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Through-Space Shielding Effects of Metal-Complexed Phenyl Rings

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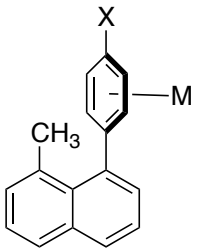


Set 1: M = $Cr(CO)_3$ and X = H; CH_3; OCH_3; $N(CH_3)_2$; F; CO_2CH_3

Set 2: M = $Cr(CO)_3$; $Mn^+(CO)_3$ BF_4^-; $RuCp^+$ PF_6^- and X = CH_3

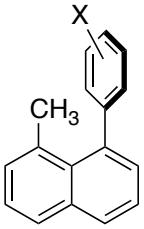
Several naphthalene compounds containing a methyl group in a 1,8-relationship to a metal-complexed phenyl ring bearing various substituents have been synthesized. The through-space shielding effects of the phenyl ring, as a function of substituent and complexing metal species, were monitored by observing the ^{1}H NMR signal of the methyl group located in the shielding zone of the ring. In all cases, the methyl signal was slightly more downfield in the complexes than in the uncomplexed analogs. A comparison of available crystal structures, however, show that the phenyl ring is slightly closer to the naphthyl methyl group in the complexes than in their metal-free counterparts. X-ray structures and DFT calculations also reveal a slight elongation in the average length of the carbon-carbon bonds of the phenyl ring upon complexation. The effect of substituents on the signal of the naphthyl methyl group is small but discernible in the uncomplexed derivatives, and consistent with our previous report. A similar trend is absent in the corresponding metal complexes, as exemplified by the chromium series, and the effect of the

metal appears to be more dominant than that of the substituents. These observations were found to be in line with NMR shift calculations.

Introduction

Following the development of a ring current model in the 1930s to describe the diamagnetic anisotropy of aromatic molecules,[1] a number of workers have investigated the interplay among ring current, aromaticity, and NMR chemical shifts in such systems.[2] It is now well known that the magnetic field induced by a diatropic ring current in aromatic species causes the peripheral (outside) protons to be deshielded and appear downfield in the ^{1}H NMR spectrum, whereas protons positioned within the ring are shielded and show an upfield chemical shift. Likewise, protons that are located opposite the face of an aromatic ring are also in the shielding zone and show chemical shifts that are upfield in the NMR spectrum.[3]

Although the influence of substituents on the chemical shifts of phenyl ring protons have been investigated in detail,[4] much less is known about how substituents affect the through-space shielding of aromatic rings.[5] In this regard, we recently reported a detailed study on the influence of substituents on the through-space shielding of phenyl rings based on our investigation of ten naphthalene derivatives (**1a-j**).[6] The chemical shift of the methyl group in **1** was carefully monitored as the substituent **X** was varied over a broad range of electronic effects.



1a: X = H
1b: X = *p*-CH_3
1c: X = *p*-OCH_3
1d: X = *p*-F
1e: X = *o*-F
1f: X = *p*-Cl
1g: X = *p*-NH_2
1h: X = *p*-CN
1i: X = *p*-CHO
1j: X = *p*-NO_2

We concluded that although the perturbation of the chemical shift of the methyl signal was quite small in **1**, a trend could still be discerned. In the ^{1}H NMR, the methyl signal was slightly upfield when **X** was an electron-withdrawing compared to when **X** was electron donating. We hypothesized that the electron withdrawing group reduced the electron density on the phenyl ring which led to slight polarization of the C-H bonds of the methyl group so that the hydrogens were

somewhat shielded (Figure 1a). An electron donating group, on the other hand, would have just the opposite effect (Figure 1b). Our computational studies were consistent with the experimental observations.[6]

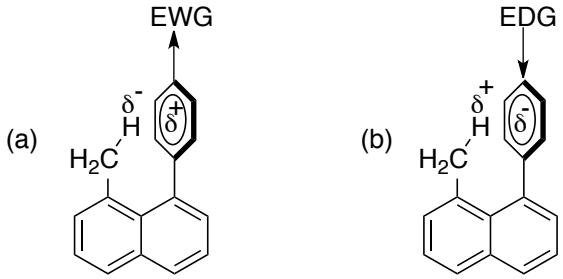


Figure 1. Proposed polarization of methyl C-H bonds in **1** dependent on the nature of the substituent X.[6]

The notion of polarization discussed above, and pictorially depicted in Figure 1, finds analogy in a computational report that examined the shielding of the proximal hydrogen of H_2 located above the face of a benzene ring complexed with a metal (alkali or alkaline) cation on the other face (Figure 2).[7] That work suggested that complexation of the benzene ring with a metal cation had a substantial synergistic influence on shielding in that "…the decreased π electron density on the side of the complexed benzene ring opposite the cation polarizes the covalent bond of diatomic hydrogen, increasing the electron density near the proximal hydrogen, with the consequence that the proximal hydrogen becomes more shielded."[7]

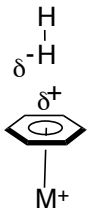
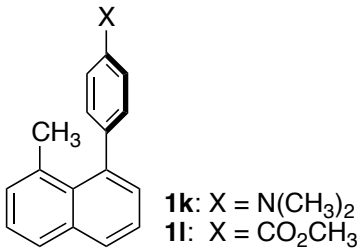


Figure 2. The cation-π complex is calculated to cause polarization of H_2 leading to enhanced shielding of the hydrogen proximal to the ring.[7]

The consequences of complexing an aromatic ring with a metal containing fragment, however, remain a controversial subject especially with respect to the question of aromaticity. The pronounced change in reactivity between aromatic compounds and their corresponding transition metal complexes (e.g. $Cr(CO)_3$, $Mn(CO)_3^+$, $RuCp^+$ systems) is well established, in which the metal dramatically facilitates the addition of nucleophiles to the aromatic ring.[8] The significant upfield shifts in the ^1H and ^{13}C NMR of nuclei bonded to the aromatic ring upon complexation of the metal has led some to propose that aromaticity is reduced in the complexed compounds.[9] In examining cyclophanes and other compounds where there are protons in the shielding region of the aromatic system, complexation usually leads to a downfield shift of those protons in the complexed compounds relative to the corresponding uncomplexed compounds, suggesting that the ring current is attenuated by complexation.[10] Many computational studies have suggested that aromaticity is diminished with coordination with a transition metal, with one going so far as to suggest that the aromatic ring becomes antiaromatic in η^6-$C_6H_6Cr(CO)_3$.[11] Other studies, both experimental and computational, however, have argued that aromaticity is either unchanged[12] or increased with complexation.[13]

In light of the foregoing reports, we considered transition metal complexes of **1** as new probe systems to experimentally investigate the effects of complexation, and the influence of substituents, on shielding by the phenyl ring. Accordingly, we synthesized eight compounds (Figure 3) where the metal is complexed to the phenyl ring on the side opposite to that facing the naphthyl methyl group. Six of these complexes are formally derived from the precursors **1a-d** and the remaining two were obtained from new compounds **1k** and **1l**. Herein we report on the chemical shift perturbations of the methyl signal and other pertinent physical properties in these complexes.



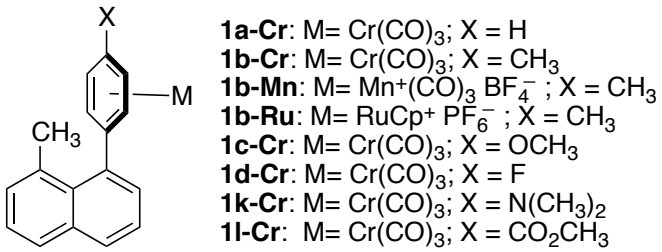
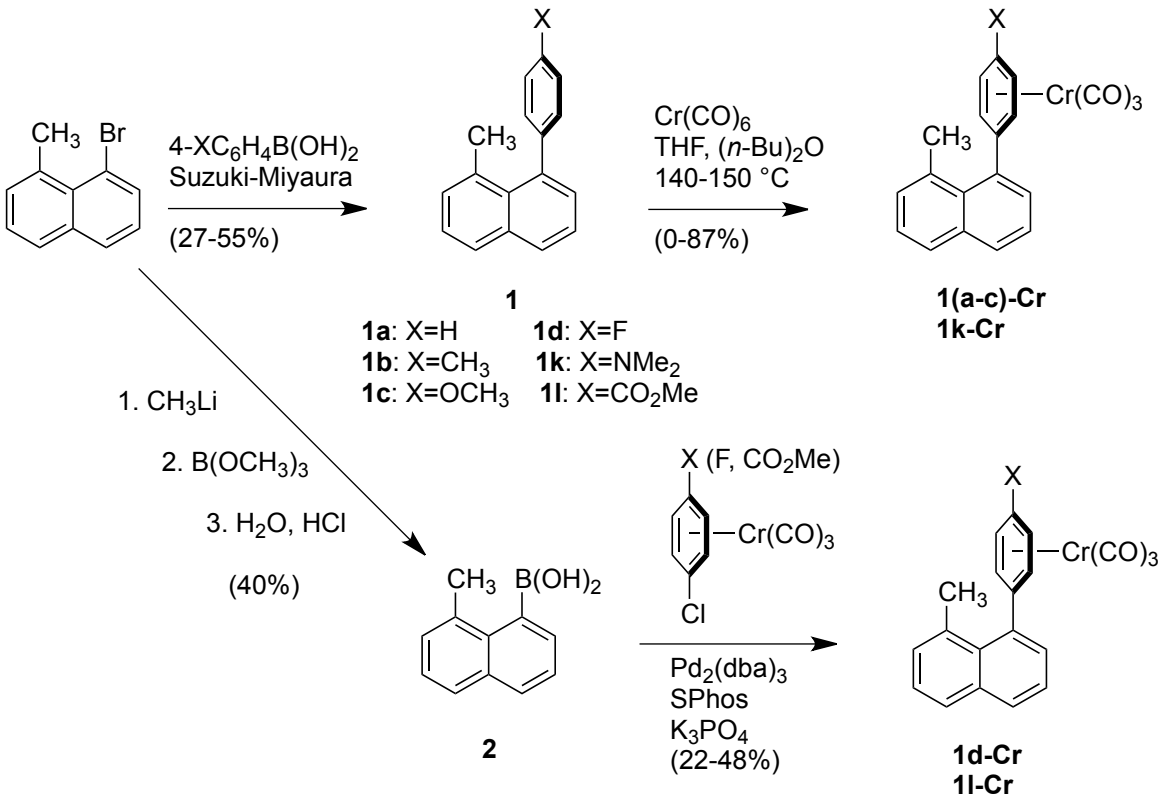


Figure 3. The eight metal complexes of compounds **1(a-d,k,l)-Cr**, **1b-Mn**, and **1b-Ru** employed in this study.

Results and Discussion

Syntheses of η⁶-arene complexes: The syntheses of **1a-d** using the Suzuki–Miyaura reaction have been previously described[6] and new compounds **1k** and **1l** were prepared in an analogous manner (Scheme 1). The direct complexation of the aryl ring of **1(a-c)** and **1k** by chromium using classical conditions[8a] for the coordination of aromatic rings by the $Cr(CO)_3$ moiety ($Cr(CO)_6$, $O(n\text{-}Bu)_2$, THF, 140-150 °C; Scheme 1) gave chromium complexes **1(a-c)-Cr** and **1k-Cr** (20-87% yield). Complexes **1(a-c)-Cr** and **1k-Cr** were readily purified, removing variable amounts of side products tentatively identified as the chromium complexes resulting from the complexation of the naphthyl ring. The very poor yields for the direct complexation of the electron-poor aromatic rings of **1d** and **1l** by the $Cr(CO)_3$ moiety necessitated an alternative approach to the synthesis of **1d-Cr** and **1l-Cr**. Several studies have shown the very high reactivity of η^6-chloroarylchromium complexes (much higher than the corresponding uncomplexed chloroarene compounds) with arylboronic acids using the Suzuki–Miyaura reaction.[14] The required boronic acid **2** was prepared by lithium-halogen exchange of 1-bromo-8-methylnaphthalene with methyllithium, followed by trimethyl borate and hydrolysis of the intermediate boronic ester (40% yield). The Suzuki–Miyaura coupling of **2** with η^6-(4-

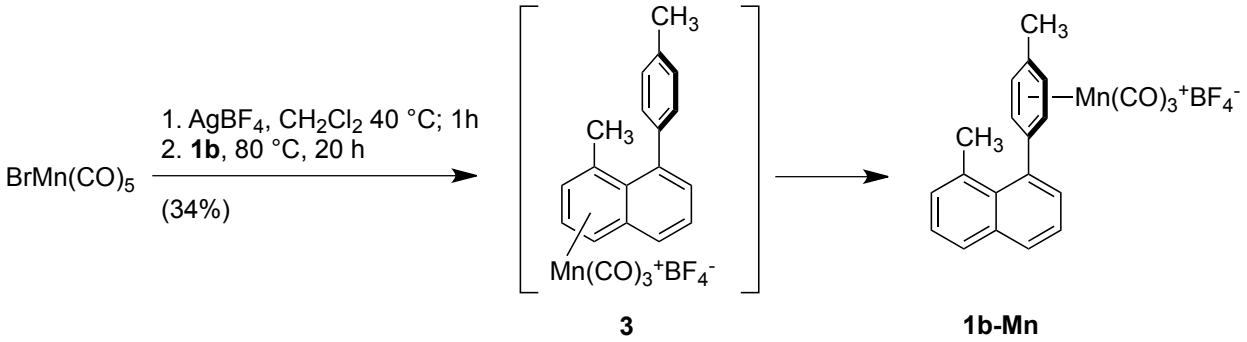
$XC_6H_4Cl)Cr(CO)_3$ complexes (X=F, CO_2CH_3)[15] gave the desired chromium complexes **1d-Cr** and **1l-Cr** in 22% and 48% yield, respectively.



Scheme 1. Synthesis of **1(a-d,k,l)** and their chromium complexes.

In our initial attempts to synthesize manganese arene complex **1b-Mn** under standard conditions ($BrMn(CO)_5$, $AgBF_4$, CH_2Cl_2, 1h, 40 °C; **1b**, 4h, 40 °C)[16] a yellow air-sensitive solid was isolated that was difficult to characterize or purify. The ^1H NMR in CD_2Cl_2 gave broad signals that pointed to the coordination of the naphthalene ring to give complex **3**. When the ^1H NMR was conducted in CD_3CN or $(CD_3)_2CO$, the only signals observed were for the uncomplexed **1b**.[17] Suspecting that under these conditions we were observing the kinetic product(s), **3** was dissolved in $ClCH_2CH_2Cl$, additional **1b** was added, and reaction mixture was heated to 80 °C for 20 h. The ^1H NMR of the resulting product was consistent with the structure

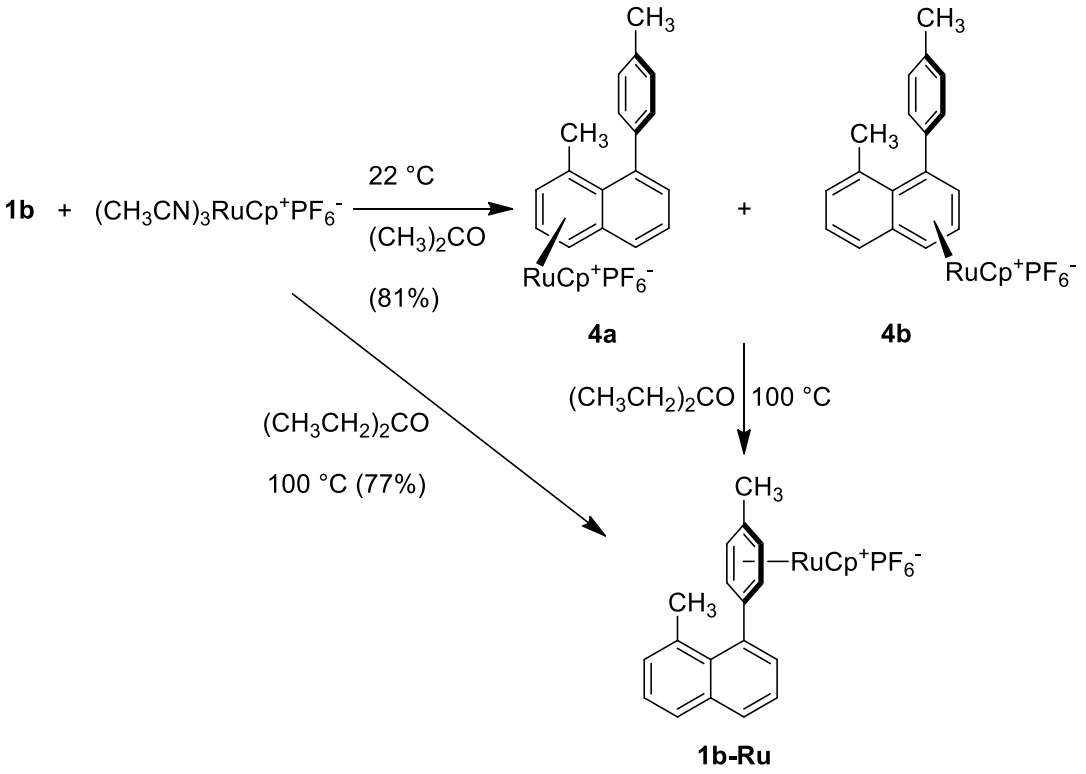
of the desired complex **1b-Mn**. Based on these observations, a simple one-pot reaction ($BrMn(CO)_5$, $AgBF_4$, $ClCH_2CH_2Cl$, 1h, 40 °C; **1b**, 20h, 80 °C) was developed (Scheme 2) to give **1b-Mn** in 34% yield.



Scheme 2. Synthesis of **1b-Mn**.

In contrast to the difficulty in isolating the kinetic product of the complexation of **1b** by $Mn(CO)_3^+$, the η^6-naphthalene complexes **4a** and **4b** formed by the complexation of **1b** by $RuCp(CH_3CN)_3PF_6$[18] were easily isolated and identified (Scheme 3). These complexes, which rapidly formed as a 2:1 mixture in acetone, exhibited clear evidence of coordination by the naphthalene ring, with signals at δ 6.25 (t) and 6.10 (d) for **4a** and at δ 6.35 (t) and 6.01 (d) for **4b**. Further purification of the major product by recrystallization allowed the conclusive assignment of the major product as **4a**, the result of coordination of the methyl-substituted ring of the naphthyl moiety. In addition to the downfield shift exhibited by the C8 methyl group (δ = 2.09) relative to the parent compound **1b** (δ = 2.02), an NOE experiment showed the close proximity of the C-7 proton at δ 6.10 with the methyl group of the coordinated naphthyl ring at δ 2.09. Further, the non-equivalency of the protons on the 4-methylphenyl ring strongly suggests that there is restricted rotation about the C1/aryl bond. As in the case of manganese arene complex **1b-Mn**, the synthesis of the ruthenium arene complex **1b-Ru** required more forcing conditions (Scheme 3). The thermodynamic product **1b-Ru** was formed under refluxing

conditions in 3-pentanone (but not in 1,2-dichloroethane) in 77% yield. These results are very similar to Mann's studies[19] for the complexation of rubrene (5,6,11,12-tetraphenyltetracene) by $RuCp^+$, in which there was rapid complexation by the polyaromatic tetracene ring at room temperature (kinetic product), with longer reaction times and higher temperatures leading to complexation by one of the phenyl rings (thermodynamic product).



Scheme 3. Synthesis of **4a**, **4b**, and **1b-Ru**.

IR Spectroscopy: The IR stretches for the carbonyl ligands of transition metal arene complexes have been correlated with the electron donating and withdrawing ability of substituents on the coordinated arene ring.[20] There are very clear trends for the $(CO)_3Cr$(arene) series, with electron-donating substituents leading to lower energy bands and electron-withdrawing substituents leading to higher energy bands for the CO ligand stretches (Table 1). Complexes **1(a-d)-Cr** and **1(k,l)-Cr** exhibited comparable trends, with electron-donating substituents (as in **1(b,c)-Cr** and

1k-Cr) on the arene ring leading to lower energy bands for the CO ligand stretch and electron-withdrawing substituents (as in **1d-Cr** and **1l-Cr**) leading to higher energy bands for the CO ligand stretch relative to the parent complex **1a-Cr** (Table 1).

Table 1. IR stretches for the carbonyl ligands of **1(a-d,k,l)-Cr** and η^6-$(XC_6H_5)Cr(CO)_3$ complexes.[a]

Substituent on phenyl[b]	Compound	CO stretches (cm^{-1})	Change from **1a-Cr** (cm^{-1})[c]	Compound	CO stretches (cm^{-1})[d]	Change from $C_6H_6Cr(CO)_3$ (cm^{-1})[e]
H	**1a-Cr**	1969, 1892	0	$\mathbf{C_6H_6Cr(CO)_3}$	1974, 1894	0
CH_3	**1b-Cr**	1965, 1887	-4, -5	$\mathbf{CH_3C_6H_5Cr(CO)_3}$	1969, 1889	-5, -5
OCH_3	**1c-Cr**	1966, 1886	-3, -6	$\mathbf{CH_3OC_6H_5Cr(CO)_3}$	1973, 1891	-1, -3
F	**1d-Cr**	1978, 1904	9, 12	$\mathbf{FC_6H_5Cr(CO)_3}$	1982, 1903	8, 9
$N(CH_3)_2$	**1k-Cr**	1953, 1870	-16, -22	$\mathbf{(CH_3)_2NC_6H_5Cr(CO)_3}$	1956, 1868	-18, -26
CO_2CH_3	**1l-Cr**	1978, 1908	9, 16	$\mathbf{CH_3CO_2C_6H_5Cr(CO)_3}$	1985, 1911	11, 17

[a] Recorded in CH_2Cl_2; [b] For Cr-complexes of the **1** series, these refer to X in Figure 3; [c] Complex minus **1a-Cr**; [d] From reference 20; [e] Complex minus $\mathbf{C_6H_6Cr(CO)_3}$.

^{13}C NMR Spectroscopy: In a similar manner, the ^{13}C NMR shifts of the carbonyl ligand of η^6-arene complexes **1**-Cr have been correlated to the electron-donating and withdrawing ability of substituents of the coordinated arene ring.[20] In a series of η^6-$(XC_6H_5)Cr(CO)_3$ complexes, the ^{13}C NMR resonance of the carbon of the carbonyl ligand for the more electron-donating substituents on the arene ring led to a downfield shift, while the more electron-withdrawing substituents on the arene ring led to an upfield shift relative to the parent complex, $C_6H_6Cr(CO)_3$ (Table 2). These results were rationalized in terms of the degree of back donation of the chromium to the carbonyl ligand. A similar trend was observed for complexes **1(b,c,k)-Cr**, with the electron-donating substituents (X = CH_3, OCH_3, $N(CH_3)_2$) on the arene ring leading to downfield shifts of

the carbonyl ligand with respect to the unsubstituted complex **1a-Cr**, while the complexes 1(d,l)-Cr with electron-withdrawing substituents (X=F, CO_2Me) on the arene ring led to upfield shifts of the carbonyl ligand with respect to **1a-Cr** (Table 2).

Table 2. ^{13}C chemical shifts for the carbonyl ligands of **1-Cr** and η^6-(4-XC_6H_5)$Cr(CO)_3$ Complexes.

Substituent on phenyl[a]	Compound	^{13}C shift for CO (ppm)[b]	Change from **1a-Cr** (ppm)[c]	Compound	^{13}C shift for CO (ppm)[d]	Change from $C_6H_6Cr(CO)_3$ (ppm)[e]
H	**1a-Cr**	233.36	0	**$C_6H_6Cr(CO)_3$**	234.00	0
CH_3	**1b-Cr**	233.74	0.38	**$CH_3C_6H_5Cr(CO)_3$**	234.29	0.29
OCH_3	**1c-Cr**	233.58	0.22	**$CH_3OC_6H_5Cr(CO)_3$**	234.25	0.25
F	**1d-Cr**	232.16	-1.20	**$FC_6H_5Cr(CO)_3$**	232.98	-1.02
$N(CH_3)_2$	**1k-Cr**	235.01	1.65	**$(CH_3)_2NC_6H_5Cr(CO)_3$**	235.52	1.52
CO_2CH_3	**1l-Cr**	231.98	-1.38	**$CH_3CO_2C_6H_5Cr(CO)_3$**	231.98	-2.02

[a]For Cr-complexes of the **1** series, these refer to X in Figure 3; [b] Recorded in CD_2Cl_2; [c] Complex minus **1a-Cr**; [d] From reference 20; [e] Complex minus **$C_6H_6Cr(CO)_3$.**

X-ray crystallographic studies: Single-crystal X-ray diffraction experiments were performed on all eight complexes and their structures are shown in Figure **4**. Of the formally uncomplexed precursors **1**, the structure of **1a**, which is a liquid at ambient temperature, was not determined while those of **1b-d** have been previously published by us[6] and are not shown here. The amine **1k** and ester **1l** are new, however, and their structures are shown in Figure **5**.

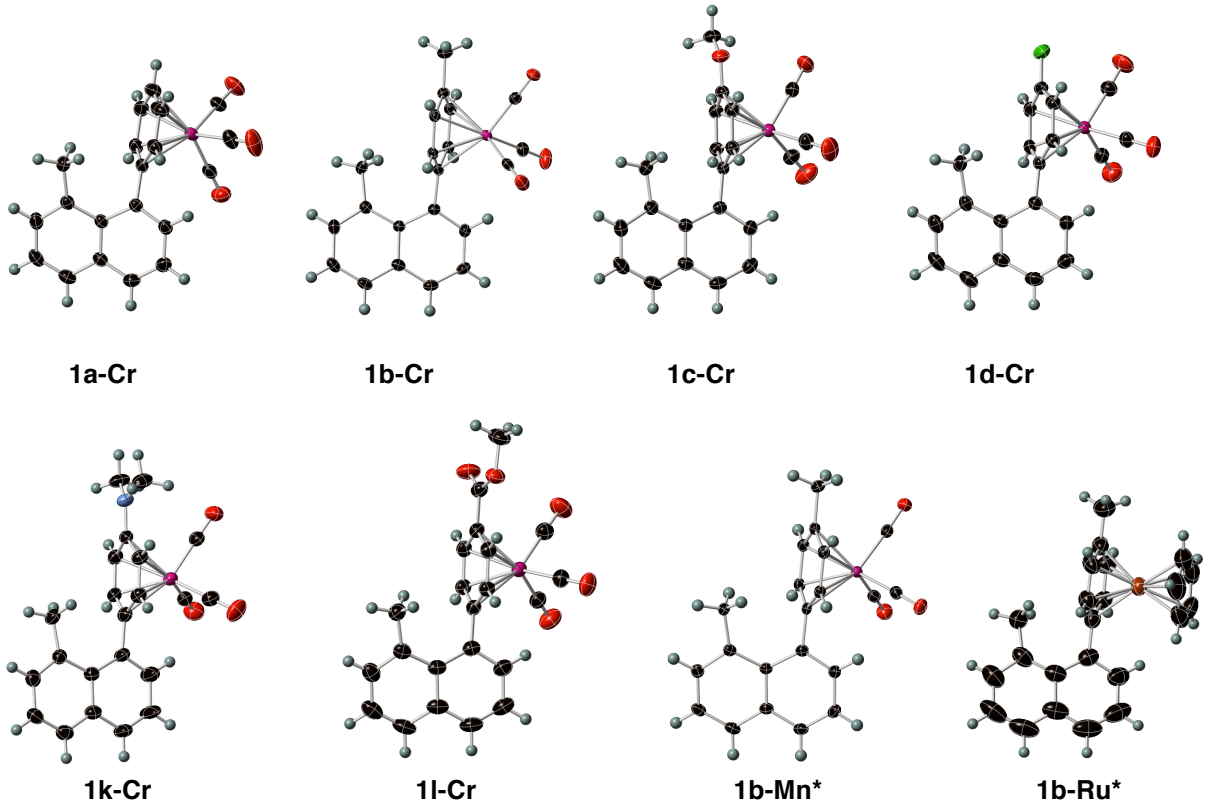


Figure 4. Single-crystal x-ray structures of **1(a-d)-Cr** (top) and **1(k,l)-Cr, 1b-Mn, and 1b-Ru** (bottom). Thermal ellipsoids are displayed at a 50% probability level. *For clarity, counter anions are not shown.

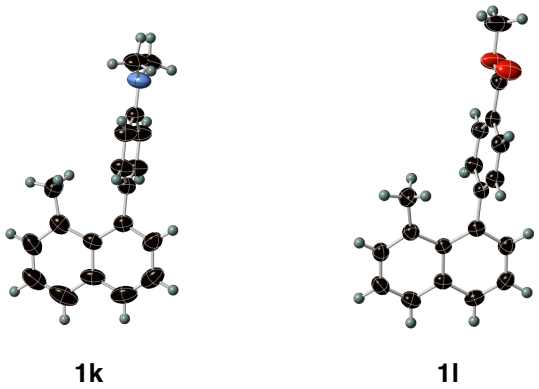
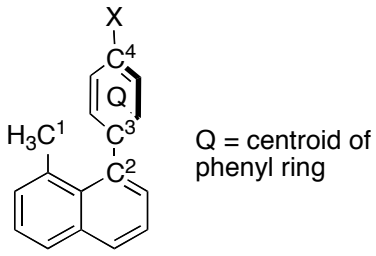


Figure 5. Single-crystal x-ray structures of **1k** and **1l.** Thermal ellipsoids are displayed at a 50% probability level.

The salient crystal structure data for the uncomplexed compounds **1(b-d**, **k**, and **l)** and their metal complexes are collected in Table 3. These data indicate that, in the solid state, the

phenyl ring is substantially twisted away from the naphthyl ring. Furthermore, the length of the carbon-carbon bond connecting the phenyl ring to the naphthyl ring, which is comparable to the corresponding bonds in 1,8-diarylnaphthalenes,[21] does not indicate any kind of conjugation between the two ring systems. Consistent with previous observations on related systems,[9a,b,22] the average length of the carbon-carbon bonds of the phenyl ring increases in the complexes but there is no indication of any length alternation among them. In any case, these changes increase the perimeter and surface area of the phenyl ring in the complexes with implications for reduced electron density. Two other interesting geometric distortions are also revealed by the X-ray structures. The first is that the distance between the naphthyl methyl group and the centroid of the phenyl ring appears to decrease slightly upon complexation. This is evident by comparing **1(b-d, k, l)** to their corresponding metal complexes. This observation is particularly significant in the context of comparing the ^{1}H NMR signals displayed by the naphthyl methyl groups in the complexed and uncomplexed compounds (*vide infra*). Second, phenyl rings bearing strong π donors show an appreciable deviation from planarity in their chromium complexes as can be seen from the structures of **1c-Cr**, **1d-Cr**, and **1k-Cr**. In these instances, the phenyl ring is slightly bowl-shaped with the convex face closer to the metal. Similar observations have been reported for the η^6-chromium tricarbonyl complexes of substituted benzenes.[23]

Table 3. Selected crystallographic data for the metal complexes and some of their metal-free precursors. Refer to structure below for parameters used in the table.



Compound	*Phenyl-naphthyl interplanar angle*	*Length of C2-C3 bond*	*Average C-C bond length of phenyl ring*	*C^1 to Q distance*	C^3-Q-C^4 angle
1a-Cr[a]	66.11°	1.50 Å	1.41 Å	3.44 Å	178.64°
1b[b]	89.40°	1.50 Å	1.38 Å	3.53 Å	179.86°
1b-Cr[a]	77.06°	1.49 Å	1.41 Å	3.34 Å	178.91°
1b-Mn[a]	66.96°	1.50 Å	1.41 Å	3.40 Å	177.88°
1b-Ru[a]	77.09°	1.51 Å	1.41 Å	3.40 Å	178.72°
1c[b]	69.08°	1.49 Å	1.39 Å	3.51 Å	179.56°
1c-Cr[a]	79.87°	1.50 Å	1.41 Å	3.26 Å	176.51°
1d[b]	67.78°	1.49 Å	1.38 Å	3.50 Å	179.51°
1d-Cr[a]	62.45°	1.49 Å	1.41 Å	3.35 Å	177.19°
1k[a]	82.66°	1.49 Å	1.39 Å	3.42 Å	179.67°
1k-Cr[a]	85.10°	1.50 Å	1.41 Å	3.34 Å	176.58°
1l[a]	81.86°	1.50 Å	1.39 Å	3.49 Å	179.62°
1l-Cr[a]	74.54°	1.50 Å	1.41 Å	3.38 Å	179.14°

a) This work. b) From reference 6.

^{1}H NMR Spectroscopy: All ^{1}H NMR spectra of **1** and, **1(a-d,k,l)-Cr**, **1b-Mn**, and **1b-Ru** were recorded in CD_2Cl_2 at 400 MHz. The methyl signal for 1-methylnaphthalene appears at δ 2.691, with a significant upfield shift with the introduction of the phenyl ring (complexed or uncomplexed) at the 8-position (Table 4). The chemical shifts for the methyl protons of **1** in CD_2Cl_2 follow the same trends observed in the previous study in $CDCl_3$,[6] in which there is a small but significant downfield shift for the more electron-rich substituents relative to X = H. In the case of **1l**, bearing an electron withdrawing ester group, the upfield shift is negligibly small compared to what we have previously noticed for other much stronger electron withdrawing groups.[6] For the chemical shifts of the methyl protons of the chromium arene complexes **1(a-d,k,l)-Cr**, there were two distinct trends: there was a significant downfield shift upon complexation of the phenyl ring (~0.25 ppm) and a smaller downfield shift associated with the more electron-rich substituents on **1(c,k)-Cr** relative to **1a-Cr**. The ^{1}H NMR of naphthyl methyl group of the η^6-manganese complex **1b-Mn** exhibited a downfield shift relative to **1b** (2.20 vs. 2.02 ppm) and was upfield relative the analogous chromium complex **1b-Cr** (2.20 vs. 2.26 ppm). Complexes **1b-Mn** and **1b-Cr** are isoelectronic but complex **1b-Mn** is cationic while **1b-Cr** is

neutral. The ^{1}H NMR of naphthyl methyl group of the cationic η^6-ruthenium complex **1b-Ru** was also downfield relative to **1b** (2.10 vs. 2.02 ppm) but not as much as either **1b-Cr** and **1b-Mn**.

Table 4. ^{1}H Chemical Shift Data for the Naphthyl Methyl Signal for **1 (a-d,k,l) and 1(a-d,k,l)-Cr** in CD_2Cl_2.

Substituent on phenyl[a]	Compound	Naphthyl CH_3 (ppm)	Change from **1a** (ppm)[b]	Compound	Naphthyl CH_3 (ppm)	Change from **1a-Cr** (ppm)[c]	Change from precursor (ppm)[d]
H	**1a**	**1.996**	**0**	**1a-Cr**	**2.265**	**0**	**0.269**
CH_3	**1b**	**2.017**	**0.021**	**1b-Cr**	**2.264**	**-0.001**	**0.247**
OCH_3	**1c**	**2.030**	**0.034**	**1c-Cr**	**2.283**	**0.018**	**0.253**
F	**1d**	**2.009**	**0.013**	**1d-Cr**	**2.263**	**-0.002**	**0.254**
$N(CH_3)_2$	**1k**	**2.073**	**0.077**	**1k-Cr**	**2.345**	**0.080**	**0.272**
CO_2CH_3	**1l**	**1.994**	**-0.002**	**1l-Cr**	**2.258**	**-0.006**	**0.264**

[a] For the **1** series, these refer to X in Figure 3; [b] Compound minus **1a**; [e] Complex minus **1a-Cr$_3$;** [d] Complex minus corresponding uncomplexed precursor in second column.

Computational Results: Structures of the complexes and their metal-free precursors were modeled using hybrid density functional methods such as B3LYP[24] and M06[25] using several basis sets as shown in Table 5. Although the chromium complexes could be,[22a] and were, fully modeled using the 6-311G (2d,p) basis set, the LANL2DZ (Los Alamos National Laboratory 2-double zeta) basis set, with relativistic effective core potentials (recp) implemented on the transition metals,[26] were also used to model all of the complexes. Where possible, the available crystal structures were used as the starting point for geometry optimizations.

The calculations are in general agreement with the observed trends. Critical structural parameters such as the C2-C3 bond length (see reference figure in Table 5), the increase in average C-C bond length of the phenyl ring upon complexation, the C1 to Q distance, and even the deviation from planarity of complexes containing π-donor substituents on the phenyl ring are reproduced closely. Only in one case (M06/6-311G(d,p), LANL2DZ) was a minor discrepancy

observed in the C1 to Q distance of the charged complexes **1b-Mn** and **1b-Ru** relative to the uncomplexed precursor **1b**.

Table 5. Selected computational data for the metal complexes and their metal-free precursors. Refer to structure in Table 3 for parameters used in this table.

Compound	*Model Chemistry*	*Phenyl-naphthyl interplanar angle*	*Length of C2-C3 bond*	*Average C-C bond length of phenyl ring*	*C^1 to Q distance*	C^3-Q-C^4 angle
1a	A	74.22°	1.50 Å	1.39 Å	3.55 Å	179.56°
	B	73.88°	1.50 Å	1.40 Å	3.55 Å	179.55°
	C	69.42°	1.48 Å	1.39 Å	3.46 Å	179.23°
1a-Cr	A	88.54°	1.50 Å	1.41 Å	3.39 Å	178.24°
	B(recp)	84.96°	1.50 Å	1.41 Å	3.38 Å	178.82°
	C(recp)	85.48°	1.49 Å	1.41 Å	3.33 Å	179.18°
1b	A	73.30°	1.50 Å	1.39 Å	3.55 Å	179.67°
	B	72.87°	1.50 Å	1.40 Å	3.55 Å	179.64°
	C	69.55°	1.48 Å	1.39 Å	3.45 Å	179.28°
1b-Cr	A	78.90°	1.50 Å	1.41 Å	3.39 Å	178.23°
	B(recp)	76.66°	1.50 Å	1.41 Å	3.40 Å	178.51°
	C(recp)	67.37°	1.49 Å	1.41 Å	3.39 Å	179.16°
1b-Mn	B(recp)	55.51°	1.49 Å	1.41 Å	3.53 Å	177.64°
	C(recp)	56.90°	1.48 Å	1.41 Å	3.47 Å	178.35°
1b-Ru	B(recp)	58.48°	1.49 Å	1.42 Å	3.51 Å	178.00°
	C(recp)	60.48°	1.48 Å	1.42 Å	3.45 Å	178.71°
1c	A	72.46°	1.49 Å	1.39 Å	3.55 Å	179.54°
	B	72.15°	1.50 Å	1.40 Å	3.55 Å	179.52°
	C	69.55°	1.49 Å	1.39 Å	3.45 Å	179.28°
1c-Cr	A	82.37°	1.50 Å	1.41 Å	3.38 Å	176.77°
	B(recp)	80.72°	1.50 Å	1.41 Å	3.38 Å	176.93°
	C(recp)	73.63°	1.49 Å	1.41 Å	3.36 Å	177.60°
1d	A	73.47°	1.50 Å	1.39 Å	3.55 Å	179.56°
	B	73.21°	1.50 Å	1.39 Å	3.55 Å	179.54°
	C	69.32°	1.48 Å	1.39 Å	3.45 Å	179.26°
1d-Cr	A	89.18°	1.50 Å	1.41 Å	3.37 Å	177.57°
	B(recp)	90.00°	1.50 Å	1.41 Å	3.37 Å	177.81°
	C(recp)	76.88°	1.49 Å	1.41 Å	3.33 Å	178.16°
1k	A	71.59°	1.49 Å	1.40 Å	3.56 Å	179.08°
	B	71.32°	1.49 Å	1.40 Å	3.56 Å	179.05°
	C	67.87°	1.48 Å	1.39 Å	3.48 Å	179.02°
1k-Cr	A	89.89°	1.50 Å	1.42 Å	3.36 Å	175.50°
	B(recp)	89.88°	1.50 Å	1.42 Å	3.36 Å	175.51°
	C(recp)	89.17°	1.49 Å	1.41 Å	3.31 Å	175.89°
1l	A	71.34°	1.50 Å	1.39 Å	3.56 Å	179.60°
	B	71.08°	1.50 Å	1.40 Å	3.56 Å	179.58°
	C	68.05°	1.48 Å	1.39 Å	3.51 Å	179.47°
1l-Cr	A	62.85°	1.50 Å	1.41 Å	3.46 Å	178.32°
	B(recp)	62.58°	1.50 Å	1.41 Å	3.46 Å	178.66°
	C(recp)	63.85°	1.49 Å	1.41 Å	3.41 Å	179.51°

A = B3LYP/6-311G(2d,p); B = B3LYP/6-311G(d,p); B(recp) = B3LYP/6-311G(d,p), LANL2DZ (transition metals); C = M06/6-311G(d,p); C(recp) = M06/6-311G(d,p), LANL2DZ (transition metals).

All of the chromium complexes and their uncomplexed precursors, which were optimized at the same B3LYP/6-311G(2d,p) level of theory, were then subjected to an NMR calculation using Cramer's WP04 functional[27] with cc-pVDZ as per the procedure of Bally and Rablen.[28] These calculations simulated dichloromethane as the solvent medium for comparison with experimental data. In particular, the chemical shifts of the three hydrogens of the naphthyl methyl group were averaged and compared to the chemical shift of TMS which was also computed in dichloromethane at the same level of theory. The differences between the computed chemical shifts of the naphthyl methyl group in the complexed and uncomplexed pairs of compounds are shown in Table 6. These results are consistent with the experimental observation that complexation of **1a-d, k, l** with **the** chromium tricarbonyl moiety causes a slight downfield shift in the methyl signal.

Table 6. Differences in the computed and experimentally observed chemical shifts of the naphthyl methyl group for the chromium complexes and their uncomplexed precursors.

Compound pairs	δCH_3 complex - δCH_3 precursor (Calculated at GIAO/WP04/cc-pVDZ)	δCH_3 complex - δCH_3 precursor (Experimental)
1a and **1a-Cr**	+ 0.07 ppm	+ 0.27 ppm
1b and **1b-Cr**	+ 0.07 ppm	+ 0.25 ppm
1c and **1c-Cr**	+ 0.05 ppm	+ 0.25 ppm
1d and **1d-Cr**	+ 0.05 ppm	+ 0.25 ppm
1k and **1k-Cr**	+ 0.06 ppm	+ 0.27 ppm
1l and **1l-Cr**	+ 0.10 ppm	+ 0.26 ppm

As can be discerned from the foregoing description, the various spectroscopic and structural data for the chromium complexes in this study are comparable to the corresponding data for typical η^6-*(arene)Cr(CO)$_3$*. The substituents on the phenyl ring of **1(a-d,k,l)-Cr** affect the CO ligands in the same way as typical η^6-*(arene)Cr(CO)$_3$* complexes, as demonstrated by the lower energy stretches and downfield ^{13}C shifts of the carbonyl ligand observed for the more electron-donating substituents. Similarly, X-ray structures indicate that deformations of the phenyl ring in **1(a-d,k,l)-Cr**, such as elongation of the carbon-carbon bonds and deviation from planarity, are also comparable to those observed for other η^6-*(arene)Cr(CO)$_3$*. Further, the structural descriptors are closely aligned with the results of computational studies.

In considering the consequences for the proton chemical shift of the naphthyl methyl group upon coordination of the metal on the opposite face of the phenyl ring, two factors favor the upfield shift of the methyl group: the well documented[8] electron-withdrawing nature of the $Cr(CO)_3$ moiety and the shortening of the distance between the centroid of the phenyl ring and the methyl group. The previous study[6] showed a small but distinct trend for the more electron-withdrawing groups on the uncoordinated phenyl ring to affect an upfield shift, perhaps through the polarization of the CH bonds of the methyl group. The crystallographic data of the complexes **1(a-d,k,l)-Cr**, however, show the methyl group deeper in the shielding zone of the phenyl ring than in the corresponding uncomplexed compounds **1(a-d,k,l)**. Yet, the chemical shift of the naphthyl methyl group in **1(a-d,k,l)** moves 0.25-0.27 ppm downfield upon complexation with $Cr(CO)_3$. As can be seen from Table 6, this trend is consistent with NMR calculations using modern methods and basis sets.

An early report, from 1978, seemed to indicate that the chemical shift of the protons in the shielding zone of the phenyl ring show a very slight *upfield* shift (0.05 ppm) upon complexing

the ring with $Cr(CO)_3$.[29] Several subsequent studies that focused on $Cr(CO)_3$ complexes of various cyclophanes, however, showed that just the opposite was true. In these cyclophane complexes, the protons in the shielding zone of the phenyl ring move *downfield* upon complexation.[30] Our results are also in line with the observations for such cyclophane systems.

Although the theoretical work of Schleyer, Sorenson, and coworkers has argued against such a notion,[12] several investigators have been inclined to attribute the downfield shift of the protons in the shielding zone of the $Cr(CO)_3$ complexes to an "attenuation" of aromaticity in the phenyl ring upon complexation.[9a,30a] The structural distortions that we have noted above for **1(a-d,k,l)-Cr**, evident from experiment and theory, also appear to support the idea of reduced aromaticity in the complexed phenyl ring. The lengthening of the carbon-carbon bonds of the phenyl ring in **1(a-d,k,l)-Cr** likely has a slight detrimental effect on conjugation. In addition, the increased surface area of the phenyl ring in these complexes and the electron withdrawing effect of the metal moiety also contributes to a slightly diminished π electron density of the phenyl ring.

The naphthyl methyl signal in the cationic complexes **1b-Mn** and **1b-Ru**, are also slightly downfield compared to the uncomplexed **1b** but, as already mentioned, the shift is not as pronounced as in **1b-Cr**. In this regard, it is noteworthy that the distance of the methyl carbon from the phenyl centroid in **1b-Cr** is shorter than the corresponding distances in **1b-Mn** and **1b-Ru**. Similar downfield shifts of protons in the shielding zone of phenyl rings of [10]-cyclophanes complexed with cationic Mn and Ru moieties have been also noted by Kreindlin et al.[31]

Conclusions: In this study, a series of naphthalene compounds in which a metal-complexed phenyl ring, bearing various substituents, is located in a 1,8-relationship to a methyl group have been synthesized. The through-space shielding effects of the phenyl ring, as a function of substituent and complexing metal species, were monitored by observing the ^{1}H NMR chemical

shift of the methyl group whose protons are pointed toward the face of the ring. In all cases, it was observed that the chemical shift of the methyl signal was slightly more downfield in the metal complexes than in the uncomplexed analogs. Furthermore, the effect of the metal fragment on the methyl signal appears to be much more pronounced compared to that of just the phenyl substituent in the uncomplexed analogs. X-ray structures of the complexes reveal a slight decrease in the distance between the naphthyl methyl group and the centroid of the phenyl ring upon complexation. There is, however, a significant elongation of the average bond lengths of the carbon-carbon bonds of the phenyl ring as compared to the formally uncomplexed precursors. The structural features determined experimentally, and the trends in the observed chemical shifts of the naphthyl methyl signal, are also consistent with DFT calculations. To the extent that shielding effects - as evaluated by NMR chemical shifts - diagnose the strength of ring current in aromatic compounds, the findings reported herein indicate an attenuation of that current in phenyl rings upon complexation with metals. The electron withdrawing effect of the metal fragment, along with an increase in the perimeter and surface area of the phenyl ring, have implications for the slightly diminished shielding of the naphthyl methyl group in the complexes.

Experimental Section

General Experimental Procedures. All reactions were carried out under Ar. All glassware was dried in the oven (110 °C) before use. IR spectra were obtained on a FT-IR using NaCl liquid cells.. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, in the indicated solvents. All chemicals shifts in the ^{1}H NMR are reported in ppm relative to TMS (δ = 0.00 ppm) and in the ^{13}C NMR are reported in ppm relative to $CDCl_3$ (δ=77.16 ppm), CD_2Cl_2 (δ=53.84 ppm), $(CD_3)_2CO$ (δ=29.84 ppm for the methyl carbon), or TMS

(δ=0.00 ppm). For the ^{1}H NMR spectra of **1(a-d,k,l)**, **1(a-d,k,l)-Cr**, **1b-Mn** and **1b-Ru**, the concentration of the compounds was 0.01-0.03 M. Flash chromatography was performed on 60 Å silica gel (40-75 μm). Anhydrous dibutyl ether, diethyl ether and THF were used without further purification. Methylene chloride was dried over powdered 4 Å molecular sieves. High resolution mass spectra were obtained on a Direct Analysis in Real Time - Time-Of-Flight (DART-TOF) mass spectrometer.

1-Bromo-8-methylnaphthalene. To a solution of 1,8-dibromonaphthalene (11.44 g, 40 mmol) in THF (200 mL) was added CH_3Li (26 mL, 42 mmol; 1.6 M in Et_2O) at 0° C over 7 min. After stirring for an additional 30 min at 0° C, CH_3I (10.0 mL, 22.8 g, 161 mmol) was added dropwise. The reaction mixture was allowed to warm to 22° C and stirred for an additional 3 h. The reaction mixture was quenched with brine (100 mL), the organic phase separated and dried over Na_2SO_4, and concentrated on the rotary evaporator. Column chromatography (silica gel; petroleum ether) gave 1-bromo-8-methylnaphthalene (6.85 g) in greater than 90% purity. Further purification by recrystallization from IPA gave 1-bromo-8-methylnaphthalene (5.71 g, 65% yield; contaminated with ~ 5% 1,8-dimethylnaphthalene) as a crystalline, white solid: mp 73-77°C (lit. mp 77-78 °C).[32] ^{1}H NMR ($CDCl_3$) δ 7.83 (dd, *J* = 1.3, 7.5 Hz, 1H), 7.77 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.71 (m, 1H), 7.37-7.34 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 3.12 (s, 3H).

General procedure for the Susuki-Muyari coupling of 1-bromo-8-methylnaphthalene with arylboronic acids. Synthesis of 1a-d and **1l.** These compounds were prepared according to the literature procedure[6] or by the following procedure. To a mixture of 1-bromo-8-methylnaphthalene (1.20 g, 5.43 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos; 0.180 g, 0.438 mmol), arylboronic acid (8.0 mmol), K_3PO_4 (3.45 g, 16.3 mmol), and $Pd_2(dba)_3$ (0.98 g, 0.107 mmol) was added toluene (10 mL) in a Schlenk flask. The reaction

mixture was degassed with argon for 5 min and then refluxed for 16-20 h. After cooling to ambient temperature, the reaction mixture was diluted with Et_2O (100 mL), filtered through Celite, and concentrated on the rotary evaporator. The crude product was purified by flash chromatography (silica gel; hexanes→5% EtOAc in hexanes). Compound **1k** was prepared by an alternative method (see below) since the yield was very low with the above procedure. Yields and characterization for new compounds **1k** and **1l** are reported below, as are the ^{1}H NMR spectra for the other known 1-methyl-8-arylnaphthalene compounds.

1-Methyl-8-phenylnaphthalene (1a).[6] ^{1}H NMR (CD_2Cl_2) δ 7.86 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.77 (br d, *J* = 8.0 Hz, 1H), 7.49-7.32 (m, 7H), 7.29 (dd, *J* = 1.5, 7.0 Hz, 1H), 7.23 (br d, *J* = 7.0 Hz, 1H), 2.00 (s, 3H).

1-Methyl-8-(4-methylphenyl)naphthalene (1b).[6] ^{1}H NMR (CD_2Cl_2) δ 7.84 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.76 (br d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 7.0, 8.1 Hz, 1H), 7.36 (dd, *J* = 7.0, 8.0 Hz, 1H), 7.27 (dd, *J* = 1.5, 7.0 Hz, 1H), 7.23-7.21 (m, 5H), 2.43 (s, 3H), 2.02 (s, 3H).

1-(4-Methoxyphenyl)-8-methylnaphthalene (1c).[6] ^{1}H NMR (CD_2Cl_2) δ 7.83 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.76 (br d, *J* = 8.2 Hz, 1H), 7.43 (dd, *J* = 7.0, 8.0 Hz, 1H), 7.36 (dd, *J* = 7.0, 8.1 Hz, 1H), 7.28 (dd, *J* = 1.5, 7.0 Hz, 1H), 7.25-7.21 (m, 3H), 6.93 (m, 2H), 3.86 (s, 3H), 2.03 (s, 3H).

1-(4-Fluorophenyl)-8-methylnaphthalene (1d).[6] ^{1}H NMR (CD_2Cl_2) δ 7.86 (dd, *J* = 1.5, 8.4 Hz, 1H), 7.77 (br d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 7.1, 8.3 Hz, 1H), 7.37 (dd, *J* = 7.3, 8.1 Hz, 1H), 7.34-7.27 (m, 3H), 7.24 (br d, *J* = 7.0 Hz, 1H), 7.10 (m, 2H), 2.01 (s, 3H).

Methyl 4-(8-methylnaphthalen-1-yl)benzoate (1l). White, crystalline solid: 0.150 g (28% yield based on 0.423 g (1.91 mmol) of 1-bromo-8-methylnaphthalene); mp 129-131° C. IR (CH_2Cl_2) 1719, 1610 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 8.06 (m , 2H), 7.89 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.79 (br d, *J* = 8.0 Hz, 1H), 7.48-7.42 (m, 3H), 7.39 (dd, *J* = 7.3, 8.0 Hz, 1H), 7.29 (dd, *J* = 1.4,

7.0 Hz, 1H), 7.26 (br d, *J* = 7.0 Hz, 1H), 3.93 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 167.2, 150.2, 139.6, 135.3, 130.9, 130.2, 130.0 (2), 129.6, 129.5, 129.0 (2), 127.7, 126.0, 124.5, 52.3, 25.3.

***N*,*N*-dimethyl-4-(8-methylnaphthalen-1-yl)aniline (1k).** To a degassed solution of $Pd(PPh_3)_4$ (0.250 g, 0.216 mmol) and 1-bromo-8-methylnaphthalene (0.884 g, 4.00 mmol) in DME (30 mL) was added a slurry of 4-(*N*,*N*-dimethylamino)phenylboronic acid (1.00 g, 6.06 mmol) in EtOH (9 mL), followed by Na_2CO_3 (1.50 g, 14.2 mmol) in degassed water (11 mL). The reaction mixture was heated to reflux for 20 h. The reaction mixture was diluted with Et_2O (100 mL), the organic phase was separated, the aqueous phase was extracted with additional Et_2O (100 mL), and the combined organic phases were washed with 1 M NaOH (100 mL). The organic phase was then extracted with 1 M HCl (2 x 100 mL). The aqueous phase was neutralized with 6 M NaOH and extracted with Et_2O (2 x 100 mL). The organic phase was concentrated on the rotary evaporator to give crude product, which was purified by flash chromatography (silica gel; hexanes→50% CH_2Cl_2 in hexanes) to give **1k** as an off-colored solid (0.50 g; ~30% (4-$(Me_2N)C_6H_4)_2$). Further recrystallization from petroleum ether gave **1k** as a crystalline off-white solid (0.280 g, 27% yield): mp 133-135° C. IR (CH_2Cl_2) 1611 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.80 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.75 (br d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 7.3, 8.1 Hz, 1H), 7.34 (dd, *J* = 7.3, 8.1 Hz, 1H), 7.28 (dd, *J* = 1.5, 7.0 Hz, 1H), 7.26 (br d, *J* = 7.0 Hz, 1H), 7.15 (m, 2H), 6.76 (m, 2H), 3.00 (s, 6H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 149.6, 140.9, 136.0, 135.2, 133.4, 131.7, 130.4, 129.9, 129.6, 128.4, 127.4, 125.4, 124.5, 111.7, 40.8, 25.3.

General Procedure for the Direct Complexation of 1 using $Cr(CO)_6$. Synthesis of 4(a-c)-Cr and 1k-Cr. A mixture of **1** (1.70 mmol) and $Cr(CO)_6$ (0.440 g, 2.00 mmol) in (n-Bu)$_2$O (12 mL) and THF (1.0 mL) was purged with Ar. The reaction mixture was then heated in an oil bath

to 140-150 °C for 44 h. The solvent was removed by vacuum to give the crude product. The crude product was purified by flash chromatography (silica gel; for **1(a-c)-Cr**, hexanes → 50% Et_2O in hexanes; for **1k-Cr**, hexanes → 50% CH_2Cl_2 in hexanes) to give **1-Cr**, in some cases contaminated by η^6-naphthalene complexed products. Further purification was accomplished by washing with hexanes.

(1-Methyl-8-(η^6-phenyl)naphthalene)Cr(CO)$_3$ (1a-Cr). Yellow, crystalline solid; 0.151 g (20% yield based on 0.46 g (2.1 mmol) of **1a**). IR (CH_2Cl_2) 1969, 1892 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.88 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.78 (br d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 1.4, 7.0 Hz, 1H), 7.47 (dd, *J* = 7.3, 8.1 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.29 (br d, *J* = 7.0 Hz, 1H), 5.84 (dd, *J* = 0.9, 6.8 Hz, 2H), 5.65 (br t, *J* = 5.9 Hz, 1H), 5.37 (t, *J* = 6.4 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 233.4, 135.2, 134.33, 134.31, 134.1, 132.1, 131.0, 130.8, 128.1, 126.1, 124.9, 119.6, 99.8, 96.4, 88.8, 27.2.

1-Methyl-8-(η^6-(4-methylphenyl))naphthalene)Cr(CO)$_3$ (1b-Cr). Yellow, crystalline solid; 0.177 g (31% yield based on 0.369 g (1.59 mmol) of **1b**). IR (CH_2Cl_2) 1965, 1887 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.87 (dd, *J* = 1.1, 8.1 Hz, 1H), 7.77 (br d, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 1.3, 7.1 Hz, 1H), 7.44 (dd, *J* = 7.4, 8.0 Hz, 1H), 7.38 (br t, *J* = 7.5 Hz, 1H), 7.28 (br d, *J* = 7.0 Hz, 1H), 5.86 (d, *J* = 6.6 Hz, 2H), 5.23 (d, *J* = 6.6 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 233.7, 135.1, 134.4 (2), 134.1, 132.2, 130.7 (2), 128.1, 126.1, 125.0, 117.5, 112.3, 100.5, 89.8, 27.3, 20.8. 1D NOE experiments confirmed the assignment of the 3H signal at δ 2.29 ppm as the methyl group on the naphthalene ring and the 3H signal at δ 2.26 ppm as the methyl group on the phenyl ring.

1-(η^6-(4-Methoxyphenyl))-8-methylnaphthalene Cr(CO)$_3$ (1c-Cr). Yellow, crystalline solid; 0.470 g (73% yield based on 0.416 g (1.68 mmol) of **1c**). IR (CH_2Cl_2) 1966, 1886 cm^{-1}; ^1H NMR

(CD_2Cl_2) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 5.91 (d, *J* = 7.0 Hz, 2H), 5.21 (d, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 233.6, 144.5, 135.1, 134.4, 133.7, 132.3, 130.9, 130.8, 128.2, 126.0, 125.0, 114.0, 100.2, 75.7, 56.2, 27.4.

(η^6-*N*,*N*-dimethyl-4-(8-methylnaphthalen-1-yl)aniline)Cr(CO)$_3$ (1k-Cr). Yellow, crystalline solid; 0.357 g (87% yield based on 0.271 g (1.04 mmol) of **1k**). IR (CH_2Cl_2) 1953, 1870 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.85 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.76 (br d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 1.5, 7.0 Hz, 1H), 7.44-7.35 (m, 2H), 7.27 (d, *J* = 7.0 Hz, 1H), 5.92 (d, *J* = 7.4 Hz, 2H), 4.89 (d, *J* = 7.3 Hz, 2H), 2.97 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 235.0, 136.3, 135.1, 134.8 (2), 134.5, 132.6, 130.7, 130.5, 128.1, 125.9, 125.1, 111.4, 101.9, 72.1, 40.0, 27.5.

(8-Methylnaphthalen-1-yl)boronic acid (2). To a solution of 1-bromo-8-methylnaphthalene (1.04 g, 4.70 mmol) in Et_2O (25 mL) was added *n*-BuLi (3.5 mL, 1.6 M in hexane, 5.6 mmol) at over 2 min. The reaction mixture was allowed to warm to 22° C, stirred for 2 h, then cooled to -78 °C. $B(OMe)_3$ (0.77 mL, 0.72 g, 6.9 mmol) in EtO_2 (10 mL) was added in one portion, allowed to warm to 22 °C, and stirred for 16 h. The reaction mixture was transferred to an Erlenmeyer flask with additional EtO_2 (20 mL), treated with aqueous HCl (2 M, 50 mL), and stirred vigorously for 16 h. The organic phase was separated, the aqueous extracted with EtO_2 (50 mL), and the combined organic extracts were concentrated on the rotary evaporator. The crude product was purified by flash chromatography (silica gel; hexanes→50% EtOAc in hexanes) to give **2** as a white solid (0.35 g, 40% yield): mp 142-145°C. IR (CH_2Cl_2) 3618, 1602 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.87 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.71 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.59 (dd, *J* = 1.3, 6.8 Hz, 1H), 7.44 (dd, *J* = 6.8, 8.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.34 (br d, *J* = 7.3 Hz, 1H), 4.74 (s,

2H), 2.79 (s, 3H); ^{13}CNMR ($(CD_3)_2CO$) δ 136.4, 135.0, 134.8, 130.5, 129.7, 128.3 ,127.9, 126.0, 125.4, 22.1; HRMS (DART-TOF) calcd for $C_{11}H_{11}BO_2$ $[M + 1]^+$ 187.0930, found 187.0934.

1-(η^6-(4-Fluorophenyl))-8-methylnaphthaleneCr(CO)$_3$ (1d-Cr). To an argon-purged solution of boronic acid **2** (0.257 g, 1.38 mmol), η^6-(4-FC_6H_4Cl) $Cr(CO)_3$[15] (0.305 g, 1.14 mmol) and SPhos (0.053 g, 0.13 mmol) in toluene (3 mL) was added K_3PO_4 (1.00 g, 4.71 mmol) and $Pd_2(dba)_3$ (0.027 g, 0.29 mmol). The reaction mixture was heated to 80 °C for 2 h and 90° C for 3 h, cooled to ambient temperature, poured into Et_2O (50 mL) and EtOAc (25 mL), filtered through a plug of silica gel, and concentrated on the rotary evaporator. Flash chromatography (silica gel; hexanes→30% toluene in hexanes) gave **1d-Cr** (0.098 g, 22% yield) as a yellow solid. IR (CH_2Cl_2) 1978, 1904 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.78 (br d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 6.6 Hz, 1H), 7.44-7.37 (m, 2H), 7.29 (d, *J* = 6.6 Hz, 1H), 5.89 (dd, *J* = 2.9, 6.6 Hz, 2H), 5.44 (dd, *J* = 5.1, 6.2 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 232.1, 147.6 ($J_{C\text{-}F}$ = 265.1 Hz), 134.1, 134.2, 133.1 (2), 132.3, 131.0 (2), 128.2, 126.2, 124.9, 115.2, 98.5 ($J_{C\text{-}F}$ = 10.7 Hz), 76.8 ($J_{C\text{-}F}$ = 20.5 Hz), 27.5.

Methyl η^6-(4-(8-methylnaphthalen-1-yl))benzoateCr(CO)$_3$ (1l-Cr). Using the procedure described in the synthesis of **1d-Cr** but employing η^6-(4-$MeCO_2C_6H_4Cl$)$Cr(CO)_3$[15] instead of η^6-(4-FC_6H_4Cl)$Cr(CO)_3$, complex **1l-Cr** was isolated as an orange, crystalline solid (0.180 g, 48% yield based on 0.28 g (0.92 mmol) of η^6-(4-$MeCO_2C_6H_4Cl$)$Cr(CO)_3$). IR (CH_2Cl_2) 1978, 1908, 1729 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.88 (dd, *J* = 1.1, 8.1 Hz, 1H), 7.78 (br d, *J* = 7.7 Hz, 1H), 7.69 (dd, *J* = 1.3, 7.1 Hz, 1H), 7.46 (dd, *J* = 7.3, 8.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 6.09 (d, *J* = 7.0 Hz, 2H), 5.84 (d, *J* = 7.0 Hz, 2H), 3.94 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 232.0, 166.5, 135.3, 134.1, 133.7 (2), 132.0, 131.2, 131.1, 128.1, 126.2, 124.7, 121.3, 97.0, 93.2, 90.5, 27.2.

(1-Methyl-8-(η^6-(4-methylphenyl))naphthalene)$Mn(CO)_3BF_4$ (1b-Mn). To a solution of $(CO)_5MnBr$ (0.256 g, 0.96 mmol) in 1,2-dichloroethane (10 mL) in a 25 mL Schlenk flask was added $AgBF_4$ (0.191 g, 0.98 mmol). The reaction mixture was heated to 40 °C for 1 h. To the reaction mixture was added **1b** (0.48 g, 2.1 mmol) and then heated to 80 °C for 20h. After cooling, the reaction mixture was filtered through a pad of Celite, washing with additional CH_2Cl_2 (2 x 5 mL). Et_2O (50 mL) was added and the precipitate was filtered to give complex **1b-Mn** (0.150 g, 34% yield) as a yellowish solid. IR (CH_2Cl_2) 2078, 2029 (sh), 2018 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.03 (br d, *J* = 7.7 Hz, 1H), 7.87 (br d, *J* = 8.4 Hz, 1H), 7.59-7.48 (m, 3H), 7.41 (br d, *J* = 6.6 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 6.2 Hz, 2H), 2.61 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (CD_2Cl_2/CD_3CN) δ 214.9, 135.2, 133.6, 132.9, 132.8, 131.9, 131.3, 129.0, 128.2, 127.0, 124.6, 124.0, 120.7, 104.4, 96.8, 27.5, 20.0.

(η^6-1,2,3,4,9,10-1-Methyl-8-(4-methylphenyl)naphthalene)$Mn(CO)_3BF_4$ (3). To a solution of $(CO)_5MnBr$ (0.310 g, 1.13 mmol) in CH_2Cl_2 (10 mL) in a 25 mL Schlenk flask was added $AgBF_4$ (0.225 g, 1.15 mmol). The reaction mixture was heated to 40 °C for 1 h. After cooling to 25 °C, **1b** (0.58 g, 2.5 mmol) was added to the reaction mixture and then heated to 40 °C for 4 h. After cooling, the solution containing **3** was decanted from the solids (AgBr) and the solids were extracted with additional CH_2Cl_2 (5 mL). Et_2O (70 mL) was added under Ar to the organic solution and the rapidly filtered to give **3** (0.28 g, 34% yield) as a bright yellow solid that was air- and water-sensitive. Further purification invariably led to decomposition of **3**. ^1H NMR (CD_2Cl_2) δ 8.19 (br d, *J* = 7.7 Hz, 1H), 7.95 (br t, *J* = 7.7 Hz, 1H), 7.78 (br d, *J* = 6.2 Hz, 1H), 7.63 (m, 1H), 7.42-7.22 (m, 3H), 7.07 (br d, *J* = 7.7 Hz, 1H), 6.89 (br s, 1H), 6.56 (br s, 1H), 2.47 (s, 3H), 2.25 (s, 3H).

1-methyl-8-(η^6-(4-methylphenyl)naphthalene))RuCpPF$_6$ (1b-Ru). To a Ar-degassed solution of **1b** (0.255 g, 1.10 mmol) in 3-pentanone (20 mL) was added CpRu(CH_3CN)$_3PF_6$ (0.434g 1.00 mmol). The reaction mixture was refluxed for 24 h. The solvent was removed on a rotary evaporator and washed with Et_2O (2x25 mL). The crude product was dissolved in CH_2Cl_2 and filtered through a plug of Celite. After removal of the volatiles, the crude product was redissolved in CH_2Cl_2 (10 mL), and Et_2O (30 mL) was added. The precipitate was filtered and washed with additional Et_2O (20 mL) to give **1b-Ru** as a tan solid (0.41g, 77% yield). ^{1}H NMR (CD_2Cl_2) δ 7.95 (dd, *J* = 2.2, 7.7 Hz, 1H), 7.81 (br d, *J* = 8.1 Hz, 1H), 7.51-7.43 (m, 3H), 7.33 (br d, *J* = 7.0 Hz, 1H), 6.36 (d, *J* = 6.2 Hz, 2H), 6.33 (d, *J* = 6.2 Hz, 2H), 5.42 (s, 5H), 2.47 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 135.2, 133.6, 133.5, 131.8, 131.6, 131.5, 131.3, 128.1, 126.7, 124.5, 114.9, 102.4, 88.9, 85.3, 82.2, 27.5, 20.5.

(η^6-1,2,3,4,9,10-1-Methyl-8-(4-methylphenyl))naphthaleneRuCp PF$_6$ (4a) and (η^6-5,6,7,8,9,10-1-methyl-8-(4-methylphenyl))naphthaleneRuCpPF$_6$ (4b). To a Ar-degassed solution of **1b** (0.150 g, 0.65 mmol) in acetone (10 mL) was added CpRu(CH_3CN)$_3PF_6$ (0.216 g, 0.497 mmol). The reaction mixture was stirred at 22 °C for 1 h. The solvent was removed on a rotary evaporator and the crude product was washed with Et_2O (2 x 25 mL). The crude product was dissolved in CH_2Cl_2 (10 mL), and Et_2O (30 mL) was added to give a yellow precipitate that was primarily complexes **4a** and **4b** as a 2:1 mixture (0.234 g). The crude product was dissolved in CH_2Cl_2 (7 mL), filtered through a Celite plug, and degassed with Ar. Slow diffusion of Et_2O into the CH_2Cl_2 solution gave **4a**·CH_2Cl_2 and **4b**·CH_2Cl_2 as yellow/orange crystals (2:1 mixture of **4a**·CH_2Cl_2:**4b**·CH_2Cl_2, 0.260 g, 81% yield). Fractional recrystallization (slow diffusion of Et_2O into the CH_2Cl_2 solution) gave **4a**·CH_2Cl_2 in greater than 95% purity. When **4a**·CH_2Cl_2 is dissolved in $(CH_3)_2CO$ and the solvent is removed, **4a** is obtained free of solvent. For **4a**: ^{1}H

NMR (CD_2Cl_2) δ 7.76 (dd, *J* = 1.3, 8.6 Hz, 1H), 7.59 (dd, *J* = 6.8, 8.6 Hz, 1H), 7.50 (dd, *J* = 1.3, 6.7 Hz, 1H), 7.36 (dm, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 2.0, 7.9 Hz, 1H), 7.26 (br d, *J* = 7.7 Hz, 1H), 7.06 (dd, *J* = 2.0, 7.9 Hz, 1H), 6.91 (d, *J* = 5.8 Hz, 1H), 6.25 (t, *J* = 6.1 Hz, 1H), 6.11 (d, *J* = 5.8 Hz, 1H), 4.93 (s, 5H), 2.45 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 141.4, 138.9, 138.4, 135.0, 131.1, 130.4, 130.0, 129.9, 129.2, 128.6, 100.0, 97.7, 95.9, 90.6, 86.6, 84.1, 80.6, 25.3, 21.4. Partial ^{1}H NMR (CD_2Cl_2) for **4b**: δ 7.64 (br d, *J* = 8.8 Hz, 1H), 7.52 (dd, *J* = 6.6, 8.8 Hz, 1H), 7.04 (dd, *J* = 0.7, 6.2 Hz, 1H), 6.35 (t, *J* = 6.0 Hz, 1H), 6.02 (dd, *J* = 0.7, 5.9 Hz, 1H), 5.07 (s, 5H), 2.47 (s, 3H), 1.94 (s, 3H). Anal Calcd for $C_{23}H_{21}F_6PRu$: C, 50.82; H, 3.90. Found: C, 50.62; 3.94.

General Procedure for X-ray Structure Determination. Crystals suitable for X-ray structure determination were prepared by the slow evaporation of Et_2O (for **1a-Cr** and **1b-Cr**), CH_2Cl_2 (for **1c-Cr** and **1l-Cr**), Et_2O/cyclohexane (for **1d-Cr**), or hexanes (for **1l**); or by recrystallization from EtOAc (for **1k** and **1k-Cr**) or CH_2Cl_2 (for **1b-Mn**); or by slow diffusion of diethyl ether into a solution of methylene chloride solution at 0° C (for **1b-Ru**).

X-ray data were acquired at 173 K on a CCD diffractometer employing graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The Apex2 suite of programs[33] was used to process the data and the SAINT software package[34] was used to integrate the frames with a narrow-frame algorithm. The multi-scan method (SADABS)[35] was used to correct the data for absorption effects. The SHELXTL software package[36] was used to perform structure solution by direct methods, and refinement by full-matrix least-squares on F^2. All nonhydrogen atoms were refined anisotropically with suggested weighting factors and the hydrogens were calculated on a

riding model. All cif files were validated with the checkCIF/Platon facility of IUCr that was accessed with the software program enCIFer.[37]

Computational methods: All calculations were carried out with Gaussian 09[38] using the methods and basis sets described in the text. The stationary points obtained from geometry optimizations were verified as minima by subsequent frequency calculations (zero imaginary frequencies). The WP04 routine may be implemented by entering the BLYP keyword and the following internal options: iop (3/76=1000001189,3/77=0961409999,3/78=0000109999).[28b]

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Supporting Information: Copies of ^{1}H and ^{13}C NMR spectra; computational data for the optimized structures and isotropic magnetic shielding values; and crystallographic information files (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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