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PAPER

Haptotropic rearrangement in tricarbonylchromium complexes of 2-aminobiphenyl and 4-aminobiphenyl†

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The *para*-aminobiphenyl compound $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}4\text{-}NH_2)]Cr(CO)_3$ (**1**) has an arene–phenyl dihedral angle of 38.01(6)°, as determined by single-crystal X-ray crystallography, and 34.7(11)°, as determined by DFT calculations. It undergoes haptotropic rearrangement at 140 °C in solution to form $[(\eta^6\text{-}C_6H_4\text{-}4\text{-}NH_2)(C_6H_5)]Cr(CO)_3$ (**2**), even though previous reports have suggested that such rearrangements should not be observed in compounds with arene–phenyl dihedral angles greater than 22°. NMR analysis gave a rate constant of $k = 5.0 \times 10^{-5}$ s^{-1} for the rearrangement of **1** to **2**. The *ortho*-substituted analog $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}2\text{-}NH_2)]Cr(CO)_3$ (**3**) has an arene–phenyl dihedral angle of 67.70(7)°, as determined by single-crystal X-ray crystallography, and 51.9(10)°, as determined by DFT calculations. Surprisingly, even though it displays a more extreme canting of arene rings, **3** rearranges to $[(\eta^6\text{-}C_6H_4\text{-}2\text{-}NH_2)(C_6H_5)]Cr(CO)_3$ (**4**) at 140 °C in solution with a rate constant of $k = 2.6 \times 10^{-4}$ s^{-1}. This approximately five-fold rate enhancement likely results from the *ortho*-amino group providing intramolecular stabilization for intermediates formed during the rearrangement.

Introduction

Organometallic compounds with π-coordinated polycyclic aromatic ligands may undergo haptotropic rearrangements where a coordinated metal fragment migrates between aromatic rings. The most commonly studied examples involve movement of metals between the rings of naphthalene, fluorene, indenyl, biphenyl, or other related ligands.[1,2] Recent examples have suggested important potential applications of this process, such as $(\eta^6$-polyarene$)Cr(CO)_3$ compounds that could be used as molecular switches when their haptotropic rearrangements can be directed by changes in electronic or steric factors.[3]

In most examples that specifically involve substituted $(\eta^6$-biphenyl$)Cr(CO)_3$ complexes, the $Cr(CO)_3$ fragment migrates from the less electron-rich ring to the more electron-rich ring, but migration has been shown to be inhibited in some cases by conformational effects, especially when substituents force the arene rings out of coplanarity.[4] In fact, a recent study describing a series of substituted compounds $[(\eta^6\text{-}C_6H_5)C_6H_4X]Cr(CO)_3$ (X = Br, D, CH_3, $SnMe_3$) showed that near coplanarity of the arene rings in the biphenyl ligand is required for haptotropic rearrangement, and indicated that a necessary condition for rearrangement is an arene–arene dihedral angle less than 22°, as determined either by calculation or single crystal X-ray crystallography.[5] Inter-ring steric hindrance effected by a non-hydrogen substituent in the *ortho* position was shown to twist the arene rings out of coplanarity to a great enough degree so as to prevent the metal from migrating between rings. We found it somewhat surprising that solid-state or gas-phase structure determination could predict this inhibition, especially considering the expected low rotational barrier about the arene–arene sigma bond in *ortho*-substituted compounds of the type $[(\eta^6\text{-}C_6H_5)C_6H_4X]Cr(CO)_3$.[6] Noting that this series of compounds had not included cases where biphenyl ligands had strongly electron-donating substituents, we wished to examine amino-substituted biphenyl compounds such as $[(\eta^6\text{-}C_6H_5)C_6H_4NH_2]Cr(CO)_3$. It seemed plausible that the strong electron donating character of the amino group could facilitate haptotropic migration even if gas-phase calculation or solid-state structure determination showed a dihedral angle greater than 22°. Here we report that the *para*-amino compound $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}4\text{-}NH_2)]Cr(CO)_3$ (**1**), which has an arene–arene dihedral angle of 38.01(6)° in the solid state, nevertheless undergoes thermal haptotropic rearrangement in solution to form $[(\eta^6\text{-}C_6H_4\text{-}4\text{-}NH_2)(C_6H_5)]Cr(CO)_3$ (**2**). Furthermore, we found that the *ortho*-amino compound $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}2\text{-}NH_2)]Cr(CO)_3$ (**3**), despite its larger arene–arene dihedral angle of 67.70(7)°, surprisingly undergoes haptotropic rearrangement to form $[(\eta^6\text{-}C_6H_4\text{-}2\text{-}NH_2)(C_6H_5)]Cr(CO)_3$ (**4**) with a rate that is approximately five times faster than that observed for the conversion of **1** to **2**.

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra and X-ray crystallographic data for compounds **1–4** and figures giving rate data for conversion of **1** to **2** and for conversion of **3** to **4**. CCDC reference numbers 778546–778549. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10994d

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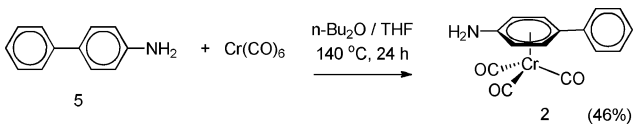
Results and discussion

When 4-aminobiphenyl (**5**) was heated with chromium hexacarbonyl in 9 : 1 dibutyl ether : tetrahydrofuran, the product obtained was the expected isomer $[(\eta^6\text{-}C_6H_4\text{-}4\text{-}NH_2)(C_6H_5)]Cr(CO)_3$ (**2**), which has a chromium tricarbonyl fragment coordinated to the *para*-amino-substituted arene ring (Scheme 1).[7] This expected predominance of $Cr(CO)_3$ coordination to the electron-rich amino-substituted ring, rather than the unsubstituted ring, has been previously observed in aminobiphenyl chromium tricarbonyl syntheses.[8–10]



Scheme 1 Synthesis of isomer **2** by direct heating.

The ^{1}H NMR spectrum of **2** in acetone-d_6 shows characteristic signals for the *para*-amino-substituted arene ring shifted markedly upfield (5.24–6.25 ppm) compared to free **5**, whereas signals for protons of the other ring appear in the free phenyl region of the spectrum (7.34–7.55 ppm). This chemical shift pattern implies that the amino-substituted ring is coordinated to the $Cr(CO)_3$ fragment.

The analog $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}4\text{-}NH_2)]Cr(CO)_3$ (**1**), is a known compound that has a *para*-amino group attached to the uncoordinated ring. It was synthesized in 18% overall yield from $Cr(CO)_6$, by repeating the method of Gubin and coworkers (Scheme 2).[7,11] In this scheme, 4-acetamidobiphenyl (**6**) reacts with $Cr(CO)_6$ to produce a mixture of $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}4\text{-}NHCOCH_3)]Cr(CO)_3$ (**7**) and $[(\eta^6\text{-}C_6H_4\text{-}4\text{-}NHCOCH_3)(C_6H_5)]Cr(CO)_3$ (**8**) which can be separated by column chromatography. Since an amide is less electron donating and more sterically demanding than an amino group, it is not surprising that the major isomer formed is **7**, which is then hydrolyzed under basic conditions to form **1**.

The ^{1}H NMR spectrum of **1** in acetone-d_6 shows characteristic signals for the *para*-amino-substituted ring in the free aromatic region of the spectrum (6.71–7.38 ppm), while signals for the metal-bound phenyl ring are shifted upfield (5.51–5.95 ppm). While **1** is a known compound, its crystallographic characterization had not been previously reported. Obtaining single-crystal X-ray crystal structures of **1** and **2** (Fig. 1 and 2) definitively showed the bonding arrangements for each compound and the arene–arene dihedral angles, which may be an important consideration for haptotropic rearrangements.

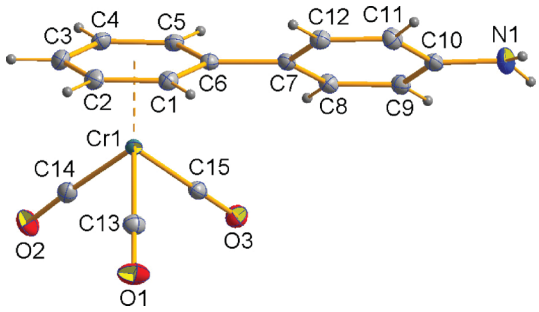


Fig. 1 X-ray crystal structure of $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}4\text{-}NH_2)]Cr(CO)_3$ (**1**).

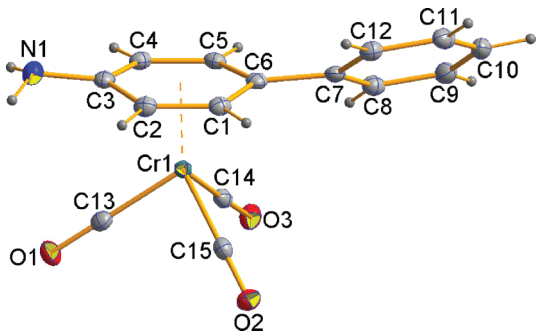
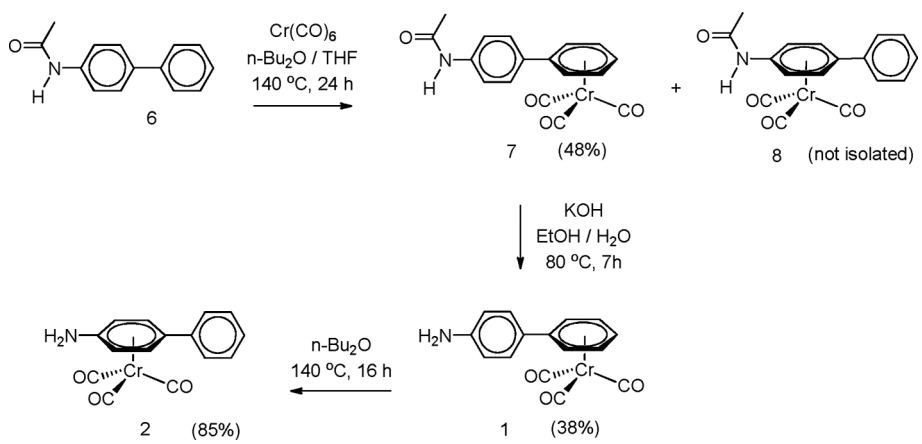


Fig. 2 X-ray crystal structure of $[(\eta^6\text{-}C_6H_4\text{-}4\text{-}NH_2)(C_6H_5)]Cr(CO)_3$ (**2**).

The crystal structure of **2** shows some notable deviations from the ideal three-legged piano-stool geometry. The coordinated ring is slightly tilted away from the carbonyl atom C13, which makes the Cr1–C2 and Cr1–C4 distances longer (av. 2.25 Å) than the Cr1–C1 and Cr–C5 distances (av. 2.20 Å). The Cr1–C3 bond length of 2.3541(14) Å substantially exceeds the Cr1–C6 distance of 2.2444(14) Å. The substituted atoms C3 and C6 are displaced from the plane of the arene ring away from the chromium, rendering a slight boat distortion to the ring. The dihedral angles between the plane defined by atoms C1, C2, C4, and C5 and planes C2–C3–C4 and C1–C5–C6 are calculated to be 6.51(19)° and 3.8(2)°,



Scheme 2 Synthesis and thermal rearrangement of isomer **1**.

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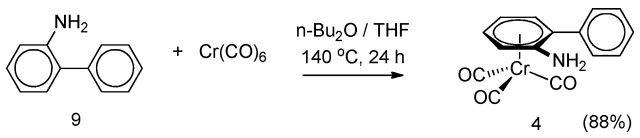
respectively. The arene–phenyl dihedral angle spans 38.01(6)°. In contrast, in **1** the dihedral angle between planes C1–C2–C4–C5 and C1–C5–C6 is only 1.24(18)°, but the arene–phenyl dihedral angle is very similar at 38.28(4)°. The Cr1–C(Ph) distances in **6** fall within the expected range.

When **1** was heated in dibutyl ether at 140 °C, thin-layer chromatography showed gradual disappearance of **1** and formation of **2**. Continued heating overnight led to the formation and isolation of **2** in 85% yield, with no **1** detectable by ^{1}H NMR spectroscopy (Scheme 2). To determine the rate of rearrangement of **1** to **2**, a degassed diglyme-d_{14} solution of **1** was sealed in an NMR tube and the solution was heated at 140 °C. Periodic collection of ^{1}H NMR spectra led to the determination of a rate constant of 5.0×10^{-5} s^{-1} (half-life ≈ 230 min) for the rearrangement of **1** to **2**. Comparison to the internal standard showed that a small amount (~10%) of decomposition to **5** occurred during this rearrangement.

The observed rearrangement of **1** to **2** was especially interesting in light of the 38.01(6)° arene–phenyl dihedral angle in **1**. It suggests that the strong electron donating effect of a substituent group, amino in this case, can predominate over steric effects, promoting haptotropic rearrangement even when the observed arene–phenyl dihedral angle is greater than 22°. In an attempt to further examine this predominance of electronic effects, we wanted to synthesize the *ortho*-substituted analog [(η^6-C_6H_5)(C_6H_4-2-NH_2)]Cr(CO)$_3$ (**3**), since we expected it to have an arene–phenyl dihedral angle even larger than that observed in **1**. Our DFT geometry optimization of **1** performed at the B3LYP/6-31G* level of theory produced a 34.7(11)° arene–phenyl dihedral angle.[12] The equivalent angle in the theoretically-optimized isomer **3** measured 51.9(10)°.

When 2-aminobiphenyl (**9**) was heated with chromium hexacarbonyl in 9 : 1 dibutyl ether : tetrahydrofuran, the single product obtained was [(η^6-C_6H_4-2-NH_2)(C_6H_5)]Cr(CO)$_3$ (**4**), which has a chromium tricarbonyl fragment coordinated to the *ortho*-amino-substituted arene ring (Scheme 3). The ^{1}H NMR spectrum of **4** in acetone-d_6 shows signals for the *ortho*-amino-substituted arene ring shifted upfield (4.02–5.90 ppm) compared to free **9**, whereas signals for the protons for the unsubstituted ring appear in the free aromatic region of the spectrum (7.4–7.6 ppm). This indicates that the amino-substituted ring is coordinated to the Cr(CO)$_3$ fragment.



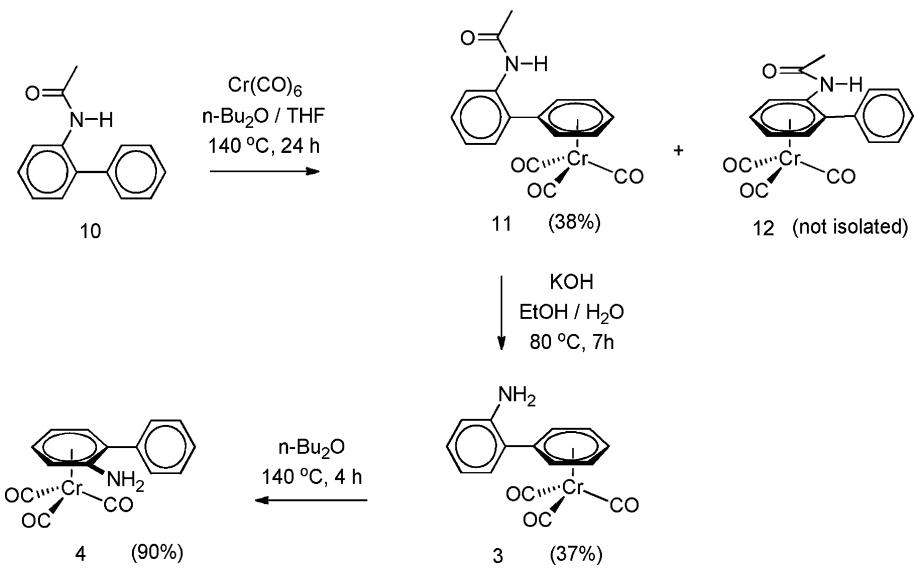
Scheme 3 Synthesis of isomer **4** by direct heating.

Analog **3** was synthesized by first reacting 2-acetamidobiphenyl (**10**) with chromium hexacarbonyl under reflux with 9 : 1 dibutyl ether : tetrahydrofuran, which led to isolation of [(η^6-C_6H_5)(C_6H_4-2-$NHCOCH_3$)]Cr(CO)$_3$ (**11**) in 38% yield.

The other isomer, [(η^6-C_6H_4-2-($NHCOCH_3$)-C_6H_5)]Cr(CO)$_3$ (**12**), though formed and observed by ^{1}H NMR, was not isolated. Basic hydrolysis of **11** gave **3** in 14% overall yield, based on the starting amount of Cr(CO)$_6$ (Scheme 4).

The ^{1}H NMR spectrum of **3** in acetone-d_6 shows signals for the *ortho*-amino-substituted ring in the free aromatic region (6.70–7.24 ppm), while signals for the protons of the unsubstituted ring are shifted upfield (5.68–5.87 ppm) into the metal-bound aryl region of the spectrum, indicating that the unsubstituted ring is coordinated to the Cr(CO)$_3$ fragment. The bonding arrangements in **3** and **4** are clearly shown in their single-crystal X-ray crystal structures (Fig. 3 and 4).

In the single crystal X-ray crystal structure of **4**, the phenyl and amino substituents of the coordinated ring are each bent slightly upwards, away from the chromium. Atoms C1 and C6 are displaced from the plane defined by atoms C2–C3–C4–C5 by 0.062(3) and 0.008(4) Å, respectively, rendering a very slight 1.69(9)° butterfly folding of the arene ring along the C2–C5 vector. The six Cr–C(arene) bond distances range from 2.2129(1) to 2.3077(18) Å, with the Cr1–C1 bond length being the longest. These features, which may result from steric interactions within **4**, are not evident in the structure of **3**, where all six Cr–C(arene) bond lengths are within 0.012 Å, with an average of 2.216(8) Å. The C1–C7 bond that connects the two arene rings is nearly coplanar



Scheme 4 Synthesis and thermal rearrangement of isomer **3**.

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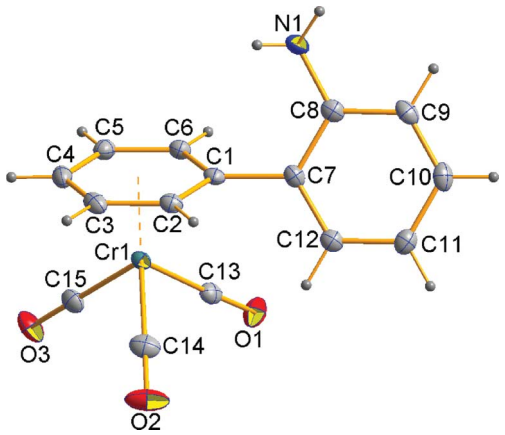


Fig. 3 X-ray crystal structure of $[(\eta^6\text{-}C_6H_5)(C_6H_4\text{-}2\text{-}NH_2)]Cr(CO)_3$ (**3**).

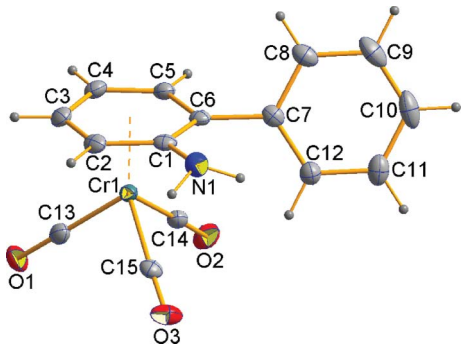


Fig. 4 X-ray crystal structure of $[(\eta^6\text{-}CH\text{-}2\text{-}NH)(CH)]Cr(CO)$ (**4**).

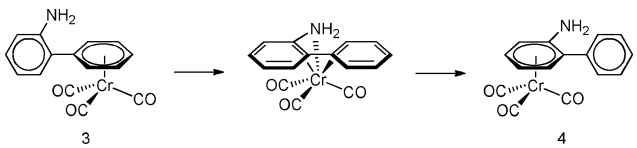
with the coordinated ring. The structures of both **3** and **4** exhibit large arene–phenyl dihedral angles spanning 67.70(7)° and 63.05(5)°, respectively. These large dihedral angles, much larger than those observed in the *para* isomers **1** and **2**, presumably result from steric interactions of the amino group with *ortho*-hydrogen atoms of the other ring.[6]

Heating **3** at 140 °C caused it to convert to **4**. TLC monitoring of a refluxing solution of **3** in dibutyl ether showed that the conversion of **3** to **4** was complete in four hours, leading to isolation of **4** in 90% yield, with no **3** detectable by ^{1}H NMR. To determine the rate of rearrangement of **3** to **4**, a degassed diglyme-d_{14} solution of **3** was sealed in an NMR tube and the solution was heated at 140 °C. Periodic collection of ^{1}H NMR spectra led to the determination of an observed rate constant of 2.6×10^{-4} s^{-1} (half-life ≈ 44 min) for the rearrangement of **3** to **4**. Comparison to the internal standard showed that less than 10% of decomposition to **9** had occurred during the rearrangement.

NMR rate measurements for conversion of **1** to **2** and **3** to **4** were repeated in *ortho*-dichlorobenzene-d_4. While the potential role of diglyme or *ortho*-dichlorobenzene in the mechanisms of these rearrangements cannot be completely discounted, polyhalogenated arenes tend not to coordinate to $Cr(CO)_3$ to form stable compounds. Heating separate samples of **1** and **3** in *ortho*-dichlorobenzene (non-deuterated) led to a rearrangement to **2** in 92% yield and **4** in 89% yield, respectively, with no observed (*ortho*-dichlorobenzene)$Cr(CO)_3$ formed in either case. NMR rate measurements were not performed in hydrocarbon solvents such as decane or decalin since compounds **1–4** are insoluble in these hydrocarbons.

A degassed *ortho*-dichlorobenzene-d_4 solution of **1** was sealed in an NMR tube and the solution was heated at 140 °C. Periodic collection of ^{1}H NMR spectra led to the determination of a rate constant of 1.7×10^{-5} s^{-1} (half-life ≈ 680 min) for the rearrangement of **1** to **2**, with less than 10% of decomposition to **5** occurring during this rearrangement. This is approximately three times slower than the rate measured in diglyme-d_{14}. Similarly, a degassed *ortho*-dichlorobenzene-d_4 solution of **3** was sealed in an NMR tube and the solution was heated at 140 °C. Periodic collection of ^{1}H NMR spectra led to the determination of a rate constant of 2.1×10^{-4} s^{-1} (half-life ≈ 54 min) for the rearrangement of **3** to **4**, showing that the rearrangement is only slightly slower in *ortho*-dichlorobenzene-d_4 than in diglyme-d_{14}. During this rearrangement, decomposition to **9** accounted for less than 10% of material at the end of the reaction.

The results of these measurements show that in diglyme-d_{14} the rearrangement of **3** to **4** is nearly five times faster than the rearrangement of **1** to **2**, and in *ortho*-dichlorobenzene-d_4 the rate enhancement is twelve-fold. This was surprising since the *ortho*-substituted isomer **3** has an arene–phenyl dihedral angle that is nearly 30 degrees greater than that found in the *para*-substituted isomer **1**. Furthermore, *ortho*-bromo $[(\eta^6\text{-}C_6H_5)C_6H_4Br]Cr(CO)_3$ has been previously reported to rearrange more slowly than its *para*-substituted isomer, and *ortho*-methyl $[(\eta^6\text{-}C_6H_5)C_6H_4CH_3]Cr(CO)_3$ does not undergo rearrangement, presumably due to a large 62.01° dihedral angle.[5] It was likewise expected that the extreme conformational twisting of rings, shown both crystallographically and by calculation, would prevent or at least somewhat decrease the observed rate of rearrangement of **3** to **4**. One possible explanation for the observed rate increase is that the *ortho*-amino group in **3** may cause a reduction of the arene–phenyl dihedral angle during the early steps of the mechanism. The amino group could donate electron density to chromium, providing intramolecular stabilization of unsaturated intermediates that would be formed during conversion to **4** (Scheme 5). Though it was not directly observed by NMR, the type of intermediate formed would be similar to $(\eta^6\text{-carbazole})Cr(CO)_3$ or $(\eta^6\text{-pyrrole})Cr(CO)_3$ compounds, which are known.[13,14] By comparison, the *para*-amino group in **1** would not be capable of providing such intramolecular stabilization during the conversion of **1** to **2**.



Scheme 5 Proposed rearrangement *via* a carbazole-like intermediate.

For both **1** to **2** and **3** to **4** the rates of rearrangement appear to be independent of concentration. For conversion of **1** to **2**, when NMR rate measurements in *ortho*-dichlorobenzene-d_4 were repeated with initial concentrations of **1** ranging between 0.03 M and 0.12 M, the observed rate constants varied from 1.3×10^{-5} s^{-1} to 1.7 x10^{-5} s^{-1}. For conversion of **3** to **4**, when NMR rate measurements in *ortho*-dichlorobenzene-d_4 were repeated with concentrations ranging from 0.03 M to 0.12 M, the observed rate constants varied from 1.8×10^{-4} s^{-1} to 2.2×10^{-4} s^{-1}, and higher initial concentrations of **1** or **3** did not necessarily

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Table 1 Crystal data and data collection parameters for **1–4**

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_{15}H_{11}CrNO_3$	$C_{15}H_{11}CrNO_3$	$C_{15}H_{11}CrNO_3$	$C_{15}H_{11}CrNO_3$
Formula weight	305.25	305.25	305.25	305.25
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$Pbca$
a (Å)	6.3121(6)	8.4228(3)	7.2106(9)	7.5427(5)
b (Å)	12.3958(12)	8.8378(3)	28.140(3)	12.7303(9)
c (Å)	16.2900(15)	9.1761(4)	7.1535(8)	26.7851(19)
α (°)	90	96.810(3)	90	90
β (°)	96.9940(10)	108.190(3)	118.175(2)	90
γ (°)	90	90.924(3)	90	90
Volume	1265.1(2) Å^3	643.32(4) Å^3	1279.5(3) Å^3	2571.9(3) Å^3
Z	4	2	4	8
Density (calculated)	1.603 Mg m^{-3}	1.576 Mg m^{-3}	1.585 Mg m^{-3}	1.577 Mg m^{-3}
Absorption coefficient	0.909 mm^{-1}	7.381 mm^{-1}	0.899 mm^{-1}	0.895 mm^{-1}
F(000)	624	312	624	1248
Crystal size/mm	0.41 × 0.39 × 0.35	0.44 × 0.29 × 0.26	0.37 × 0.36 × 0.20	0.47 × 0.42 × 0.19
Theta range for data collection	2.52 to 29.97°	5.05 to 71.55°	2.90 to 26.47°	3.04 to 26.39°
Index ranges	$-8 \le h \le 8$ $-17 \le k \le 16$ $-22 \le l \le 22$	$-8 \le h \le 9$ $-10 \le k \le 10$ $-11 \le l \le 10$	$-9 \le h$ 8 $-35 \le k \le 34$ $-8 \le l \le 8$	$-9 \le h \le 9$, $-15 \le k \le 15$ $-33 \le l \le 33$
Reflections collected	17223	12763	10331	19756
Independent reflections	3465 [R(int) = 0.0242]	2365 [R(int) = 0.0168]	2615 [R(int) = 0.0254]	2629 [R(int) = 0.0288]
Completeness to resolution of 0.84 Å	99.1%	94.2%	99.3%	99.7%
Absorption correction	Multi-scan with SADABS	Empirical with SADABS	Multi-scan with SADABS	Multi-scan with SADABS
Max. and min. transmission	0.7414 and 0.7068	0.2489 and 0.1412	0.8406 and 0.7320	0.8484 and 0.6785
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3465 / 0 / 187	2365 / 0 / 189	2615 / 0 / 187	2629 / 1 / 187
Goodness-of-fit on F^2	1.042	1.013	1.060	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0275$ w$R_2 = 0.0770$	$R_1 = 0.0214$ w$R_2 = 0.0586$	$R_1 = 0.0292$ w$R_2 = 0.0804$	$R_1 = 0.0350$ w$R_2 = 0.0980$
R indices (all data)	$R_1 = 0.0305$ w$R_2 = 0.0795$	$R_1 = 0.0216$ w$R_2 = 0.0587$	$R_1 = 0.0304$ w$R_2 = 0.0813$	$R_1 = 0.0391$ w$R_2 = 0.1011$
Largest diff peak and hole	0.488 and –0.237 e.Å^{-3}	0.288 and –0.238 e.Å^{-3}	0.410 and –0.307 e.Å^{-3}	0.746 and –0.392 e.Å^{-3}

correspond to a faster observed rate of rearrangement. The results of these observations at various concentrations are consistent with a unimolecular reaction and intramolecular haptotropic rearrangement for both **1** and **3**. It is worth noting that the observed rate constants for the *para* isomer **1** are within an order of magnitude of the rate constants previously reported for the series [(η^6-C_6H_5)C_6H_4X]Cr(CO)$_3$ (X = Br, D, CH_3, $SnMe_3$), while the observed rate constants for the *ortho* isomer **3** are an order of magnitude greater.[5]

To further examine the intermolecular *versus* intramolecular nature of the rearrangements of **1** to **2** and **3** to **4**, the NMR rate determinations were repeated in the presence of free aminobiphenyl ligand, with the reaction progress monitored for signs of crossover products. When a solution of **1** in *ortho*-dichlorobenzene-d_4 was heated at 140 °C in the presence of an equimolar amount of **9**, the expected rearrangement to **2** occurred, with an observed rate constant of 1.8×10^{-4} s^{-1}, along with approximately 12% formation of **4** after four half-lives. Similarly, when **3** in *ortho*-dichlorobenzene-d_4 was heated at 140 °C in the presence of an equimolar amount of **5**, the expected rearrangement to **4** occurred, with an observed rate constant of 2.2×10^{-5} s^{-1}, along with approximately 10% formation of **2** after four half-lives. The results of these crossover experiments indicate that while the observed rearrangements of **1** and **3** may involve some intermolecular exchange of ligands, they are predominantly intramolecular.

Conclusions

The observed thermal rearrangements of **1** and **3** demonstrate that haptotropic rearrangements can occur in substituted (η^6-biphenyl)Cr(CO)$_3$ compounds even if calculations or single crystal X-ray crystallography show a large canting of arene rings. At least in the case of the strongly electron-donating amino substituent, electronic factors can predominate over steric effects. These results emphasize that while single crystal X-ray crystallography and DFT calculations can indicate the presence of strong steric effects or unfavorable conformations within a compound, they might not be the ultimate predictor of the possibility of haptotropic rearrangement in solution, where near coplanarity of arene rings can be readily achieved through C–C single bond rotation.[6] At the very least, these results suggest that any upper limit on arene–arene dihedral angle should likely be higher than 22°. The unexpectedly

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accelerated rearrangement of **3** to **4** indicates that in specific cases, where the ring substituent could also coordinate to the metal as a donor ligand, the predicted solid state or calculated arene–arene dihedral angle of the starting compound may be even less important in predicting the possibility of inter-ring haptotropic rearrangement. These results may be especially important for the further design of (η^6-arene)$Cr(CO)_3$ compounds that can act as molecular switches.

Experimental

General methods

Reactions and manipulations of air-sensitive materials were performed under a nitrogen atmosphere using standard glove box and Schlenk techniques. NMR spectra were obtained on a Bruker AC300 spectrometer (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz) and a Bruker Avance III 400 spectrometer (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz). Solution infrared spectra were recorded on a MIDAC Prospect-IR PRS-102 using CsI solution cells. Mass spectra were obtained on an AutoSpec magnetic sector mass spectrometer (Waters (Micromass)). Elemental analyses were performed by Columbia Analytical Services (Tucson, AZ). Hexane, tetrahydrofuran, and diethyl ether were purified using a Vacuum Atmospheres Company 103991 Solvent Purifier immediately prior to use. Di-*n*-butyl ether was stirred over sodium and vacuum distilled prior to use. Chromium hexacarbonyl, 2-aminobiphenyl, 4-aminobiphenyl, acetic anhydride, and 2,6-difluorotoluene, obtained from Aldrich Chemical Company, were used without further purification. $CDCl_3$, acetone-d_6, diglyme-d_{14}, and *ortho*-dichlorobenzene-d_4 were obtained from Cambridge Isotope Laboratories, Inc. and were used without further purification.

Syntheses

[(η^6-C_6H_4-4-NH_2)(C_6H_5)]$Cr(CO)_3$ (2). A mixture of chromium hexacarbonyl (1.00 g, 4.54 mmol) and 4-aminobiphenyl (0.780 g, 4.61 mmol) in di-*n*-butyl ether (27 mL) and tetrahydrofuran (3 mL) was degassed and heated under reflux for 24 h under a nitrogen atmosphere. Solvents were removed by vacuum distillation. Column chromatography (silica gel, 80 : 20 hexane : diethyl ether) of the remaining yellow solid gave a fast-moving yellow band from which **2** was isolated as a yellow, air-stable solid (0.640 g, 46% yield), mp 173–175 °C. ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.55 (m, 2H, aryl), 7.34 (m, 3H, aryl), 6.25 (d, J = 6.9 Hz, 2H, metal-bound aryl), 5.40 (s, 2H, NH_2), 5.24 (d, J = 6.9 Hz, 2H, metal-bound aryl). ^{13}C{^{1}H} NMR (acetone-d_6, 75 MHz) δ 236.1, 129.9, 128.7, 127.4, 126.8, 115.9, 98.3, 78.1, 76.0. IR (CH_2Cl_2) 3451, 3390, 1949, 1866 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}CrNO_3$ 305.0144, found 305.0139. Anal. calcd for $C_{15}H_{11}CrNO_3$: C, 59.02; H, 3.63; N, 4.59. Found: C, 59.14; H, 3.60; N, 4.52.

[(η^6-C_6H_5)(C_6H_4-4-$NHCOCH_3$)]$Cr(CO)_3$ (7). This compound was prepared according to the method described by Gubin.[8] A mixture of chromium hexacarbonyl (2.10 g, 9.55 mmol) and 4-acetamidobiphenyl[15] (2.03 g, 9.62 mmol) in di-*n*-butyl ether (27 mL) and tetrahydrofuran (3 mL) was degassed and heated under reflux for 24 h under a nitrogen atmosphere. Solvents were removed by vacuum distillation. Column chromatography (silica gel, 75 : 25 diethyl ether : hexane) of the remaining oily residue gave two yellow bands. Collection of the second yellow band led to isolation of **7** as an air-stable yellow solid (1.60 g, 48%). ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.95 (s, 1H, NH), 7.94 (d, J = 6.9 Hz, 2H), 7.29 (d, J = 6.9 Hz, 2H), 5.90 (d, J = 6.5 Hz, 2H), 5.73 (t, J = 6.5 Hz, 2H), 5.44 (t, J = 6.5 Hz, 1H), 2.80 (s, 3H, CH_3).

[(η^6-C_6H_5)(C_6H_4-4-NH_2)]$Cr(CO)_3$ (1). This was prepared according to the method described by Gubin.[7] A mixture of **7** (1.10 g, 3.17 mmol) and KOH (3.5 g, 62.4 mmol) in 3 : 1 ethanol : water (25 mL) was degassed and heated at 80 °C for 7 h under a nitrogen atmosphere. The solution was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and purified by column chromatography (silica gel, 50 : 50 hexane : diethyl ether) to give **1** as a yellow air-stable solid (0.354 g, 37%), mp 150–152 °C (lit. 156–157 °C). ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.39 (d, J = 6.9 Hz, 2H), 6.71 (d, J = 6.9 Hz, 2H), 5.95 (d, J = 6.5 Hz, 2H), 5.78 (t, J = 6.5 Hz, 2H), 5.50 (t, J = 6.5 Hz, 1H), 4.96 (s, 2H).

[(η^6-C_6H_4-2-NH_2)(C_6H_5)]$Cr(CO)_3$ (4). A mixture of chromium hexacarbonyl (1.050 g, 4.77 mmol) and 2-aminobiphenyl (0.810 g, 4.79 mmol) in di-*n*-butyl ether (27 mL) and tetrahydrofuran (3 mL) was degassed and heated under reflux for 24 h under a nitrogen atmosphere. Solvents were removed by vacuum distillation. Column chromatography (silica gel, 50 : 50 hexane : diethyl ether) of the remaining yellow solid gave a yellow band from which **4** was isolated as a yellow, air-stable solid (1.28 g, 88% yield), mp 153–156 °C. ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.4–7.6 (m, 5H, aryl), 5.90 (m, 2H, metal-bound aryl), 5.22 (d, J = 6.9 Hz, 1H, metal-bound aryl), 4.02 (m, 3H, NH_2 overlapping with metal-bound aryl). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.4–7.6 (m, 5H, aryl), 5.72 (d, J = 6.9 Hz, 1H, metal-bound aryl), 5.65 (t, J = 6.9 Hz, 1H, metal-bound aryl), 4.89 (d, J = 6.9 Hz, 1H, metal-bound aryl), 4.87 (t, J = 6.9 Hz, 1H, metal-bound aryl), 3.64 (s, 2H, NH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 234.2, 130.6, 129.8, 129.1, 128.7, 107.4, 100.0, 96.3, 92.0, 82.3, 75.3. IR (CH_2Cl_2) 3462, 3362, 1958, 1877 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}CrNO_3$ 305.0144, found 305.0140. Anal. calcd for $C_{15}H_{11}CrNO_3$: C, 59.02; H, 3.63; N, 4.59. Found C, 58.73; H, 3.46; N, 4.54.

[(η^6-C_6H_5)(C_6H_4-2-$NHCOCH_3$)]$Cr(CO)_3$ (11). A mixture of chromium hexacarbonyl (2.00 g, 9.09 mmol) and 2-acetamidobiphenyl (2.00 g, 9.48 mmol) in di-*n*-butyl ether (27 mL) and tetrahydrofuran (3 mL) was degassed and heated under reflux for 24 h under a nitrogen atmosphere. Solvents were removed by vacuum distillation. Column chromatography (silica gel, 75 : 25 diethyl ether : hexane) of the remaining oily residue gave two yellow bands. Collection of the second yellow band led to isolation of **11** as an air-stable yellow solid (1.20 g, 38%). ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.79 (s, 1H, NH), 7.65 (d, J = 6.9 Hz, 1H, aryl), 7.47 (d, J = 6.9 Hz, 1H, aryl), 7.36 (t, J = 6.9 Hz, 1H, aryl), 7.28 (t, J = 6.9 Hz, 1H, aryl), 5.89 (dt, J = 6.5, 1.0 Hz, 2H, metal-bound aryl), 5.73, (m, 3H, metal-bound aryl), 2.87 (s, 3H, CH_3). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, J = 6.9 Hz, 1H, aryl), 7.88 (s, 1H, NH), 7.37 (m, 2H, aryl), 7.21 (t, J = 6.9 Hz, 1 H, aryl), 5.50 (m, 5H, metal-bound aryl), 2.27 (s, 3H, CH_3). ^{13}C{^{1}H} NMR

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($CDCl_3$, 75 MHz) δ 232.0, 168.8, 134.8, 131.3, 130.2, 125.3, 123.7, 108.6, 107.8, 94.6, 92.9, 92.5, 24.8. IR (CH_2Cl_2) 3326, 1973, 1896, 1696 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}CrNO_4$ 347.0250, found 347.0233. Anal. calcd for $C_{17}H_{13}CrNO_4$: C, 58.79; H, 3.77; N, 4.03. Found C, 58.78; H, 3.57; N, 4.41.

[(η⁶-C_6H_5)(C_6H_4-2-NH_2)]$Cr(CO)_3$ (3). A mixture of **11** (1.00 g, 2.88 mmol) and KOH (3.0 g, 53.5 mmol) in 3 : 1 ethanol : water (25 mL) was degassed and heated at 80 °C for 7 h under a nitrogen atmosphere. The solution was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic extracts were dried ($MgSO_4$), filtered, concentrated, and purified by column chromatography (silica gel, 50 : 50 hexane : diethyl ether) to give **3** as a yellow air-stable solid (0.322 g, 37%), mp 128–130 °C. ^{1}H NMR (acetone-d_6, 300 MHz) δ 7.24 (d, J = 6.9 Hz, 1H, aryl), 7.09 (t, J = 6.9 Hz, 1H, aryl), 6.81 (d, J = 6.9 Hz, 1H, aryl), 6.70 (t, J = 6.9 Hz, 1H, aryl), 5.87 (d, J = 6.5 Hz, 2H, metal-bound aryl), 5.68, (m, 3H, metal-bound aryl), 4.82 (s, 2H, NH_2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 (d, J = 6.9 Hz, 1H, aryl), 7.19 (t, J = 6.9 Hz, 1H, aryl), 6.84 (t, J = 6.9 Hz, 1H, aryl), 6.77 (d, J = 6.9 Hz, 1H, aryl), 5.67 (d, J = 6.5, 2H, metal-bound aryl), 5.44, (m, 3H, metal-bound aryl), 4.13 (s, 2H, NH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ = 232.4, 144.4, 131.3, 130.4, 129.5, 119.2, 116.8, 110.3, 94.9, 93.0, 92.5. IR (CH_2Cl_2) 3429, 3330, 1970, 1892 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}CrNO_3$ 305.0144, found 305.0140. Anal. calcd for $C_{15}H_{11}CrNO_3$: C, 59.02; H, 3.63; N, 4.59. Found C, 59.19; H, 3.80; N, 4.53.

Rate constant determinations

In a typical experiment, **1** or **3** (0.010–0.015 g) and the internal standard 2,6-difluorotoluene (0.005–0.010 g), which does not coordinate to $Cr(CO)_3$ even upon prolonged heating at 140 °C, were placed in an NMR tube. Diglyme-d_{14} or *ortho*-dichlorobenzene-d_4 (0.500–0.600 mL) was added to establish a 0.06 M concentration of the chromium arene complex and approximately a 0.06 M concentration of 2,6-difluorotoluene. For concentration dependence studies, the starting masses of **1** or **3** ranged from 0.005–0.008 g for ~0.03 M solutions to 0.020–0.030 g for ~0.12 M solutions. The solution was subjected to three freeze-pump-thaw cycles and sealed under vacuum. An initial ^{1}H NMR spectrum was collected at ambient temperature and the tube was completely immersed in a silicone oil bath with a Glas-Col DigiTrol II thermostat controller maintaining the temperature at 140 ± 0.5 °C. Periodically, the rearrangement reaction was quenched simply by removing the tube from the oil bath, collecting a spectrum, and returning the tube to the bath for continued heating. The process was continued for at least four half-lives. For conversion of **1** to **2**, the disappearance of metal-coordinated arene peaks of **1** was monitored and these peaks were integrated relative to the CH_3 peak of the internal standard. For conversion of **3** to **4**, disappearance of the upfield metal-coordinated arene peak of **3** was monitored, since this peak is well-separated from the metal-coordinated arene peaks of **4**. This peak was integrated relative to the CH_3 peak of the internal standard. For each series of spectra, logarithms (of arene area/initial arene area) were plotted *versus* time to yield a straight line from which half-lives and rate constants were calculated. For each of the NMR-scale rearrangements of **1** to **2** and **3** to **4**, final spectra showed that the free ligands 4-aminobiphenyl and 2-aminobiphenyl, respectively, constituted less than 10% of the products.

Preparative scale rearrangement of 1 to 2

A solution of **1** (0.200 g, 0.656 mmol) in di-*n*-butyl ether (10 mL) in a Schlenk flask equipped with a condenser was degassed and heated under reflux under a nitrogen atmosphere. Periodic monitoring by thin layer chromatography showed gradual disappearance of **1** and formation of **2**. After heating for 16 h, the solvent was removed by vacuum distillation and the remaining yellow residue was taken up in diethyl ether and filtered through a pad of silica gel. Evaporation of the solvent gave **2** as a yellow powder (0.169 g, 85% yield, > 95% pure by ^{1}H NMR).

Preparative scale rearrangement of 3 to 4

A solution of **3** (0.210 g, 0.688 mmol) in di-*n*-butyl ether (10 mL) in a Schlenk flask equipped with a condenser was degassed and heated under reflux under a nitrogen atmosphere. Periodic monitoring by thin layer chromatography showed gradual disappearance of **3** and formation of **4**. After heating for 4 h, the solvent was removed by vacuum distillation and the remaining yellow residue was taken up in diethyl ether and filtered through a pad of silica gel. Evaporation of the solvent gave **4** as a yellow powder (0.190 g, 90% yield, > 95% pure by ^{1}H NMR).

Aminobiphenyl crossover in the rearrangement of 1 to 2

In an NMR tube were placed **1** (0.020 g, 0.066 mmol), 2,6-difluorotoluene (0.010 g, 0.078 mmol), 2-aminobiphenyl (0.012 g, 0.071 mmol), and *ortho*-dichlorobenzene-d_4 (0.550 mL). The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. An initial ^{1}H NMR spectrum was collected at ambient temperature and the tube was completely immersed in a thermostat-controlled oil bath at 140 °C. After 4 half-lives, a ^{1}H NMR spectrum at ambient temperature showed that the rearrangement of **1** to **2** had occurred with approximately 12% formation of the intermolecular crossover product **4**.

Aminobiphenyl crossover in the rearrangement of 3 to 4

In an NMR tube were placed **3** (0.018 g, 0.059 mmol), 2,6-difluorotoluene (0.010 g, 0.078 mmol), 4-aminobiphenyl (0.011 g, 0.065 mmol), and *ortho*-dichlorobenzene-d_4 (0.490 mL). The tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. An initial ^{1}H NMR spectrum was collected at ambient temperature, and the tube was completely immersed in a thermostat-controlled oil bath at 140 °C. After 4 half-lives, a ^{1}H NMR spectrum at ambient temperature showed that the rearrangement of **3** to **4** had occurred with approximately 10% formation of the intermolecular crossover product **2**.

X-ray crystallographic analysis

Under a nitrogen atmosphere at ambient temperature, slow evaporation of diethyl ether solutions of **1–4** led to the formation of single crystals of each compound suitable for X-ray crystallographic analysis. Crystallographic and data collection parameters are provided in Table 1. Molecular drawings of **1–4** showing the atom numbering schemes are provided in Fig. 1, 2, 3, and 4, respectively. Additional crystallographic details are available in the ESI.†

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