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Convenient syntheses of "heavy fluorous" cyclopentadienes and cyclopentadienyl complexes with three to five ponytails†

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Reactions of (η^5-$C_5H_{5-x}Br_x$)M(CO)$_3$ (M = Re, Mn; x = 1, 3, 4, 5) and IZn(CH_2)$_2$R$_{f8}$ in the presence of Cl_2PdL_2 catalysts give the title complexes (η^5-C_5H_{5-x}((CH_2)$_2$R$_{f8}$)$_x$)M(CO)$_3$, accompanied in the case of x = 5 by hydride-transfer byproducts. Extremely high fluorophilicities are realized, and the cyclopentadienyl ligands are readily detached ($h\nu$) from the manganese complexes.

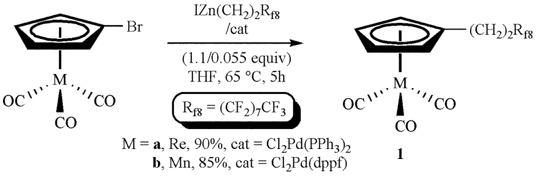
Cyclopentadienyl metal complexes see extensive use in catalysis,[1] and numerous methods have been investigated for their recovery and re-use. One increasingly popular recycling strategy involves "fluorous" catalysts that have been derivatized with "ponytails", often of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ (abbreviated $(CH_2)_mR_{fn}$).[2,3] When sufficient CF_2 moieties are present, high affinities for perfluoroalkanes and other fluorous phases are achieved. Reactions can be conducted under a variety of single- or multiphase conditions. Catalyst/product separation, as traditionally practiced, utilizes a perfluoralkane/organic solvent mixture, which is commonly biphasic at room temperature. The organic products partition predominantly into the organic phase (>95%). In newer fluorous-solvent-free variants, the temperature-dependent solubilities of such catalysts in organic solvents are exploited.[4]

Little attention has been given to developing fluorous cyclopentadienyl metal complexes that exhibit very high fluorous phase affinities (*e.g.*, >99 : <1 $CF_3C_6F_{11}$/toluene). Unlike the phosphine ligands in many catalysts, cyclopentadienyl ligands remain bound for the entire catalytic cycle. Thus, fluorous cyclopentadienyl ligands have distinct advantages over fluorous phosphine ligands for catalyst immobilization. In early studies, Hughes and Horváth synthesized several iron, manganese, cobalt, and rhodium cyclopentadienyl complexes with one ponytail per ring ($(CH_2)_2R_{fn}$, n = 6, 8, 10).[5,6] Although fluorophilicities were generally modest, the ferrocene (η^5-$C_5H_4(CH_2)_2R_{f10}$)$_2$Fe exhibited a $CF_3C_6F_{11}$/toluene partition coefficient of *ca.* 95 : 5. More recently, routes to free cyclopentadienes with two ponytails have been reported ($(CH_2)_2R_{fn}$ with n = 4, 6, 8), and iron and rhodium derivatives prepared.[7] Certain ferrocenes gave $CF_3C_6F_{11}$/toluene partition coefficients as high as 98.6 : 1.4.

In order to obtain cyclopentadienyl complexes with still higher fluorophilicities and the lowest possible leaching susceptibilities, we sought routes to "heavy fluorous" species with three to five ponytails per ring. It was recently shown that dibromo- and tribromopyridines undergo efficient substitution when treated with the fluorous organozinc reagent IZn(CH_2)$_2$R$_{f8}$ in the presence of the catalyst $Cl_2Pd(PPh_3)_2$.[8] We wondered whether this method could be extended to polyhalocyclopentadienyl systems, numerous types of which are readily available.[9,10] The successful implementation of this strategy is described below.[11,12]

As shown in Scheme 1, screening experiments were conducted with the rhenium and manganese monobromocyclopentadienyl complexes (η^5-C_5H_4Br)M(CO)$_3$.[13] Reactions with IZn(CH_2)$_2$R$_{f8}$ (1.1 equiv) and Cl_2PdL_2 (0.055 equiv)[14] in THF at 65 °C gave the corresponding fluorous cyclopentadienyl complexes (η^5-$C_5H_4(CH_2)_2R_{f8}$)M(CO)$_3$ (**1**; M = **a**/Re, **b**/Mn) in 90–85% yields after workup. Both were air stable and highly soluble in common organic solvents as well as $CF_3C_6F_{11}$. The $CF_3C_6F_{11}$/toluene partition coefficients were determined by HPLC. As summarized in Table 1, both complexes were preferentially soluble in toluene. The IR ν_{CO} values were at slightly higher frequencies than those of the parent compounds (η^5-C_5H_5)M(CO)$_3$, indicating diminished metal/CO backbonding (Table 1). This shows, as expected from other studies,[5,15] that the $(CH_2)_2$ spacer does not completely insulate the cyclopentadienyl ligand and metal from the electron-withdrawing R_{f8} segment.

Next, a more challenging application was sought. The rhenium pentabromocyclopentadienyl complex (η^5-C_5Br_5)Re(CO)$_3$ was prepared from BrRe(CO)$_5$ and tetrabromodiazocyclopentadiene[16] in $CF_3C_6H_5$ at 120 °C (45% after recrystallization).[17] A 0.500 g sample was treated with IZn(CH_2)$_2$R$_{f8}$ (5.5 equiv) and Cl_2PdL_2 (0.11 equiv per C–Br bond) in THF at 65 °C. Workup gave the product mixture shown in Scheme 2, which was separated by chromatography on fluorous silica gel (8 : 1 v/v hexanes/$CF_3C_6H_5$).[18] The compounds eluted in inverse order of their fluorous content. The last fraction contained the target complex with five ponytails, (η^5-$C_5((CH_2)_2R_{f8})_5$)Re(CO)$_3$ (**5a**), which was isolated in 15% yield (0.263 g). The penultimate fraction contained the major product, (η^5-$C_5H((CH_2)_2R_{f8})_4$)Re(CO)$_3$ (**4a**), in which one of the bromine atoms had been replaced by hydrogen and the other four by ponytails (30%, 0.435 g). Two earlier fractions contained analogous species with three ponytails (1,2,4 isomer **3a**, 2%, 0.023 g; 1,2,3 isomer **3′a**, 5%, 0.057 g). Authentic samples of **4a** and **3′a** were prepared from the corresponding tetra- and



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Scheme 1 Screening experiments.

Table 1 Selected data for fluorous cyclopentadienyl complexes

	Complex	Partition coefficient ($CF_3C_6F_{11}$/toluene)[a]	IR ν_{CO} ($C_6H_5CF_3$)/cm^{-1}
5a	(η^5-$C_5((CH_2)_2R_{f8})_5$)Re(CO)$_3$	>99.5 : <0.5	2030/1942
4a	(η^5-$C_5H((CH_2)_2R_{f8})_4$)Re(CO)$_3$	>99.5 : <0.5	2026/1939
3a	(η^5-1,2,4-$C_5H_2((CH_2)_2R_{f8})_3$)Re(CO)$_3$	>99.5 : <0.5	2026/1938
3′a	(η^5-1,2,3-$C_5H_2((CH_2)_2R_{f8})_3$)Re(CO)$_3$	>99.5 : <0.5	2026/1938
1a	(η^5-$C_5H_4(CH_2)_2R_{f8}$)Re(CO)$_3$	26.1 : 73.9	2026/1930
	(η^5-C_5H_5)Re(CO)$_3$		2026/1926
5b	(η^5-$C_5((CH_2)_2R_{f8})_5$)Mn(CO)$_3$	>99.5 : <0.5	2026/1949
4b	(η^5-$C_5H((CH_2)_2R_{f8})_4$)Mn(CO)$_3$	>99.5 : <0.5	2026/1945
3b	(η^5-1,2,4-$C_5H_2((CH_2)_2R_{f8})_3$)MnCO)$_3$	>99.5 : <0.5	2026/1943
3′b	(η^5-1,2,3-$C_5H_2((CH_2)_2R_{f8})_3$)Mn(CO)$_3$	>99.5 : <0.5	2026/1943
2b	(η^5-1,3-$C_5H_3((CH_2)_2R_{f8})_2$)MnCO)$_3$	93.5 : 6.5	2026/1942
2′b	(η^5-1,2-$C_5H_3((CH_2)_2R_{f8})_2$)MnCO)$_3$	93.8 : 6.2	2026/1942
1b	(η^5-$C_5H_4(CH_2)_2R_{f8}$)Mn(CO)$_3$	44.4 : 55.6	2026/1938
	(η^5-C_5H_5)Mn(CO)$_3$		2023/1922

[a] 23 °C, determined by HPLC.

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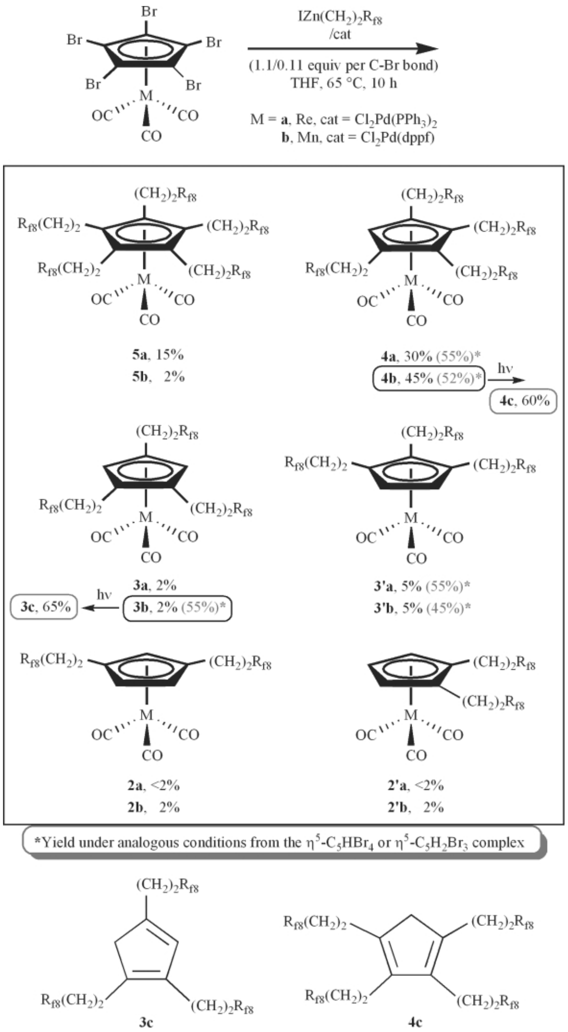
tribromocyclopentadienyl complexes (4.4 or 3.3 equiv $IZn(CH_2)_2R_{f8}$, 0.11 equiv Cl_2PdL_2 per C–Br bond, 55% yields).

Although more selective reactions are often sought, Scheme 2 can be viewed as a facile one-pot synthesis of an easily-separable library of fluorous compounds, all of which were desired at the outset of this study. Because of the high formula weights of the ponytails, the combined mass of **5a** and **4a** isolated is much greater than that of the educt. The tetra- and trisubstituted complexes presumably arise *via* hydride transfer from the organozinc reagent.[14b] All complexes are low-melting white solids that are soluble in $CF_3C_6F_{11}$ and $CF_3C_6H_5$. Solubilities in organic solvents decrease markedly in the order **3a**/**3′a** > **4a** > **5a**. Among eight solvents screened, only THF and acetone could dissolve trace amounts of **5a** at room temperature. As summarized in Table 1, the $CF_3C_6F_{11}$/toluene partition coefficients were in all cases $>99.5 : <0.5$, and the IR ν_{CO} values showed the expected trends.

A number of protocols have been developed for detaching cyclopentadienyl ligands from transition metals.[19] One of the most reliable involves the photolysis of manganese tricarbonyl adducts. Thus, the preceding chemistry was repeated with $(\eta^5\text{-}C_5Br_5)Mn(CO)_3$.[16a] As summarized in Scheme 2, workup gave **5b**, **4b**, **3b**, **3′b**, **2b**, and **2′b** in 2%, 45%, 2%, 5%, 2%, and 2% yields, respectively.[14] All properties were very similar to those of the rhenium analogs, and authentic samples of **4b**, **3b**, and **3′b** were independently synthesized from the corresponding tetra- and tribromocyclopentadienyl complexes (52%, 55%, 45%). Next, $CF_3C_6H_5$ solutions of **4b** and **3b** were irradiated with a Heraeous TQ150 high-pressure mercury lamp. After 20 min, a chromatographic workup gave the free fluorous cyclopentadienes **4c** and **3c**, with four and three ponytails respectively, in 60% and 65% yields. The NMR spectra indicated a tautomeric purity of > 95%, with the major isomers as depicted in Scheme 2.



Scheme 2 Syntheses of cyclopentadienyl complexes and cyclopentadienes with three to five ponytails.

In summary, complexes **5a,b** contain to our knowledge the first examples of "totally ponytailed" or "perfluorous" π ligands. They are obtained as part of a library of partially ponytailed complexes, all of which can be independently synthesized from the corresponding bromocyclopentadienyl complexes. The fluorous ligands are easily detached from the manganese adducts, and their transfer to other metals will be described in future reports. Thus, families of cyclopentadienyl complexes with gradated fluorophilicities and other properties are now accessible, including the first cases with highly biased partition coefficients that are suitable for application in "heavy fluorous" chemistry.

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