Supporting Information

Haptotropic Rearrangement in Tricarbonylchromium Complexes of

2-Aminobiphenyl and 4-Aminobiphenyl

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X-ray Crystallographic Studies. Yellow crystals of each compound with approximate dimensions (**1**, 0.41 x 0.39 x 0.35 mm³; **2**, 0.44 x 0.29 x 0.26 mm³; **3**, 0.37 x 0.36 x 0.20 mm³; **4**, 0.47 x 0.42 x 0.19 mm³) were selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount[©] for **1** and **2** or a nylon loop for **3** and **4**. In all cases, the crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. For **1**, **3**, and **4** the crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_a ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. For **2** the crystal evaluation and data collection were performed on a Bruker MART APEXII diffractometer with Cu K_a ($\lambda = 1.54178$ Å) radiation and the diffractometer to crystal distance of 4.03 cm.

For 1: The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 164 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 9917 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.71 Å. A total of 17223 data were harvested by collecting three sets of frames with 0.36° scans in ω and one set with 0.45° scans in φ with an exposure time 22 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.¹ The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement.² A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps.² All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms attached to carbon atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The hydrogen atoms attached to nitrogen atoms were located in the difference map and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There is one intermolecular hydrogen bonding interaction present. The final least-squares refinement of 187 parameters against 3465 data resulted in residuals *R* (based on F^2 for $I \ge 2\sigma$) and *wR* (based on F^2 for all data) of 0.0275 and 0.0795, respectively. The final difference Fourier map was featureless. The molecular diagram is drawn with 50% probability ellipsoids.

For 2: The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 41 frames collected at intervals of 0.6° in a 25° range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 9962 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.82 Å. A total of 12763 data were harvested by collecting 15 sets of frames with 0.7° scans in ω with an exposure time 4-10 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.¹ The systematic absences in the diffraction data were consistent for the space groups $P\overline{1}$ and P1. The E-statistics strongly suggested the centrosymmetric space group P_1 that yielded chemically reasonable and computationally stable results of refinement.^{2,3}. A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms attached to C atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The amine H atoms were refined freely. The final least-squares refinement of 189 parameters against 2365 data resulted in residuals R (based on F^2 for $I \ge 2\sigma$) and wR (based on F^2 for all data) of 0.0214 and 0.0587, respectively. The final difference Fourier map was featureless. The molecular diagram is drawn with 50% probability ellipsoids.

For **3**: The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 106 reflections was obtained. The reflections were

successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 7505 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 10331 data were harvested by collecting three sets of frames with 0.25° scans in ω with an exposure time 15 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.⁴ The systematic absences in the diffraction data were uniquely consistent for the space group $P_{21/c}$ that yielded chemically reasonable and computationally stable results of refinement.⁴ A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms attached to carbon atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. All hydrogen atoms attached to nitrogen atoms were located in the difference map but were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 187 parameters against 2615 data resulted in residuals R (based on F^2 for $I \ge 2\sigma$) and wR (based on F^2 for all data) of 0.0292 and 0.0813, respectively. The final difference Fourier map was featureless. The molecular diagram is drawn with 50% probability ellipsoids.

For 4: The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 15 seconds per frame. A total of 112 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 7826 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 19756 data were harvested by collecting three sets of frames with 0.25° scans in ω with an exposure time 24 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.⁴ The systematic absences in the diffraction data were uniquely consistent for the space group *Pbca* that yielded chemically reasonable and computationally stable results of refinement.⁴ A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms except the amino group hydrogens were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Atom H(1N) and H(2N) were refined as equidistant from atom N. The final least-squares refinement of 187 parameters against 2629 data resulted in residuals *R* (based on F^2 for $I \ge 2\sigma$) and *wR* (based on F^2 for all data) of 0.0350 and 0.1011, respectively. The final difference Fourier map was featureless. The ORTEP diagram is drawn with 50% probability ellipsoids.

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(3) Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. "OLEX2: a complete structure solution, refinement and analysis program". *J. Appl. Cryst.* **2009**, *42*, 339-341.

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