116(6)	O(10)–C(10)	1.164(7)
		O(20)–C(20)	1.141(7)
		O(30)–C(30)	1.142(7)
C(11)–Br(11)	1.970(4)		
C(12)–Br(12)	1.864(4)	C(11)–Br(11)	1.859(5)
C(13)–Br(13)	1.866(4)	C(12)–Br(12)	1.864(5)
C(14)–Br(15)	1.864(4)	C(13)–Br(13)	1.866(5)
C(15)–Br(15)	1.869(5)	C(14)–Br(14)	1.868(5)
		C(15)–Br(15)	1.870(5)
C(1)–Re(1)–C(11)	93.46(18)	C(10)–Re(1)–C(20)	90.4(2)
C(2)–Re(1)–C(11)	86.53(17)	C(10)–Re(1)–C(30)	89.1(2)
C(3)–Re(1)–C(11)	174.67(18)	C(20)–Re(1)–C(30)	90.3(2)
C(4)–Re(1)–C(11)	91.46(18)		
C(3)–Re(1)–C(1)	90.5(2)		
C(3)–Re(1)–C(2)	89.6(2)		
C(3)–Re(1)–C(4)	92.3(2)		
C(4)–Re(1)–C(1)	87.21(19)		

strongly temperature-dependent product selectivity are discussed further below. To probe one hypothesis, the bromide-bridged dirhenium complex [ReBr(CO)₄]₂ [23] was prepared. No reaction occurred with tetrabromodiazocyclopentadiene at 120 °C in CF₃C₆H₅.

Complex **5a** exhibited spectroscopic properties similar to those of the other η^5 -cyclopentadienyl complexes. TGA measurements showed an onset of mass loss (130 °C, *T*_g) very close to the melting point (134–136 °C). Thus, **5a** is thermally less stable than **5'a** (onset of mass loss 160 °C). The crystal structures of **5a** and **5'a** were determined as summarized in Table 2 and Section 4. The molecular structures are illustrated in Fig. 2, while key metrical parameters are listed in Table 4. These represent the first pair of formally analogous η^1 - and η^5 -cyclopentadienyl complexes to be structurally characterized, and selected features are analyzed below.

3. Discussion

3.1. Syntheses

The successful syntheses of the new di- and tribromodiazocyclopentadienes in Scheme 3 allow the target rhenium and manganese η^5 -1,2,3-tribromocyclopentadienyl and tetrabromocyclopentadienyl complexes **3a,b** and **4a,b** (Scheme 4) to be readily accessed. We have

never encountered any explosions with the any of the diazo compounds in this study. They further allow possible alternative procedures involving the mercuriation of cyclopentadienyl complexes [3] to be avoided. Diazocyclopentadienes are known to insert into many other types of metal-halogen bonds (e.g., Rh, Fe, Ru) [10,24]. Thus, **1** and **2** can very likely be used to access polybromocyclopentadienyl complexes of other metals. Although it does not appear feasible to synthesize the isomeric η^5 -1,2,4-tribromocyclopentadienyl complexes via this methodology, the alternative route shown in Scheme 5 constitutes at least a partial solution.

Given the previously reported synthesis of the manganese η^5 -pentabromocyclopentadienyl complex **5b** from tetrabromodiazocyclopentadiene and $\text{BrMn}(\text{CO})_5$ (Scheme 1, top), the similar preparation of the rhenium analog was not expected to hold any surprises. The rhenium η^1 -cyclopentadienyl complex $(\eta^1\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_5$ readily decarbonylates to $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in the solid state at 22 °C [21], and **4'a** cleanly decarbonylates to **4a** in solution at 90 °C (Scheme 1, bottom). Thus, the isolation of an η^1 -cyclopentadienyl complex (**5'a**, Scheme 1) that was resistant to thermal decarbonylation was unexpected. Furthermore, the manganese η^1 -pentachlorocyclopentadienyl complex $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$ undergoes clean conversion to $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_3$ upon melting at 100 °C or heating in pentane [10].

Nonetheless, the target η^5 -cyclopentadienyl complex **5a** can be isolated in reasonable yields when reactions are conducted at 120 °C. The origin of this dramatic temperature dependence is not obvious, but previous studies of the reaction of tetrachlorodiazocyclopentadiene and $\text{ClMn}(\text{CO})_5$ may be relevant [10]. The η^1 - and η^5 -pentachlorocyclopentadienyl complexes $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$ and $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_3$ are obtained in varying ratios, depending upon conditions. The data are consistent with the intermediacy of the tetracarbonyl complex $\text{ClMn}(\text{CO})_4$, which combines with tetrachlorodiazocyclopentadiene to give some type of 1:1 adduct. Under CO-rich conditions, $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$ is the dominant product, and when CO is removed by a nitrogen stream, $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_3$ is the only product.

If the reactions in Scheme 6 were to involve some type of common tetracarbonyl $\text{BrRe}(\text{CO})_4$ (tetrabromodiazocyclopentadiene) species, the subsequent formation of the pentacarbonyl **5'a** would likely have a near-zero ΔS^\ddagger value (CO must be recaptured, N_2 must evolve). On the other hand, decarbonylation to the tricarbonyl **5a** would have a markedly positive ΔS^\ddagger value. Thus, the product distribution may be under enthalpy control below ca. 100 °C, and entropy control above 120 °C. In any event, once **5'a** is formed, it is stable with respect to **5a** and carbon monoxide. When pyrolyzed, other decomposition modes are kinetically faster. As noted above, the lower nucleophilicity of halogenated η^1 -cyclopentadienyl ligands is likely a factor. As more

halide substituents are introduced, the metal also becomes a stronger Lewis acid, disfavoring carbonyl ligand dissociation.

3.2. Spectroscopy and structure

As summarized in Table 1, the IR spectra of the η^5 -cyclopentadienyl complexes show several expected trends. First, the IR ν_{CO} values of the rhenium complexes increase in the order **3a** < **4a** < **5a** (2038/1953, 2042/1961, 2046/1965 cm^{-1}), consistent with diminished backbonding due to the increasing numbers of electron-withdrawing bromine atoms. The manganese complexes follow an analogous trend (**3b** < **3c** < **4b** < **5b**; 2038/1961, 2042/1965, 2042/1972, 2045/1976 cm^{-1}). The values for the monobromocyclopentadienyl and nonbrominated complexes are lower still.

The rhenium and manganese complexes **3a** and **3b** exhibit bond lengths and angles similar to those in related compounds [3b,25]. As expected for homologous third- and first-row transition metal complexes, the metal-ligand bonds in **3a** are 6.8–7.2% longer than those of **3b**. This is readily seen in the distances from the metals to the centroids of the cyclopentadienyl ligands (1.969 Å vs. 1.766 Å). Otherwise, the geometric features of **3a** are nearly identical to those of **3b**.

The crystal structure of the η^1 -pentabromocyclopentadienyl complex **5'a** is very similar to that of the related pentachloro manganese species $(\eta^1\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_5$ [10]. In both cases, the metal-carbon bond length for the carbonyl group trans to the η^1 -cyclopentadienyl ligand is shorter than the average bond length for the four *cis* carbonyl groups (1.972(5) vs. 2.009 Å in **5'a**), consistent with enhanced backbonding. The rhenium- η^1 -cyclopentadienyl bond length (2.298(4) Å) is only slightly shorter than the average distances between the rhenium and η^5 -cyclopentadienyl carbons in **3a** (2.301 Å) and **5a** (2.314 Å). The structures of two other octahedral rhenium η^1 -cyclopentadienyl complexes have been reported, both bis(phosphines) of the formula *fac*-($\eta^1\text{-C}_5\text{H}_5$) $\text{Re}(\text{CO})_3(\text{L})_2$ [17,26]. The rhenium- η^1 -cyclopentadienyl bond lengths were 2.360(10) Å ($\text{L} = \text{PMe}_3$) and 2.379(6) Å ($(\text{L})_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$).

The crystal structure of the η^5 -pentabromocyclopentadienyl complex **5a** is in most ways similar to that of **3a**. The average rhenium-ligand bond lengths are virtually identical, and in both cases the carbon-bromine bonds bend slightly away from rhenium. For the carbonyl groups, the average rhenium-carbon bond length in **5a** (1.923 Å) is much shorter than that in η^1 -pentabromocyclopentadienyl complex **5'a** (2.002 Å), consistent with greater backbonding. This is a logical consequence of the replacement of two strongly π accepting carbonyl ligands by the C=C moieties of the poorly π accepting η^5 -pentabromocyclopentadienyl ligand. Two formally analogous η^1 - and η^5 -indenyl $\text{Re}(\text{CO})_n$ complexes have

been structurally characterized, and exhibit similar trends [27,28].

3.3. Conclusion

When the new syntheses described above are combined with existing literature reports, practical routes to manganese η^5 -cyclopentadienyl tricarbonyl complexes with one, three, four, and five bromine substituents are now available. Both isomers of the tribromo complex can be accessed. In the rhenium series, only the dibromo and 1,2,4-tribromo complexes remain unknown. There are several obvious approaches to filling these remaining gaps, such as via the monobromination of diazocyclopentadiene, or debromination sequences as exemplified in Scheme 5. These complexes are very useful building blocks for fluoros and other functionalized cyclopentadienyl complexes, as described elsewhere [5a]. Finally, **5'a** represents an interesting curiosity in that it is the only rhenium η^1 -cyclopentadienyl pentacarbonyl complex that cannot be easily decarbonylated to an η^5 analog, at least under conditions investigated to date.

4. Experimental

4.1. General data

Reactions of rhenium and manganese complexes were conducted under N_2 . Chemicals were treated as follows: THF, distilled from Na/benzophenone; $CF_3C_6H_5$ (Fluorochem or ABCR), distilled from CaH_2 ; NBS, recrystallized from water (boiling, then 0 °C); CsF (Arcos) and others, used as received from common commercial sources. NMR spectra were recorded on Bruker or Jeol 400 MHz FT instruments and referenced to residual THF- d_8 or C_6D_6 signals. IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC and TGA data were recorded with a Mettler-Toledo DSC821 instrument and treated by standard methods [20]. Microanalyses were conducted with a Carlo Erba EA1110 instrument (in-house facility).

4.2. 2,5-Dibromodiazocyclopentadiene (**1**)

A round bottom flask was charged with diazocyclopentadiene (5.002 g, 54.33 mmol) [14] and acetonitrile (250 mL) and placed in a -40 °C bath. Then NBS (14.51 g, 81.53 mmol, 1.5 equiv) was slowly added with stirring over 0.5 h. After an additional hour, the flask was transferred to a 0 °C bath. Aqueous $NaHSO_4$, cold water, and ether were added. The ether layer was separated, and the aqueous layer was extracted twice with ether. The combined ether extracts were dried ($MgSO_4$) and filtered through a silica plug. The solvent was re-

moved by rotary evaporation and oil pump vacuum at room temperature. The residue was chromatographed (silica gel column, pentane) to give **1** as a bright orange liquid (5.478 g, 21.74 mmol, 40%). Some **2** also formed, and eluted later; the fractions were monitored by TLC.

IR (cm^{-1} , neat) ν_{CH} 3107 m, ν_{NN} 2092 s. NMR (δ , $CDCl_3$): 1H 6.03 (s, 2CH); $^{13}C\{^1H\}$ 99.75 (s, CBr), 120.85 (s, CH) [29].

4.3. 2,3,5-Tribromodiazocyclopentadiene (**2**)

Diazocyclopentadiene (5.002 g, 54.33 mmol) [14], acetone (350 mL), and NBS (24.18 g, 135.9 mmol, 2.5 equiv) were reacted in a procedure similar to that for **1**. An identical workup gave **2** as a bright orange liquid (5.359 g, 16.30 mmol, 30%).

IR (cm^{-1} , neat) ν_{CH} 3111 m, ν_{NN} 2096 s. NMR (δ , $CDCl_3$): 1H 6.09 (s, CH); $^{13}C\{^1H\}$ 99.74 (s, CBr), 100.61 (s, CBr), 106.23 (s, CBr), 122.74 (s, CH) [29].

4.4. Tetrabromodiazocyclopentadiene [9,30,31]

Diazocyclopentadiene (5.004 g, 54.33 mmol) [14], acetone (350 mL), and NBS (29.02 g, 163.1 mmol, 3.0 equiv) were reacted in a procedure similar to that for **1**. A comparable workup (flash chromatography on silica gel using pentane) gave an orange residue. Crystallization from warm hexanes (-4 °C) gave orange needles of tetrabromodiazocyclopentadiene (11.841 g, 28.81 mmol, 53%).

IR (cm^{-1} , $CF_3C_6H_5$) ν_{NN} 2100 s, 2069 s. NMR (δ , $CDCl_3$): $^{13}C\{^1H\}$ 100.20 (s, 2 CBr), 109.25 (s, 2 CBr) [29].

4.5. (η^5 -1,2,3- $C_5H_2Br_3$) $Re(CO)_3$ (**3a**)

A Schlenk flask was charged with $BrRe(CO)_5$ (1.003 g, 2.467 mmol) [32] and $CF_3C_6H_5$ (20 mL) and transferred to a 80 °C oil bath. After most of the $BrRe(CO)_5$ had dissolved, a solution of **1** (0.585 g, 2.34 mmol) in $CF_3C_6H_5$ was added via cannula with stirring. After 14 h at 80 °C, the solvent was removed by rotary evaporation and the crude dark product was flash chromatographed (silica gel, hexanes). The hexanes were removed by rotary evaporation and the crude greenish product was chromatographed (silica gel, hexanes). Recrystallization from hot hexanes gave opaque colorless crystals of **3a** (1.200 g, 1.99 mmol, 85%), m.p. 52–57 °C (capillary). Calc. for $C_8H_2Br_3O_3Re$: C, 16.80; H, 0.35. Found: C, 16.82; H, 0.30%.

IR (cm^{-1} , $CF_3C_6H_5$) ν_{CO} 2038 s, 1953 s. NMR (δ , C_6D_6): 1H 4.25 (s, 2CH); $^{13}C\{^1H\}$ 84.84 (s, CH), 85.09 (s, 2CBr), 86.66 (s, 1CBr), 192.24 (s, CO). MS (positive FAB, m/z) 572 (M^+ , 100%).

4.6. (η^5 -1,2,3- $C_5H_2Br_3$) $Mn(CO)_3$ (**3b**) [13]

The complex $BrMn(CO)_5$ (1.002 g, 3.645 mmol) [33], $CF_3C_6H_5$ (20 mL), and a solution of **1** (0.910 g, 3.64 mmol) in $CF_3C_6H_5$ were combined in a procedure analogous to that for **3a**. An identical workup gave dark yellow crystals of **3b** (1.363 g, 3.094 mmol, 85%), m.p. 68–72 °C (capillary; lit. [13] 71–72 °C). Calc. for $C_8H_2Br_3O_3Mn$: C, 21.80; H, 0.46. Found: C, 21.82; H, 0.40%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2038 s, 1961 s. NMR (δ): 1H (C_6D_6 or $CDCl_3$) 4.45 or 3.79 (s, 2CH); $^{13}C\{^1H\}$ (C_6D_6) 81.42 (s, CH), 85.77 (s, 2CBr), 90.64 (s, 1CBr), 223.09 (s, CO). MS (positive FAB, m/z): 440 (M^+ , 30%), 384 ($[M^+ - 2CO]$, 50%), 356 ($[M^+ - 3CO]$, 100%).

4.7. (η^1 - C_5HBr_4) $Re(CO)_5$ (**4'a**)

A Schlenk flask was charged with $BrRe(CO)_5$ (0.253 g, 0.623 mmol) [32] and $CF_3C_6H_5$ (20 mL), and transferred to a 65 °C oil bath. After most of the $BrRe(CO)_5$ had dissolved, a solution of **2** (0.202 g, 0.614 mmol) in $CF_3C_6H_5$ (10 mL) was added via cannula with stirring. After 10 h, the solvent was removed by oil pump vacuum. The black residue was flash chromatographed (silica gel, 1:1 v/v toluene/hexanes). The solvents were removed by rotary evaporation (35 °C) and the brown residue was chromatographed (silica gel, hexanes). The first band to elute contained **4a**. The solvent was removed from the second band and the residue was recrystallized several times from ether/hexanes (–20 °C) to give yellow crystals of **4'a** (0.193 g, 0.270 mmol, 44%), m.p. 122–125 °C (capillary, CO loss). TGA: onset of mass loss, 123.5 °C (T_g). DSC: endotherm, 122.5 °C (T_g). Calc. for $C_{10}HBr_4O_5Re$: C, 16.99. Found: C, 16.97%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2142 w, 2077 w, 2038 s, 2003 s. NMR (δ , THF- d_8): 1H , 65 °C, 4.97 (s); 25 °C, 4.86 (br s); –75 °C, 4.70 (s, 96%), 6.42 (s, 3%), 6.92 (s, 1%); ^{13}C , –100 °C, 49.45 (s, ReCH) [34], 109.73 (s, =CBr) [34], 131.75 (s, =CBr) [34], 180.68 (s, 1CO), 184.71 (s, 4CO).

4.8. (η^5 - C_5HBr_4) $Re(CO)_3$ (**4a**)

The complex $BrRe(CO)_5$ (1.005 g, 2.474 mmol) [32], $CF_3C_6H_5$ (20 mL), and a solution of **2** (0.769 g, 2.34 mmol) in $CF_3C_6H_5$ were combined in a procedure analogous to that for **3a**. After 14 h, the sample was heated at 90 °C (2 h) or 100 °C (1 h) to ensure the complete conversion of intermediate **4'a**. An identical workup gave opaque colorless crystals of **4a** (1.142 g, 1.755 mmol, 75%), m.p. 119–123 °C (capillary). TGA: onset of mass loss, 141.2 °C (T_g). DSC: 123.6 °C (T_g). Calc. for $C_8HBr_4O_3Re$: C, 14.76; H, 0.15. Found: C, 14.83; H, 0.30%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2042 s, 1961 s. NMR (δ , C_6D_6): 1H 4.44 (s, CH); $^{13}C\{^1H\}$ 84.63 (s, CH), 85.21 (s, CBr), 86.66 (s, CBr), 192.24 (s, CO). MS (positive FAB, m/z): 651 (M^+ , 100%).

4.9. (η^5 - C_5HBr_4) $Mn(CO)_3$ (**4b**) [13]

The complex $BrMn(CO)_5$ (1.009 g, 3.641 mmol) [33], $CF_3C_6H_5$ (20 mL), and a solution of **2** (1.197 g, 3.640 mmol) in $CF_3C_6H_5$ were combined in a procedure analogous to that for **3a**. An identical workup gave yellow crystals of **4b** (1.607 g, 3.094 mmol, 85%), m.p. 78–82 °C (capillary; lit. [13] 80.5 °C). Calc. for $C_8HBr_4O_3Mn$: C, 18.49; H, 0.19. Found: C, 18.47; H, 0.30%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2042 s, 1972 s. NMR (δ , C_6D_6): 1H 4.44 (s, CH); $^{13}C\{^1H\}$ 82.59 (s, CH), 85.90 (s, CBr), 89.08 (s, CBr), 222.70 (s, CO). MS (positive FAB, m/z): 521 (M^+ , 100%), 492 ($[M^+ - CO]$, 28%), 464 ($[M^+ - 2CO]$, 70%), 436 ($[M^+ - 3CO]$, 68%).

4.10. (η^1 - C_5Br_5) $Re(CO)_5$ (**5'a**)

A Schlenk flask was charged with $BrRe(CO)_5$ (1.003 g, 2.469 mmol) [32] and $CF_3C_6H_5$ (20 mL), and transferred to a 80 °C oil bath. After most of the $BrRe(CO)_5$ had dissolved, a solution of tetrabromodiazocyclopentadiene (0.954 g, 2.34 mmol) in $CF_3C_6H_5$ (20 mL) was added via cannula with stirring. After 5 h at 80 °C, the solvent was removed by rotary evaporation. The residue was flash chromatographed (silica gel, first with hexanes and then with 1:1 v/v toluene/hexanes). The solvents were removed by rotary evaporation and the brown residue was recrystallized several times from hot hexanes (0 °C). This gave tan crystals of **5'a** (1.361 g, 1.732 mmol, 74%), m.p. 165–167 °C (capillary, dec). TGA: onset of mass loss, 160 °C (T_g). DSC: exotherm, 167.9 °C (T_g). Calc. for $C_{10}Br_5O_5Re$: C, 15.28. Found: C, 15.19%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2146 w, 2081 w, 2034 s, 2003 s. $^{13}C\{^1H\}$ NMR (δ): C_6D_6 , 25 °C, 182.06 (br s, CO); THF- d_8 , –80 °C, 48.95 (s, ReCBr), 113.50 (s, =CBr), 140.51 (s, =CBr), 180.90 (s, 1CO), 184.61 (s, 4CO). MS (positive FAB, m/z): 786 (M^+ , 100).

4.11. (η^5 - C_5Br_5) $Re(CO)_3$ (**5a**)

A Schlenk flask was charged with $BrRe(CO)_5$ (1.002 g, 2.460 mmol) [32] and $CF_3C_6H_5$ (20 mL) and transferred to a 120 °C oil bath. After the $BrRe(CO)_5$ had dissolved, a solution of tetrabromodiazocyclopentadiene (0.954 g, 2.34 mmol) in $CF_3C_6H_5$ was added via cannula with stirring. After 1 h at 120 °C, the solvent was removed by rotary evaporation. The dark residue was triturated and flash chromatographed (silica gel, hexanes). The hexanes were removed by rotary evaporation and the crude greenish product was chromatographed (silica

gel, hexanes). Recrystallization from hot hexanes gave opaque colorless crystals of **5a** (0.769 g, 1.05 mmol, 45%), m.p. 134–136 °C (capillary). TGA: onset of mass loss, 130 °C (T_c). Calc. for $C_8Br_5O_3Re$: C, 13.17. Found: C, 13.36%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2046 s, 1965 s. NMR (δ , C_6D_6): $^{13}C\{^1H\}$ 86.00 (s, CBr), 192.06 (s, CO). MS (positive FAB, m/z): 729 (M^+ , 100%), 673 ($[M^+ - 2CO]$, 20%), 645 ($[M^+ - 3CO]$, 24%).

4.12. (η^5 -1,2,4- $C_5H_2Br_3$) $Mn(CO)_3$ (**3c**) [13]

A Schlenk flask was charged with (η^5 -1,2,4- $C_5(SiMe_3)_2Br_3$) $Mn(CO)_3$ (1.002 g, 1.710 mmol) [19], CsF (0.530 g, 3.50 mmol), THF (5 mL) and MeOH (5 mL). After 5 min, the solvents were removed by oil pump vacuum. The residue was extracted with hexane. The hexane was removed by rotary evaporation to give an orange solid. Recrystallization from pentane gave dark yellow crystals of **3c** (0.641 g, 1.45 mmol, 85%), m.p. 41–44 °C (capillary; lit. [13] 61 °C). Calc. for $C_8H_2Br_3O_3Mn$: C, 21.80; H, 0.46. Found: C, 22.00; H, 0.54%.

IR (cm^{-1} , $CF_3C_6H_5$): ν_{CO} 2042 s, 1965 s. NMR (δ , C_6D_6): 1H 4.08 (s, 2CH); $^{13}C\{^1H\}$ 83.23 (s, CH), 83.40 (s, 2CBr), 86.72 (s, 1CBr), 223.09 (s, CO). MS (positive FAB, m/z): 440 (M^+ , 30%), 384 ($[M^+ - 2CO]$, 50%), 356 ($[M^+ - 3CO]$, 100%).

4.13. Crystallography

(A) Complex **3a** was dissolved in hot hexanes and stored at room temperature. After a few days, colorless translucent prisms were taken directly to a Nonius KappaCCD diffractometer for data collection as summarized in Table 2. Cell parameters were obtained from 10 frames using a 10° scan and refined with 5075 reflections. Lorentz, polarization, and absorption corrections [35] were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 using SHELXL-97 [36]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from the literature [37]. Two independent molecules were found in a unit cell. After refinement, quite high rest electron densities remained (poor crystal quality). (B) Complex **3b** was dissolved in hot hexanes and stored at room temperature. After a few days, the yellowish prisms were analyzed as described for **3a** (cell parameters from 10 frames using a 10° scan; refined with 2536 reflections). The structure was solved and refined as described for **3a**. (C) Complex **5a** was dissolved in hot hexanes and stored at room temperature. After a few days, the translucent prisms were analyzed as

described for **3a** (cell parameters from 10 frames using a 10° scan; refined with 2833 reflections). The structure was solved and refined as described for **3a**. (D) Complex **5'a** was dissolved in hot hexanes and stored at room temperature. After a few days, the brownish prisms were analyzed as described for **3a** (cell parameters obtained from 10 frames using a 10° scan; refined with 3848 reflections). The structure was solved and refined as described for **3a**.

5. Supplementary material

CCDC-247943 (**3a**), CCDC-247944 (**3b**), CCDC-247945 (**5'a**), and CCDC-247946 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving/html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

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