

# Organotransition Metal Compounds for Photonics: Syntheses and Structures of a Series of (Nitrostilbene)chromium Tricarbonyl Complexes

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Treatment of  $\text{Cr}(\text{CO})_6$  with 4-substituted benzaldehyde dialkyl acetals provides the new arene complexes  $[4\text{-RC}_6\text{H}_4\text{CH}(\text{OR}')_2]\text{Cr}(\text{CO})_3$  ( $\text{R} = \text{Me}_2\text{N}, \text{H}, \text{Me}_3\text{Si}, \text{F}_3\text{C}$ ;  $\text{R}' = \text{Me}, \text{Et}$ ), which are readily hydrolyzed to the benzaldehyde complexes  $(4\text{-RC}_6\text{H}_4\text{CHO})\text{Cr}(\text{CO})_3$ . These react with the Wittig reagent  $\text{Bu}_3\text{P}=\text{CHC}_6\text{H}_4\text{NO}_2$  to provide nitrostilbene complexes  $(4\text{-RC}_6\text{H}_4\text{CH}=\text{CH}-4'\text{-C}_6\text{H}_4\text{NO}_2)\text{Cr}(\text{CO})_3$ , a new class of organometallic complexes with potential nonlinear optics applications. The *E* isomers of the nitrostilbene compounds may be separated from the *Z* isomers; the former were characterized by spectroscopic and crystallographic means. For  $(4\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}=\text{CH}-4'\text{-C}_6\text{H}_4\text{NO}_2)\text{Cr}(\text{CO})_3$ , **13E**, monoclinic,  $P2_1/c$ ,  $a = 7.710(3) \text{ \AA}$ ,  $b = 13.953(3) \text{ \AA}$ ,  $c = 17.016(4) \text{ \AA}$ ,  $\beta = 99.80(3)^\circ$ , and  $Z = 4$ . For  $(\text{C}_6\text{H}_5\text{CH}=\text{CH}-4'\text{-C}_6\text{H}_4\text{NO}_2)\text{Cr}(\text{CO})_3$ , **14E**, monoclinic,  $P2_1/c$ ,  $a = 10.141(4) \text{ \AA}$ ,  $b = 13.767(3) \text{ \AA}$ ,  $c = 11.768(3) \text{ \AA}$ ,  $\beta = 108.82(3)^\circ$ , and  $Z = 4$ . For  $(4\text{-Me}_3\text{SiC}_6\text{H}_4\text{CH}=\text{CH}-4'\text{-C}_6\text{H}_4\text{NO}_2)\text{Cr}(\text{CO})_3$ , **15E**, orthorhombic,  $Pbca$ ,  $a = 11.745(8) \text{ \AA}$ ,  $b = 15.644(4) \text{ \AA}$ ,  $c = 22.255(6) \text{ \AA}$ , and  $Z = 8$ . For  $(4\text{-F}_3\text{CC}_6\text{H}_4\text{CH}=\text{CH}-4'\text{-C}_6\text{H}_4\text{NO}_2)\text{Cr}(\text{CO})_3$ , **16E**, monoclinic,  $P2_1/c$ ,  $a = 18.305(6) \text{ \AA}$ ,  $b = 12.641(4) \text{ \AA}$ ,  $c = 15.208(5) \text{ \AA}$ ,  $\beta = 92.59(3)^\circ$ , and  $Z = 8$ . The structural data show that the stilbene fragments maintain planarity with only slight deviations attributed to crystal packing forces and thermal motion. The absorption spectra of these deep red compounds are interpreted in light of theoretical studies of models.

The application of organotransition metal chemistry to photonics and nonlinear optics (NLO) is in its infancy, but several groups have already reported studies demonstrating that selected organometallic compounds exhibit significant hyperpolarizabilities. While the greatest amount of effort has been devoted to molecules based on the ferrocene moiety and related species,<sup>1-7</sup>  $\beta$  (first order hyperpolarizability; related to second harmonic generation) and/or  $\gamma$  (second order hyperpolarizability; related to third harmonic generation) values of compounds as diverse as  $\text{Cp}_2\text{ZrX}_2$  ( $\text{X} = \text{halide}, \text{acetylide}$ ),<sup>8</sup>  $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{-Cr}(\text{CO})_3$ ,<sup>9</sup>  $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-E})\text{-CCH}=\text{CHC}_6\text{H}_4\text{-}p\text{-NMe}_2)]^+\text{CF}_3\text{SO}_3^-$ ,<sup>10</sup> and  $(\text{RC}\equiv\text{C})\text{-Pt}(\text{PR}_3)_2\text{-C}(\text{C}=\text{CR})$ <sup>11</sup> have been obtained. These studies have generally demonstrated, as is true in purely organic molecules, that molecules incorporating conjugated  $\pi$  systems show larger nonlinearities than those which do not.

Donor-acceptor  $\alpha,\omega$ -diphenyl polyenes  $\text{D-Ph-(CH=CH)}_n\text{-Ph-A}$  are among the many organic molecules which display sizable  $\beta$  values.<sup>12-15</sup> Compounds of this general type appear ideal for attachment to transition metals, since a wide range of (arene)metal complexes exist.<sup>16,17</sup> One might predict such attachment to provide two useful effects: one, the poor solubilities exhibited by such molecules as the chain length increases may be improved by the addition of a "greasy" metal fragment, and two, proper matching of the donor-acceptor characteristics of the transition metal moiety to those of a diphenyl polyene ligand could lead to enhanced NLO response. Exemplifying the latter point, calculations indicate that (4-amino-4'-nitrostilbene)tris(amine)chromium,  $(\text{H}_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2)\text{Cr}(\text{NH}_3)_3$ , will exhibit a  $\beta$  value approximately 6 times that of the free stilbene.<sup>18</sup>

The widest class by far of (arene)metal compounds is the (arene)chromium tricarbonyl group  $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_3$ , of which over 1000 examples exist.<sup>19</sup> Because of their ready preparation and typical air and thermal

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stability, several examples of these were among the first organotransition metal complexes to be investigated for NLO activity.<sup>9</sup> Frazier and co-workers found that only 11 of 22 (arene)chromium tricarbonyls exhibited solid-state second harmonic generation (SHG); they surmised that the other chromium compounds crystallized in centrosymmetric space groups, prohibiting them from creating the bulk polarity necessary to influence the incident light. Regardless, three of the (arene)chromium tricarbonyls displayed significant SHG, suggesting that correctly designed molecules of this type could act as useful NLO materials.

More recently, Cheng and co-workers observed  $\beta$  for six (arene)chromium tricarbonyls by the EFISH technique,<sup>20</sup> which can be applied to any polar molecule. The values determined were small and negative, requiring the somewhat surprising conclusion that the chromium tricarbonyl fragment functions as a ground state acceptor, but an excited state donor. Intriguingly, the stilbene complex (*E*)-(C<sub>6</sub>H<sub>5</sub>CH=CHC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub> displayed a  $\beta$  twice as large as that of any other system, again pointing out the need for conjugated  $\pi$  systems if molecules are to behave as good NLO materials.

The above-cited work argues that synthesizing (arene)chromium tricarbonyl complexes which will find use as NLO materials will prove demanding. However, their atypical air and thermal stability and the proven capacity of the chromium tricarbonyl moiety for improving the solubility of conjugated and polymeric arene-containing organics<sup>21-23</sup> make such species attractive targets. We have therefore begun a program designed to generate a variety of  $\alpha,\omega$ -diphenyl polyene transition metal compounds, initially involving the synthesis of (stilbene)chromium tricarbonyls. A few examples already exist,<sup>24,25</sup> including the parent (C<sub>6</sub>H<sub>5</sub>CH=CHC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub>,<sup>26</sup> but these typically employ donor-donor stilbenes such as 4,4'-dimethoxystilbene rather than the donor-acceptor systems preferred in NLO applications. Drefahl and co-workers showed that Wittig reagents readily attack the aldehyde function of (C<sub>6</sub>H<sub>5</sub>CHO)Cr(CO)<sub>3</sub>,<sup>26</sup> we have taken advantage of this methodology to prepare and characterize several (nitrostilbene)Cr(CO)<sub>3</sub> compounds. This paper describes our results.

## Experimental Section

**General Information.** Unless otherwise noted, all reactions and manipulations were performed under an inert atmosphere, either through standard Schlenk techniques or in a Vacuum Atmospheres glovebox equipped with an MO-40-2 Dri-Train. Evaporations of solvent were performed *in vacuo*. Reagents were used as received from commercial sources; solvents were purified and freed from dissolved oxygen and water by standard techniques. Silica gel (70-230 mesh, Aldrich) and neutral alumina I (Merck) were heated at 100 °C under vacuum overnight.

Benzaldehydes were converted to the dimethyl and diethyl acetals by a reported method.<sup>27</sup> The phosphonium salt Bu<sub>3</sub>P-

(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)Cl was prepared by warming a mixture of PBu<sub>3</sub> and ClCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> to 70 °C overnight, cooling the resultant slurry to room temperature, filtering out the beige powder, washing it with toluene and pentane, and drying it under vacuum.<sup>12</sup>

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker WA-200 spectrometer at ambient temperature; chemical shifts are reported as ppm downfield of tetramethylsilane. IR spectra were obtained on a Perkin-Elmer 1310 spectrometer; the data appear in Table 7. Absorption spectra were obtained on a Cary 3 spectrometer (Varian) in spectroscopy grade CH<sub>2</sub>Cl<sub>2</sub> vacuum distilled from 3-Å molecular sieves; the data appear in Table 8. Elemental analyses were performed by Ms. Paulanne Rider, NIU Chemistry Analytical Services.

[4-R<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH(OR')<sub>2</sub>]Cr(CO)<sub>3</sub> (R = Me<sub>2</sub>N, H, Me<sub>2</sub>Si, F<sub>3</sub>C; R' = Me, Et). All these were prepared by minor variations of the method of Mahaffy and Pauson.<sup>28</sup> Occasionally, 5-10% v/v butyl acetate<sup>29</sup> (Me<sub>2</sub>Si systems) or 5-10% v/v dioxane (F<sub>3</sub>C systems) was added to the THF/Bu<sub>2</sub>O solvent mixture as a reaction catalyst. The solutions were heated overnight at 135-140 °C and then at 150-160 °C (reflux) for the periods specified. An air-cooled condenser was employed;<sup>30</sup> this allowed the THF to stay sufficiently warm in the condenser to efficiently wash down sublimed Cr(CO)<sub>6</sub>. Evaporation of the solvent at 60 °C and pumping at this temperature for 2 h typically left the product as a dark oil or yellow solid uncontaminated by Cr(CO)<sub>6</sub>. The material was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the solution filtered through Celite. The solvent was then evaporated, generally giving the product as a yellow or yellow-orange solid. This was triturated with pentane, filtered out, and dried to give analytically pure material. Cooling of the mother liquor generally provided a second crop of material.

These compounds decompose very slowly (half-life of several weeks) in the air as solids, but much more rapidly (hours to days) in solution.

[4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub>, 1. Heated for 36 h at reflux. Yield: 78%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.78 (d, *J*<sub>HH</sub> = 7.2 Hz, 2H, Ph), 4.96 (s, 1H, CH), 4.77 (d, *J*<sub>HH</sub> = 7.2 Hz, 2H, Ph), 3.38 (s, 6H, OCH<sub>3</sub>), 2.88 (s, 6H, NMe<sub>2</sub>). Anal. Calcd for C<sub>14</sub>H<sub>17</sub>CrNO<sub>5</sub>: C, 50.76; H, 5.17; N, 4.23. Found: C, 50.56; H, 5.25; N, 4.10.

[4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(OEt)<sub>2</sub>]Cr(CO)<sub>3</sub>, 2. Heated for 48 h at reflux. Yield: 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.82 (d, *J*<sub>HH</sub> = 7.1 Hz, 2H, Ph), 5.04 (s, 1H, CH), 4.76 (d, *J*<sub>HH</sub> = 7.1 Hz, 2H, Ph), 3.63 (m, 4H, OCH<sub>2</sub>), 2.86 (s, 6H, NMe<sub>2</sub>), 1.23 (t, *J*<sub>HH</sub> = 7.0 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  234.2 (s, CO), 135.2 (s, ipso C, probably attached to N), 99.9 (d, *J*<sub>CH</sub> = 163 Hz, acetal CH), 98.7 (s, ipso C, probably attached to C), 95.5 (d, *J*<sub>CH</sub> = 173 Hz, Ph ortho or meta C), 73.2 (d, *J*<sub>CH</sub> = 173 Hz, Ph ortho or meta C), 62.4 (t, *J*<sub>CH</sub> = 143 Hz, OCH<sub>2</sub>), 39.6 (q, *J*<sub>CH</sub> = 135 Hz, NMe<sub>2</sub>), 15.1 (q, *J*<sub>CH</sub> = 126 Hz, CH<sub>3</sub>). Anal. Calcd for C<sub>16</sub>H<sub>21</sub>CrNO<sub>5</sub>: C, 53.48; H, 5.89; N, 3.90. Found: C, 53.79; H, 5.90; N, 3.79.

[C<sub>6</sub>H<sub>5</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub>, 3. Heated for 90 h at reflux. Yield: 92%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.52→5.23 (complex m, 5H, Ph), 5.11 (s, 1H, CH), 3.38 (s, 6H, OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  232.5 (s, CO), 107.3 (s, ipso C), 101.2 (d, *J*<sub>CH</sub> = 166 Hz, acetal CH), 92.2 (d, *J*<sub>CH</sub> = 175 Hz, Ph para C), 92.1 (d, *J*<sub>CH</sub> = 175 Hz, Ph ortho or meta C), 91.3 (d, *J*<sub>CH</sub> = 175 Hz, Ph ortho or meta C), 53.2 (q, *J*<sub>CH</sub> = 143 Hz, OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (dmso-*d*<sub>6</sub>):  $\delta$  233.4 (s, CO), 109.1 (s, ipso C), 101.1 (s, acetal CH), 94.5 (s, Ph para C), 94.0 (s, Ph ortho or meta C), 92.8 (s, Ph ortho or meta C), 53.5 (s, OCH<sub>3</sub>). Anal. Calcd for C<sub>12</sub>H<sub>12</sub>CrNO<sub>5</sub>: C, 50.01; H, 4.20. Found: C, 49.81; H, 4.06.

[C<sub>6</sub>H<sub>5</sub>CH(OEt)<sub>2</sub>]Cr(CO)<sub>3</sub>, 4. Heated for 90 h at reflux. Yield: 60%. This compound has been reported several times;<sup>26,31</sup> we have collected the following additional data. <sup>13</sup>C{<sup>1</sup>H} NMR

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(dmso-*d*<sub>6</sub>):  $\delta$  232.7 (s, CO), 109.0 (s, ipso C), 98.9 (s, acetal CH), 93.5 (s, Ph para C), 92.7 (s, Ph ortho or meta C), 92.1 (s, Ph ortho or meta C), 61.4 (s, OCH<sub>2</sub>), 14.7 (s, CH<sub>3</sub>).

[4-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub>, 5. Heated for 56 h at reflux. Yield: 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.45 (d, *J*<sub>HH</sub> = 6.6 Hz, 2H, Ph), 5.34 (d, *J*<sub>HH</sub> = 6.6 Hz, 2H, Ph), 5.18 (s, 1H, CH), 3.38 (s, 6H, OCH<sub>3</sub>), 0.28 (s, 9H, SiMe<sub>3</sub>). Anal. Calcd for C<sub>15</sub>H<sub>20</sub>CrO<sub>5</sub>-Si: C, 49.99; H, 5.59. Found: C, 49.77; H, 5.71.

[4-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH(OEt)<sub>2</sub>]Cr(CO)<sub>3</sub>, 6. Heated for 48 h at reflux. Yield: 95%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.41 (AB quartet, near d, *J*<sub>HH</sub> = 6.9 Hz, 4H, both Ph), 5.28 (s, 1H, CH), 3.65 (m, 4H, OCH<sub>2</sub>), 1.24 (t, *J*<sub>HH</sub> = 7.0 Hz, 6H, CH<sub>3</sub>), 0.28 (s, 9H, SiMe<sub>3</sub>). Anal. Calcd for C<sub>17</sub>H<sub>24</sub>CrO<sub>5</sub>-Si: C, 52.56; H, 6.23. Found: C, 52.18; H, 6.33.

[4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub>, 7. Heated for 96 h at reflux. Yield: 67% [83% based on unreacted Cr(CO)<sub>6</sub>]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.66 (d, *J*<sub>HH</sub> = 6.8 Hz, 2H, Ph), 5.43 (d, *J*<sub>HH</sub> = 6.8 Hz, 2H, Ph), 5.17 (s, 1H, CH), 3.38 (s, 6H, OCH<sub>3</sub>). Anal. Calcd for C<sub>13</sub>H<sub>11</sub>CrF<sub>3</sub>O<sub>5</sub>: C, 43.83; H, 3.11. Found: C, 44.23; H, 2.89.

[4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CH(OEt)<sub>2</sub>]Cr(CO)<sub>3</sub>, 8. Heated for 72 h at reflux. Yield: 65%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.66 (d, *J*<sub>HH</sub> = 6.8 Hz, 2H, Ph), 5.49 (d, *J*<sub>HH</sub> = 6.8 Hz, 2H, Ph), 5.28 (s, 1H, CH), 3.65 (m, 4H, OCH<sub>2</sub>), 1.25 (t, *J*<sub>HH</sub> = 7.1 Hz, 6H, CH<sub>3</sub>). Anal. Calcd for C<sub>15</sub>H<sub>15</sub>-CrF<sub>3</sub>O<sub>5</sub>: C, 46.88; H, 3.93. Found: C, 46.80; H, 3.69.

[4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO]Cr(CO)<sub>3</sub>, 9. [4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(OEt)<sub>2</sub>]Cr(CO)<sub>3</sub> (2, 5.39 g, 15.0 mmol) was dissolved in 75 mL of THF, and the solution was treated dropwise with 0.5 mL of 1.0 M HCl (ca. 30 mmol of H<sub>2</sub>O).<sup>32</sup> The yellow solution became cloudy and orange. It was stirred vigorously at room temperature for 24 h, during which it reddened. The solution was then treated with a small amount of Na<sub>2</sub>CO<sub>3</sub> and a small amount of CaCl<sub>2</sub>. The mixture was stirred for 1 h and then filtered through Celite packed in a D frit. The filter cake was washed with THF until the washings were colorless. The volatiles were evaporated from the combined extracts, and the resulting orange solid was pumped on for 2 h. The solid was triturated with pentane, filtered out, washed with pentane, and dried to give analytically pure [4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO]Cr(CO)<sub>3</sub> (4.11 g, 14.4 mmol, 96%). This compound has been prepared previously, but only a partial <sup>13</sup>C{<sup>1</sup>H} NMR spectrum was reported.<sup>31</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.39 (s, 1H, CHO), 6.08 (d, *J*<sub>HH</sub> = 6.3 Hz, 2H, Ph), 4.87 (d, *J*<sub>HH</sub> = 6.3 Hz, 2H, Ph), 2.86 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  231.4 (s, CO), 187.0 (s, CHO), 136.8 (s, ipso C, probably attached to N), 96.4 (s, Ph ortho or meta C), 89.1 (s, ipso C probably attached to C), 73.0 (s, Ph ortho or meta C), 39.0 (s, NMe<sub>2</sub>). Anal. Calcd for C<sub>12</sub>H<sub>11</sub>-CrNO<sub>4</sub>: C, 50.53; H, 3.89; N, 4.91. Found: C, 50.69; H, 4.02; N, 5.14.

[C<sub>6</sub>H<sub>5</sub>CHO]Cr(CO)<sub>3</sub>, 10. [C<sub>6</sub>H<sub>5</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub> (3, 5.76 g, 20.0 mmol) was dissolved in 75 mL of THF, and the solution treated dropwise with 1.4 mL of 1.0 M HCl (ca. 80 mmol of H<sub>2</sub>O). The yellow solution became cloudy and orange. It was stirred vigorously at room temperature for 24 h, during which it reddened. The solution was then treated with 1 g of Na<sub>2</sub>CO<sub>3</sub> and 10 g of CaCl<sub>2</sub>. The mixture was stirred for 1 h and then filtered through Celite packed in a D frit. The filter cake was washed with THF until the washings were colorless. The volatiles were evaporated from the combined extracts, and the resulting red solid was pumped on for 2 h. The solid was triturated with pentane, filtered out, and dried to give analytically pure [C<sub>6</sub>H<sub>5</sub>CHO]Cr(CO)<sub>3</sub> (4.73 g, 19.5 mmol, 98%). This compound has been prepared previously.<sup>26</sup> The reported <sup>1</sup>H NMR spectral data<sup>31</sup> are incorrect. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.45 (s, 1H, CHO), 5.94 (d, *J*<sub>HH</sub> = 6.0 Hz, 2H, ortho Ph), 5.69 (t, *J*<sub>HH</sub> = 6.3 Hz, 1H, para H), 5.28 ("t" (actually a dd), *J*<sub>HH</sub> = 6.4 Hz, 2H, meta Ph).

[4-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CHO]Cr(CO)<sub>3</sub>, 11. [4-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub> (5, 10.8 g, 30.0 mmol) was dissolved in 150 mL of THF, and the solution was treated dropwise with 0.75 mL of 1.0 M CF<sub>3</sub>SO<sub>3</sub>H (ca. 42 mmol of H<sub>2</sub>O). The yellow solution was stirred

vigorously at room temperature for 42 h, during which it reddened. The solution was then treated with 1 g of Na<sub>2</sub>CO<sub>3</sub> and 10 g of MgSO<sub>4</sub>. The mixture was stirred for 1 h and then filtered through Celite packed in a D frit. The filter cake was washed with THF until the washings were colorless. The volatiles were evaporated from the combined extracts, and the resulting red oil was pumped on for 2 h.

At this point, the <sup>1</sup>H NMR spectrum of the material showed it to contain ca. 10% unreacted starting material. It was therefore redissolved in 150 mL of THF, and the solution was treated with 0.4 mL of 1.0 M CF<sub>3</sub>SO<sub>3</sub>H and stirred for 36 h. The solution was neutralized, dehydrated, and filtered as above. Evaporation of solvent gave a red oil. To this was added 50 mL of heptane. The mixture was stirred for 10 min, whereupon the heptane was evaporated, giving an orange solid. This was pumped on for 15 min, triturated with (Me<sub>3</sub>Si)<sub>2</sub>O, filtered out, washed with (Me<sub>3</sub>-Si)<sub>2</sub>O, and dried to give analytically and spectroscopically pure [4-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CHO]Cr(CO)<sub>3</sub> (9.16 g, 29.1 mmol, 97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.54 (s, 1H, CHO), 5.82 (d, *J*<sub>HH</sub> = 6.7 Hz, 2H, Ph), 5.33 (d, *J*<sub>HH</sub> = 6.7 Hz, 2H, Ph), 0.33 (s, 9H, SiMe<sub>3</sub>). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>CrO<sub>4</sub>-Si: C, 49.67; H, 4.49. Found: C, 47.65; H, 4.28. We have attempted several analyses of different batches of material, and consistently find the carbon analysis to be 2% low. This appears to result partly from the extremely hygroscopic nature of the material; IR spectra invariably exhibit large broad bands near 3500 cm<sup>-1</sup>, indicating the presence of water in the samples. Since water does not inhibit the Wittig reaction, we have not attempted to remove it completely.

[4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CHO]Cr(CO)<sub>3</sub>, 12. [4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CH(OMe)<sub>2</sub>]Cr(CO)<sub>3</sub> (7, 6.40 g, 18.0 mmol) was dissolved in 80 mL of THF, and the solution was treated dropwise with 0.4 mL of 1.0 M CF<sub>3</sub>SO<sub>3</sub>H (ca. 22 mmol of H<sub>2</sub>O). The yellow solution was stirred vigorously at room temperature for 5 days, during which it reddened. The solution was then treated with 1 g of Na<sub>2</sub>CO<sub>3</sub> and 10 g of MgSO<sub>4</sub>. The mixture was stirred for 1 h and then filtered through Celite packed in a D frit. The filter cake was washed with THF until the washings were colorless. The volatiles were evaporated from the combined extracts, and the resulting red solid was pumped on for 2 h.

At this point, the <sup>1</sup>H NMR spectrum of the material showed it to contain ca. 20% unreacted starting material. It was therefore redissolved in 80 mL of THF, and the solution was treated with 0.40 mL of 1.0 M CF<sub>3</sub>SO<sub>3</sub>H and stirred for 3 days. The solution was neutralized, dehydrated, and filtered as above. Evaporation of solvent gave a red solid, which was triturated with pentane, filtered out, and dried to give analytically and spectroscopically pure [4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CHO]Cr(CO)<sub>3</sub> (4.70 g, 15.2 mmol, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.53 (s, 1H, CHO), 5.94 (d, *J*<sub>HH</sub> = 6.3 Hz, 2H, Ph), 5.57 (d, *J*<sub>HH</sub> = 6.3 Hz, 2H, Ph). Anal. Calcd for C<sub>11</sub>H<sub>5</sub>-CrF<sub>3</sub>O<sub>4</sub>: C, 42.60; H, 1.62. Found: C, 42.86; H, 1.73.

(E)-[4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH=CH-4'-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]Cr(CO)<sub>3</sub>, 13E, and (Z)-[4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH=CH-4'-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]Cr(CO)<sub>3</sub>, 13Z. An ethanolic solution of 9 (2.85 g, 10.0 mmol) and Bu<sub>3</sub>P(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)-Cl (3.93 g, 10.5 mmol) was treated dropwise with an ethanolic solution of NaOEt (1 M, 11.0 mL, 11.0 mmol). The reaction mixture darkened and then lightened as a bright red-orange solid precipitated. After complete addition of base, the slurry was stirred overnight at room temperature and then 1 h at 90 °C. The mixture was then cooled to room temperature, and the solid was filtered out, washed with cold ethanol, and dried, giving analytically and isomerically pure 13E (1.40 g, 3.46 mmol, 35%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.19 (d, *J*<sub>HH</sub> = 8.9 Hz, 2H, ortho or meta PhNO<sub>2</sub>), 7.54 (d, *J*<sub>HH</sub> = 8.9 Hz, 2H, ortho or meta PhNO<sub>2</sub>), 6.80 (AB quartet, *J*<sub>HH</sub> = 16.2 Hz, 2H, olefin CH), 5.84 (d, *J*<sub>HH</sub> = 7.3 Hz, 2H, ortho or meta PhNMe<sub>2</sub>), 4.69 (d, *J*<sub>HH</sub> = 7.3 Hz, 2H, ortho or meta PhNMe<sub>2</sub>), 2.87 (s, 6H, NMe<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>CrN<sub>2</sub>O<sub>5</sub>: C, 56.44; H, 3.99; N, 6.93. Found: C, 56.38; H, 3.95; N, 7.05.

The solvent was evaporated from the mother liquor, giving a red solid (1.71 g). <sup>1</sup>H NMR spectroscopic analysis of this solid demonstrated it to be a mixture of O=PBU<sub>3</sub>, 13E, and 13Z. The mixture was chromatographed on neutral alumina I, eluting first with pentane to remove Bu<sub>3</sub>P=O. The column was then eluted

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with  $\text{CH}_2\text{Cl}_2$ . A red band with a considerable tail separated from the material at the top of the column and was collected. The solvent was evaporated from this fraction, giving a sample of the pure *Z* isomer **13Z** (0.500 g, 1.24 mmol, 12%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.16 (d,  $J_{\text{HH}} = 8.8$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 7.48 (d,  $J_{\text{HH}} = 8.8$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 6.51 (d,  $J_{\text{HH}} = 12.0$  Hz, 1H, olefinic CH), 6.23 (d,  $J_{\text{HH}} = 12.0$  Hz, 1H, olefin CH), 5.48 (d,  $J_{\text{HH}} = 7.3$  Hz, 2H, ortho or meta  $\text{PhNMe}_2$ ), 4.69 (d,  $J_{\text{HH}} = 7.3$  Hz, 2H, ortho or meta  $\text{PhNMe}_2$ ), 2.87 (s, 6H,  $\text{NMe}_2$ ). Anal. Calcd for  $\text{C}_{19}\text{H}_{16}\text{CrN}_2\text{O}_5$ : C, 56.44; H, 3.99; N, 6.93. Found: C, 56.14; H, 4.00; N, 7.00.

The column was last eluted with THF, giving a deep red fraction. Evaporation of the solvent from this gave material shown by  $^1\text{H NMR}$  spectroscopy to be a mixture of **13E** and **13Z** isomers, enriched in *E* isomer from the initial mixture. This material was not further separated.

(*E*)-[ $\text{C}_6\text{H}_5\text{CH}=\text{CH}-4'-\text{C}_6\text{H}_4\text{NO}_2$ ] $\text{Cr}(\text{CO})_3$ , **14E**. A slurry of 10 (4.84 g, 20.0 mmol) and  $\text{Bu}_3\text{P}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2)\text{Cl}$  (8.23 g, 22.0 mmol) in THF (175 mL) was warmed to 50 °C, whereupon solid  $\text{NaOEt}$  (1.50 g, 22.0 mmol) was added in small portions over 30 min by means of a powder addition funnel. The solid slowly dissolved, and the solution reddened. After complete addition of base, the mixture was stirred overnight at 50–60 °C. The resultant solution was cooled to room temperature and then transferred by cannula into 1500 mL of argon-sparged water. The yellowish-brown slurry was stirred vigorously for 1.5 h, whereupon the liquid was removed by cannula. The dark, sticky semisolid which remained was pumped on in a vacuum oven at room temperature for 4 h. It was then triturated with heptane; the heptane extracts were discarded. The material was then extracted into toluene, and the toluene extracts were filtered through a silica column (8 cm  $\times$  3 cm) packed in a frit. The column was washed with toluene until the eluent was nearly colorless (ca. 1200 mL total), giving a deep red solution. The solvent was evaporated to 150 mL, at which point the bright red solid which had precipitated was filtered out, washed with pentane, and dried, giving analytically and isomerically pure **14E** (2.58 g, 7.14 mmol, 36%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.22 (d,  $J_{\text{HH}} = 8.9$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 7.59 (d,  $J_{\text{HH}} = 8.9$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 6.87 (AB quartet,  $J_{\text{HH}} = 16.2$  Hz, 2H, olefin CH), 5.58–5.29 (m, 5H, ortho, meta, and para Ph). Anal. Calcd for  $\text{C}_{17}\text{H}_{11}\text{CrNO}_5$ : C, 56.52; H, 3.07; N, 3.88. Found: C, 56.86; H, 2.97; N, 4.22.

The solvent was evaporated from the mother liquor, giving a red solid (1.71 g, 4.73 mmol, 24%).  $^1\text{H NMR}$  spectroscopic analysis of this solid demonstrated it to be a 1:2 mixture of **14E** and **14Z**. This material was not further separated.

(*E*)-[4- $\text{Me}_3\text{SiC}_6\text{H}_4\text{CH}=\text{CH}-4'-\text{C}_6\text{H}_4\text{NO}_2$ ] $\text{Cr}(\text{CO})_3$ , **15E**. A slurry of 11 (4.72 g, 15.0 mmol) and  $\text{Bu}_3\text{P}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2)\text{Cl}$  (6.17 g, 16.5 mmol) in THF (100 mL) was warmed to 45 °C, whereupon a solution of LDA (1.77 g, 16.5 mmol) in 50 mL of THF was added dropwise over 20 min. The solid slowly dissolved, and the solution reddened. After complete addition of base, the mixture was stirred for 1 h at 50 °C and then at room temperature overnight. The resultant solution was then transferred by cannula into 1400 mL of argon-sparged water. The yellowish-brown slurry was stirred vigorously for 1.5 h, whereupon the liquid was removed by cannula. The dark, crystalline material remaining was pumped on in a vacuum oven at room temperature for 4 h. It was then triturated with heptane; the heptane extracts were discarded. The material was then extracted into toluene, and the toluene extracts were filtered through a silica column (8 cm  $\times$  3 cm) packed in a frit. The column was washed with toluene until the eluent was nearly colorless (ca. 1000 mL total), giving a deep red solution. The solvent was evaporated to dryness. The red solid which resulted was extracted into a minimum of warm toluene (ca. 50 mL), filtered to remove a small amount of insoluble matter, and cooled to –30 °C overnight. The red solid which precipitated was filtered out, washed with pentane, and dried, giving analytically and isomerically pure **15E** (2.27 g, 5.24 mmol, 35%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.22 (d,  $J_{\text{HH}} = 8.8$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 7.60 (d,  $J_{\text{HH}} = 8.8$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 6.93 (AB quartet,

$J_{\text{HH}} = 16.2$  Hz, 2H, olefin CH), 5.48 (AB quartet,  $J_{\text{HH}} = 6.7$  Hz, 4H, ortho and meta  $\text{PhSiMe}_3$ ), 0.31 (s, 9H,  $\text{SiMe}_3$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{19}\text{CrNO}_5\text{Si}$ : C, 55.42; H, 4.42; N, 3.23. Found: C, 55.56; H, 4.37; N, 3.11.

The solvent was evaporated from the mother liquor, giving a red solid (2.40 g, 5.54 mmol, 37%).  $^1\text{H NMR}$  spectroscopic analysis of this solid demonstrated it to be a 1.2:1 mixture of **15E** and **15Z**. This material was not further separated.

(*E*)-[4- $\text{F}_3\text{CC}_6\text{H}_4\text{CH}=\text{CH}-4'-\text{C}_6\text{H}_4\text{NO}_2$ ] $\text{Cr}(\text{CO})_3$ , **16E**. A slurry of 12 (6.05 g, 19.5 mmol) and  $\text{Bu}_3\text{P}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2)\text{Cl}$  (8.22 g, 22.0 mmol) in THF (160 mL) was warmed to 55 °C, whereupon solid  $\text{NaOEt}$  (1.50 g, 22.0 mmol) was added in small portions over 30 min by means of a powder addition funnel. The solid slowly dissolved, and the solution reddened. After complete addition of base, the mixture was stirred for 1 h at 50–60 °C and then overnight at room temperature. The resultant solution was transferred by cannula into 1500 mL of argon-sparged water. The yellowish-brown slurry was stirred vigorously for 1.5 h, whereupon the dark, sticky semisolid was filtered out into a coarse frit. The semisolid was pumped on in a vacuum oven at room temperature for 4 h. It was then triturated with heptane; the heptane extracts were discarded. The material was then extracted into toluene, and the toluene extracts were filtered through a silica column (8 cm  $\times$  3 cm) packed in a frit. The column was washed with toluene until the eluent was nearly colorless (ca. 1500 mL total), giving a deep red solution. The solvent was evaporated to 75 mL, at which point the bright red solution was cooled to –30 °C overnight. The red solid which precipitated was filtered out, washed with pentane, and dried, giving analytically and isomerically pure **16E** (2.92 g, 6.80 mmol, 35%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.24 (d,  $J_{\text{HH}} = 8.8$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 7.61 (d,  $J_{\text{HH}} = 8.8$  Hz, 2H, ortho or meta  $\text{PhNO}_2$ ), 6.94 (AB quartet,  $J_{\text{HH}} = 16.2$  Hz, 2H, olefin CH), 5.76 (d,  $J_{\text{HH}} = 6.8$  Hz, 2H, ortho or meta  $\text{PhCF}_3$ ), 5.49 (d,  $J_{\text{HH}} = 6.8$  Hz, 2H, ortho or meta  $\text{PhCF}_3$ ). Anal. Calcd for  $\text{C}_{18}\text{H}_{10}\text{CrF}_3\text{NO}_5$ : C, 50.36; H, 3.26; N, 2.35. Found: C, 50.03; H, 3.77; N, 2.06.

The solvent was evaporated from the mother liquor, giving a red solid (2.49 g, 5.80 mmol, 30%).  $^1\text{H NMR}$  spectroscopic analysis of this solid demonstrated it to be a 2:1 mixture of **16E** and **16Z**. This material was not further separated.

**Single Crystal X-ray Diffraction Studies of 13E–16E.** Crystals of **13E–16E** suitable for study were grown either from a slowly cooled  $\text{CH}_2\text{Cl}_2$  solution (**13E**) or from  $\text{CH}_2\text{Cl}_2$ /pentane mixtures (**14E–16E**). These were inspected in air and then sealed in argon-flushed capillaries. Data were collected on an Enraf-Nonius CAD-4 diffractometer, employing  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å) and  $\omega$ - $2\theta$  scans. Data collection and structure refinement parameters appear in Table 1. The structures were solved using SHELXS,<sup>34</sup> and the data were refined using SHELXL.<sup>35</sup> All non-hydrogen atoms were refined anisotropically in the last least squares cycles; the stilbene hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å<sup>2</sup>. The methyl hydrogen atoms of **13E** and **15E** were included as a rigid group with rotational freedom at the bonded carbon, with  $d(\text{C}-\text{H}) = 0.95$  Å and  $B = 5.5$  Å<sup>2</sup>. The only disorder involved the  $\text{CF}_3$  group in one of the molecules in the asymmetric unit of **16E**. The disorder was modeled by setting F(4)–F(6) to 60% occupancy, and an alternate set of positions (F(4')–F(6')) to 40% occupancy. The disordered atoms were refined in alternate least squares cycles. Positional parameters and equivalent isotropic thermal parameters for **13E–16E** appear in Tables 2–5, respectively; selected bond distances and angles appear in Table 6. More extensive data are available as supplementary material.

## Results and Discussion

We attempted several times to generate the (4-(dimethylamino)-4'-nitrostilbene)chromium tricarbonyl complex

(34) Sheldrick, G. M. *Acta Crystallogr.* 1990, *A46*, 467–473.

(35) Sheldrick, G. M. *SHELX76*, a system of computer programs for X-ray structure determination, as locally modified. University of Cambridge, England, 1976.

Table 1. Data Collection and Refinement Parameters for 13E–16E

	13E	14E	15E	16E
formula	C <sub>19</sub> H <sub>16</sub> CrN <sub>2</sub> O <sub>5</sub>	C <sub>17</sub> H <sub>11</sub> CrNO <sub>5</sub>	C <sub>20</sub> H <sub>19</sub> CrNO <sub>5</sub> Si	C <sub>18</sub> H <sub>10</sub> CrF <sub>3</sub> NO <sub>5</sub>
fw	404.35	361.28	433.46	429.28
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	Pbca	P2 <sub>1</sub> /c
temp, K	173	292	295	293
cell constants				
a, Å	7.710(3)	10.141(4)	11.745(8)	18.305(6)
b, Å	13.953(3)	13.767(3)	15.644(4)	12.641(4)
c, Å	17.016(4)	11.768(3)	22.255(6)	15.208(5)
β, deg	99.80(3)	108.82(3)		92.59(3)
vol, Å <sup>3</sup>	1804	1555.1	4089	3515.4
formula units/cell	4	4	8	8
D <sub>calc</sub> , g cm <sup>-3</sup>	1.49	1.54	1.41	1.62
μ <sub>calc</sub> , cm <sup>-1</sup>	6.98	7.97	6.73	7.47
decay of std reflns, %	±1	±2.5	±3.7	±3
2θ range, deg	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50
no. of reflns measd	3561	3014	4051	6676
no. of reflns obsd [F <sub>o</sub> > 5σF <sub>o</sub> ]	2226	1942	1302	4306
no. of params	250	217	262	532
weights	[σ(F <sub>o</sub> ) <sup>2</sup> + 0.0004F <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	[σ(F <sub>o</sub> ) <sup>2</sup> + 0.0015F <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	[σ(F <sub>o</sub> ) <sup>2</sup> + 0.002F <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	[σ(F <sub>o</sub> ) <sup>2</sup> + 0.00042F <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>
GOF	0.90	0.92	1.59	1.52
R	0.042	0.044	0.046	0.040
R <sub>w</sub>	0.053	0.060	0.066	0.053

Table 2. Fractional Coordinates for 13E

atom	x/a	y/b	z/c	B <sub>eq</sub> , <sup>a</sup> Å <sup>2</sup>
Cr	0.45716(7)	0.75779(4)	0.03066(3)	1.08
O(1)	0.3182(4)	0.8839(2)	-0.1085(2)	2.76
O(2)	0.3115(4)	0.5880(2)	-0.0661(2)	2.08
O(3)	0.1257(4)	0.7883(2)	0.0966(2)	2.24
O(4)	1.0807(5)	0.4829(2)	-0.3860(2)	2.91
O(5)	1.1250(5)	0.3492(2)	-0.3229(2)	3.37
N(1)	0.5383(4)	0.8396(2)	0.2235(2)	1.70
N(2)	1.0739(5)	0.4331(2)	-0.3278(2)	1.93
C(1)	0.3728(5)	0.8360(3)	-0.0544(2)	1.73
C(2)	0.3638(5)	0.6546(3)	-0.0281(2)	1.42
C(3)	0.2515(5)	0.7772(2)	0.0698(2)	1.46
C(4)	0.7212(5)	0.8214(2)	0.0359(2)	1.44
C(5)	0.6516(5)	0.8609(2)	0.0995(2)	1.39
C(6)	0.5980(5)	0.8021(3)	0.1590(2)	1.50
C(7)	0.6018(5)	0.7008(3)	0.1461(2)	1.47
C(8)	0.6713(5)	0.6624(2)	0.0825(2)	1.33
C(9)	0.7370(5)	0.7213(2)	0.0259(2)	1.25
C(10)	0.8060(5)	0.6830(3)	-0.0428(2)	1.37
C(11)	0.8272(5)	0.5913(3)	-0.0589(2)	1.46
C(12)	0.8919(5)	0.5528(2)	-0.1286(2)	1.25
C(13)	0.9401(5)	0.6110(2)	-0.1887(2)	1.57
C(14)	0.9970(5)	0.5725(2)	-0.2542(2)	1.51
C(15)	1.0081(5)	0.4737(2)	-0.2598(2)	1.50
C(16)	0.9640(5)	0.4136(2)	-0.2021(2)	1.53
C(17)	0.9045(5)	0.4535(3)	-0.1369(2)	1.47
C(18)	0.4978(6)	0.9416(3)	0.2250(2)	2.24
C(19)	0.4605(6)	0.7761(3)	0.2768(2)	2.41

<sup>a</sup> In this and subsequent tables of fractional coordinates, B<sub>eq</sub> = 4/3[a<sup>2</sup>β<sub>11</sub> + b<sup>2</sup>β<sub>22</sub> + c<sup>2</sup>β<sub>33</sub> + ab(cos γ)β<sub>12</sub> + ac(cos β)β<sub>13</sub> + bc(cos α)β<sub>23</sub>].

through the direct reaction of the stilbene with Cr(CO)<sub>6</sub> under Pauson–Mahaffey conditions<sup>28</sup> and were unable to do so. We found this surprising, as (4,4'-dimethylstilbene)- and (4,4'-dimethoxystilbene)chromium tricarbonyl<sup>24,25,28</sup> were prepared this way, albeit in low yield. It appears either that the (dimethylamino)nitrostilbene is too insoluble in the reaction medium to allow the reaction to occur at a reasonable rate or that the electron-withdrawing characteristics of the nitro group overwhelm the electron-donating properties of the dimethylamino group, and thereby retard the ability of the reaction to proceed. The thermal stability of 13E, once prepared by the method detailed below, suggests that the difficulty in the reaction stems from such kinetic factors rather than thermodynamic ones.

It seemed likely that reactions involving other nitrostilbenes would also fail. We therefore opted to explore

Table 3. Fractional Coordinates for 14E

atom	x/a	y/b	z/c	B <sub>eq</sub>
Cr	0.00346(6)	0.67317(4)	0.17562(5)	2.31
O(1)	-0.1431(4)	0.8295(2)	0.2638(3)	4.57
O(2)	-0.0746(4)	0.5302(3)	0.3348(4)	6.51
O(3)	-0.2644(4)	0.6275(3)	-0.0166(3)	4.63
O(4)	0.4922(5)	0.2661(3)	0.9105(4)	6.42
O(5)	0.5844(4)	0.4013(3)	0.9843(3)	5.17
N	0.5161(4)	0.3514(3)	0.9017(4)	3.96
C(1)	-0.0871(5)	0.7682(3)	0.2288(3)	3.00
C(2)	-0.0456(5)	0.5854(3)	0.2722(4)	3.73
C(3)	-0.1604(5)	0.6453(3)	0.0567(4)	3.19
C(4)	0.1807(4)	0.5812(3)	0.1734(4)	3.01
C(5)	0.1202(4)	0.6217(3)	0.0584(3)	3.28
C(6)	0.1051(5)	0.7229(3)	0.0458(4)	3.43
C(7)	0.1493(5)	0.7820(3)	0.1459(4)	3.46
C(8)	0.2106(4)	0.7421(3)	0.2603(4)	3.16
C(9)	0.2267(4)	0.6417(3)	0.2764(3)	2.73
C(10)	0.2873(5)	0.6076(3)	0.4013(4)	3.58
C(11)	0.2928(5)	0.5180(4)	0.4340(4)	3.93
C(12)	0.3529(4)	0.4793(3)	0.5594(4)	3.18
C(13)	0.3407(5)	0.3827(4)	0.5743(4)	3.89
C(14)	0.3939(5)	0.3399(3)	0.6874(4)	3.59
C(15)	0.4573(4)	0.3983(3)	0.7827(4)	3.07
C(16)	0.4706(4)	0.4953(3)	0.7737(4)	3.32
C(17)	0.4166(5)	0.5371(3)	0.6580(4)	3.49

the method first exploited by Drefahl,<sup>26</sup> whose elegant route converted the parent chromium-bound benzaldehyde (C<sub>6</sub>H<sub>5</sub>CHO)Cr(CO)<sub>3</sub> to a series of (phenyl-substituted stilbene)chromium tricarbonyl compounds in good to excellent yields through the Wittig reaction. Notably, Drefahl discovered that the difficulties inherent in coordinating benzaldehyde to a (tricarbonyl)chromium moiety (owing to the electron-withdrawing characteristics of the aldehyde function) were readily overcome by first protecting the aldehyde group as the diethyl acetal, coordinating the protected arene to the metal, and then hydrolyzing the coordinated arene acetal to the benzaldehyde. This provided (C<sub>6</sub>H<sub>5</sub>CHO)Cr(CO)<sub>3</sub> in considerably greater yield than the direct reaction did.

A number of workers have since reproduced this synthesis of (C<sub>6</sub>H<sub>5</sub>CHO)Cr(CO)<sub>3</sub>,<sup>31,36,37</sup> and some have expanded the concept into new areas such as the synthesis of (chalcone)chromium tricarbonyl derivatives,<sup>38</sup> but the

Table 4. Fractional Coordinates for 15E

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>eq</sub>
Cr	-0.9063(1)	-0.24622(8)	-0.18098(5)	2.67
Si	-1.0772(2)	-0.0454(1)	-0.1608(1)	3.15
O(1)	-0.9129(7)	-0.2532(6)	-0.3146(3)	7.37
O(2)	-0.7066(8)	-0.3657(6)	-0.1856(5)	8.31
O(3)	-0.7414(7)	-0.1023(6)	-0.1875(3)	6.03
O(4)	-0.8695(8)	-0.8556(5)	-0.0119(4)	6.24
O(5)	-0.7262(7)	-0.8090(5)	0.0404(4)	5.74
N	-0.8073(9)	-0.7990(6)	0.0069(4)	4.24
C(1)	-0.9105(9)	-0.2508(6)	-0.2628(4)	4.30
C(2)	-0.784(1)	-0.3211(7)	-0.1843(5)	4.74
C(3)	-0.8035(8)	-0.1568(6)	-0.1857(4)	3.60
C(4)	-0.9477(8)	-0.2733(5)	-0.0872(4)	3.06
C(5)	-0.9715(7)	-0.1877(5)	-0.0986(4)	2.83
C(6)	-1.0435(7)	-0.1625(5)	-0.1461(4)	2.43
C(7)	-1.0907(7)	-0.2283(5)	-0.1803(4)	2.85
C(8)	-1.0702(7)	-0.3163(6)	-0.1690(4)	3.07
C(9)	-0.9971(7)	-0.3397(5)	-0.1214(4)	2.75
C(10)	-0.9727(8)	-0.4299(5)	-0.1092(4)	3.36
C(11)	-0.9061(7)	-0.4586(5)	-0.0680(4)	3.27
C(12)	-0.8818(7)	-0.5483(5)	-0.0511(4)	3.04
C(13)	-0.7957(8)	-0.5626(5)	-0.0094(4)	3.67
C(14)	-0.7708(8)	-0.6450(6)	0.0088(4)	3.81
C(15)	-0.8337(9)	-0.7115(6)	-0.0140(4)	3.27
C(16)	-0.9186(8)	-0.6995(5)	-0.0553(4)	3.68
C(17)	-0.9413(8)	-0.6178(5)	-0.0743(4)	3.26
C(18)	-1.2343(7)	-0.0331(6)	-0.1563(5)	4.11
C(19)	-1.0248(9)	-0.0137(6)	-0.2353(4)	4.35
C(20)	-1.007(1)	0.0193(6)	-0.1025(5)	4.87

exploration of the range of benzaldehydes for which the method may be used has lagged.

We find that a variety of 4-substituted benzaldehyde dialkyl acetals will coordinate to the chromium tricarbonyl center in good yield. As anticipated from previous work,<sup>19</sup> the reaction rate depends significantly on the electron-donating ability of the substituent, with arenes containing donating groups coordinating more rapidly than those containing withdrawing groups. However, the reaction proceeds acceptably even when the substituent is the highly electron-withdrawing CF<sub>3</sub> group, indicating that the  $\sigma$ -donating properties of the dialkyl acetal function counteract the acceptor properties of the substituent to some degree. Only in the cases of chloro- and bromobenzaldehyde dialkyl acetals, where apparent oxidative addition of the carbon-halide bond competes with arene coordination, and of nitrobenzaldehyde dialkyl acetals, where rapid and total decomposition of the reactants occurs during warming of the solution, do we isolate less than 60% of the desired product.

The resulting (arene dialkyl acetal)chromium tricarbonyl compounds 1–8 display reasonable air and thermal stability, and so are easily characterized. Their notable spectroscopic features include the normal upfield shifts of the resonances corresponding to the arene protons in the <sup>1</sup>H NMR spectra, and the strong A<sub>1</sub> and E carbonyl stretching bands in the IR spectra (Table 7). The IR frequencies suggest a substituent donor ability order of Me<sub>2</sub>N ≫ Me<sub>3</sub>Si > H ≫ CF<sub>3</sub>, qualitatively consistent with  $\sigma_I$  values but not with  $\sigma_R$  values.<sup>39</sup> However, in general  $\nu_{CO}$  does not quantitatively correlate with either of these parameters exclusively,<sup>32,37</sup> so no conclusions can be drawn from this ordering.

Somewhat surprisingly, 1–8 all hydrolyze smoothly to the corresponding (4-substituted benzaldehyde)metal

Table 5. Fractional Coordinates for 16E

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>eq</sub>
Cr(1)	0.48288(3)	-0.12818(4)	0.75084(3)	2.62
F(1)	0.4917(2)	-0.2647(2)	0.5077(1)	5.41
F(2)	0.4394(1)	-0.1140(2)	0.5205(1)	5.12
F(3)	0.5469(1)	-0.1228(2)	0.4757(1)	4.74
O(1)	0.3787(2)	-0.2939(2)	0.8054(2)	6.76
O(2)	0.4507(2)	-0.0147(2)	0.9174(2)	5.72
O(3)	0.3553(2)	-0.0107(3)	0.6687(2)	6.00
O(4)	0.8109(2)	-0.2991(2)	1.3091(2)	5.41
O(5)	0.7952(2)	-0.1330(2)	1.3202(2)	5.88
N(1)	0.7902(2)	-0.2156(3)	1.2795(2)	3.81
C(1)	0.4182(2)	-0.2304(3)	0.7838(3)	4.00
C(2)	0.4639(2)	-0.0579(3)	0.8536(2)	3.55
C(3)	0.4041(2)	-0.0560(3)	0.6991(2)	3.75
C(4)	0.5752(2)	-0.2397(3)	0.7639(2)	3.30
C(5)	0.5427(2)	-0.2483(2)	0.6778(2)	3.22
C(6)	0.5343(2)	-0.1587(3)	0.6253(2)	2.94
C(7)	0.5588(2)	-0.0599(3)	0.6585(2)	3.17
C(8)	0.5913(2)	-0.0522(3)	0.7432(2)	3.20
C(9)	0.6005(2)	-0.1431(3)	0.7971(2)	3.10
C(10)	0.6344(2)	-0.1323(3)	0.8868(2)	3.29
C(11)	0.6647(2)	-0.2101(3)	0.9311(2)	3.32
C(12)	0.6975(2)	-0.2061(3)	1.0210(2)	3.02
C(13)	0.7193(2)	-0.3011(3)	1.0602(2)	3.33
C(14)	0.7486(2)	-0.3053(3)	1.1438(2)	3.34
C(15)	0.7567(2)	-0.2122(3)	1.1898(2)	3.05
C(16)	0.7361(2)	-0.1162(3)	1.1550(2)	3.45
C(17)	0.7063(2)	-0.1132(3)	1.0700(2)	3.40
C(18)	0.5025(2)	-0.1656(3)	0.5330(2)	3.71
Cr(2)	-0.79056(3)	0.73514(4)	-0.98996(3)	2.96
F(4) <sup>a</sup>	-0.7721(3)	0.9264(4)	-0.8074(4)	7.89
F(5)	-0.8802(3)	0.9176(5)	-0.7706(4)	9.09
F(6)	-0.8194(3)	0.9972(3)	-0.9019(4)	7.44
F(4)'	-0.7784(4)	0.9012(5)	-0.7847(4)	7.16
F(5)'	-0.8891(5)	0.9591(7)	-0.8096(7)	8.33
F(6)'	-0.8655(8)	0.9939(6)	-0.8783(6)	10.89
O(6)	-0.7688(2)	0.8590(2)	-1.1533(2)	6.90
O(7)	-0.7081(2)	0.5581(2)	-1.0711(2)	5.63
O(8)	-0.6510(2)	0.8347(3)	-0.9196(2)	6.54
O(9)	-0.9647(2)	0.0592(3)	-1.2796(3)	7.64
O(10)	-0.9456(3)	-0.0311(3)	-1.1607(3)	9.08
N(2)	-0.9506(2)	0.0513(4)	-1.2013(3)	5.79
C(19)	-0.7773(2)	0.8115(3)	-1.0901(3)	4.34
C(20)	-0.7385(2)	0.6263(3)	-1.0388(3)	3.76
C(21)	-0.7040(2)	0.7942(3)	-0.9460(3)	4.22
C(22)	-0.8440(2)	0.6240(3)	-0.9020(2)	3.95
C(23)	-0.8277(2)	0.7164(3)	-0.8568(2)	4.30
C(24)	-0.8523(2)	0.8145(3)	-0.8918(3)	4.10
C(25)	-0.8935(2)	0.8158(3)	-0.9704(3)	4.22
C(26)	-0.9097(2)	0.7225(3)	-1.0155(3)	3.92
C(27)	-0.8857(2)	0.6249(3)	-0.9834(2)	3.55
C(28)	-0.9046(2)	0.5279(3)	-1.0348(2)	3.67
C(29)	-0.8982(2)	0.4313(3)	-1.0064(2)	3.69
C(30)	-0.9163(2)	0.3361(3)	-1.0583(2)	3.49
C(31)	-0.9006(2)	0.2385(3)	-1.0196(2)	3.95
C(32)	-0.9131(2)	0.1465(3)	-1.0652(3)	4.40
C(33)	-0.9408(2)	0.1509(3)	-1.1500(3)	4.12
C(34)	-0.9578(2)	0.2441(3)	-1.1896(3)	4.19
C(35)	-0.9457(2)	0.3373(3)	-1.1445(2)	3.85
C(36)	-0.8369(3)	0.9177(4)	-0.8428(4)	6.08

<sup>a</sup> F(4)–F(6) were assigned occupancy factors of 0.60; F(4)'–F(6)' were assigned occupancy factors of 0.40.

complexes 9–12 without evident decomposition. Even the presumably extremely electron-poor trifluoromethylbenzaldehyde complex 12 exhibits hydrolytic stability during the reaction, and acceptable thermal and air stability once isolated. The electronic characteristics of the substituent affect the efficacy of this reaction significantly, in that complexes 1 and 2, containing the electron-donating dimethylamino group, are wholly converted to the benzaldehyde 9 in a few hours, while complexes 7 and 8, containing the electron-withdrawing CF<sub>3</sub> group, require a few days and evaporative removal of alcohol (along with spiking of the reaction mixture with aqueous acid) for

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(39) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper Collins: New York, 1987.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 13E–16E<sup>a</sup>

	13E	14E	15E	16E
Cr–C (arene)	2.245 (4, 57, 6)	2.215 (4, 12, 6)	2.209 (8, 26, 6)	2.201 (4, 23, 12)
Cr–Centroid	1.74	1.72	1.70	1.70 (–, 1, 2)
Cr–C (carbonyl)	1.837 (4, 8, 3)	1.830 (4, 8, 3)	1.84 (1, 2, 3)	1.843 (4, 8, 6)
C–O (carbonyl)	1.158 (4, 8, 3)	1.159 (5, 5, 3)	1.14 (1, 2, 3)	1.147 (5, 6, 6)
C(6)–X	1.363 (4) (N(1))		1.903 (8) (Si)	1.510 (6, 18, 2) (CF <sub>3</sub> )
C–C (coordinated ring)	1.414 (5, 14, 6)	1.402 (6, 12, 6)	1.41 (1, 1, 6)	1.401 (5, 15, 12)
C(9)–C(10)	1.465 (5)	1.475 (5)	1.47 (1)	1.483 (5, 6, 2)
C(10)–C(11)	1.324 (5)	1.289 (6)	1.29 (1)	1.300 (5, 4, 2)
C(11)–C(12)	1.465 (5)	1.501 (6)	1.48 (1)	1.469 (5, 0, 2)
C–C (nitro ring)	1.388 (5, 12, 6)	1.376 (6, 27, 6)	1.38 (1, 1, 6)	1.376 (5, 14, 12)
C(15)–N (nitro)	1.455 (5)	1.482 (5)	1.48 (1)	1.479 (5, 13, 2)
N–O	1.226 (4, 10, 2)	1.210 (5, 1, 2)	1.22 (1, 0, 2)	1.211 (6, 5, 4)
C (carbonyl)–Cr–C (carbonyl)	90.0 (2, 15, 3)	89.0 (2, 5, 3)	88.4 (5, 10, 3)	87.9 (2, 11, 6)
Centroid–Cr–C (carbonyl)	125.3 (–, 27, 3)	126.0 (–, 9, 3)	126.4 (–, 8, 3)	126.7 (–, 15, 6)
Cr–C (carbonyl)–O (carbonyl)	177.9 (3, 9, 3)	178.9 (4, 1, 3)	178.8 (9, 8, 3)	178.5 (3, 8, 6)
C(9)–C(10)–C(11)	126.2 (3)	124.4 (4)	125.9 (9)	124.9 (3, 14, 2)
C(10)–C(11)–C(12)	126.4 (3)	126.7 (4)	129.0 (8)	126.2 (3, 12, 2)
C(15)–N (nitro)–O (nitro)	118.7 (3, 12, 2)	118.0 (4, 5, 2)	117 (1, 2, 2)	117.8 (4, 8, 4)
O(4)–N (nitro)–O(5)	122.6 (3)	124.1 (4)	126 (1)	124.4 (4, 15, 2)

<sup>a</sup> Esds of averaged values are given in the form (a, b, c), where a is the average esd, b is the standard deviation of the values from the average, and c is the number of trials.

Table 7. IR Spectral Data (cm<sup>-1</sup>) for 1–16E in CH<sub>2</sub>Cl<sub>2</sub> Solvent, NaBr Cells

	$\nu_{\text{CO}}, A_1$	$\nu_{\text{CO}}, E$
[Me <sub>2</sub> NPhCH(OMe) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 1	1960	1870
[Me <sub>2</sub> NPhCH(OEt) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 2	1957	1870
[Me <sub>2</sub> NPhCHO]Cr(CO) <sub>3</sub> , 9	1969	1890
(E)-[Me <sub>2</sub> NPhCHCHPhNO <sub>2</sub> ]Cr(CO) <sub>3</sub> , 13E	1957	1874
[PhCH(OMe) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 3	1974	1892
[PhCH(OEt) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 4	1974	1894
[PhCHO]Cr(CO) <sub>3</sub> , 10	1991	1920
(E)-[PhCHCHPhNO <sub>2</sub> ]Cr(CO) <sub>3</sub> , 14E	1975	1900
[Me <sub>3</sub> SiPhCH(OMe) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 5	1970	1890
[Me <sub>3</sub> SiPhCH(OEt) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 6	1968	1890
[Me <sub>3</sub> SiPhCHO]Cr(CO) <sub>3</sub> , 11	1984	1915
(E)-[Me <sub>3</sub> SiPhCHCHPhNO <sub>2</sub> ]Cr(CO) <sub>3</sub> , 15E	1969	1895
[F <sub>3</sub> CPhCH(OMe) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 7	1990	1920
[F <sub>3</sub> CPhCH(OEt) <sub>2</sub> ]Cr(CO) <sub>3</sub> , 8	1990	1918
[F <sub>3</sub> CPhCHO]Cr(CO) <sub>3</sub> , 12	2002	1942
(E)-[F <sub>3</sub> CPhCHCHPhNO <sub>2</sub> ]Cr(CO) <sub>3</sub> , 16E	1990	1922

complete formation of 12. These observations are consistent with a nucleophilic attack mechanism analogous to that observed in the purely organic systems, wherein the rate is controlled by the ability of the substituent to stabilize the positive charge brought by the acid catalyst. They are also consistent with the qualitative rates of the acetalization reaction, which is fast for trifluoromethylbenzaldehyde and slow for (dimethylamino)benzaldehyde.

The infrared spectra of 9–12 indicate that, as expected, the amount of electron density donated to the metal by the ring diminishes considerably after hydrolysis of the acetal. As may be seen in Table 7, the A<sub>1</sub> carbonyl stretching band increases ca. 10–15 cm<sup>-1</sup> in energy in each case, while the broader E stretching band increases 15–20 cm<sup>-1</sup>. This reflects considerably decreased metal→carbonyl back-bonding in the benzaldehyde complexes, consistent with a decrease in the level of ring → metal donation.

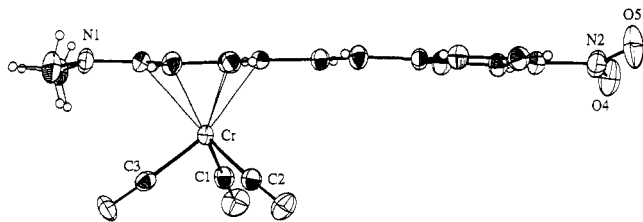
Complexes 9–12 react with the ylide Bu<sub>3</sub>P=CH-4-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub> to give the corresponding (4'-nitrostilbene)chromium tricarbonyls 13–16 as mixtures of E and Z isomers. These represent the first examples of (stilbene)chromium tricarbonyl complexes containing electron-withdrawing substituents. The relative E:Z ratios apparently depend upon subtle electronic factors as well as on reaction conditions; for example, employing either electron-rich 9 or electron-poor 12 in ethanol results in E:Z ratios for 13 and 16 of ca. 3:1; however, 10 and 11 under identical conditions give 14 and 15 with E:Z ratios of 1:1. When less-polar THF

is used as solvent, the E:Z ratios of 14–16 are all increased by a factor of 2, but the E:Z ratio of 13 is unchanged. We have not attempted to carefully optimize the reactions, but in no case have we been able to eliminate the formation of one isomer, nor have we ever observed preferential formation of the Z isomer.

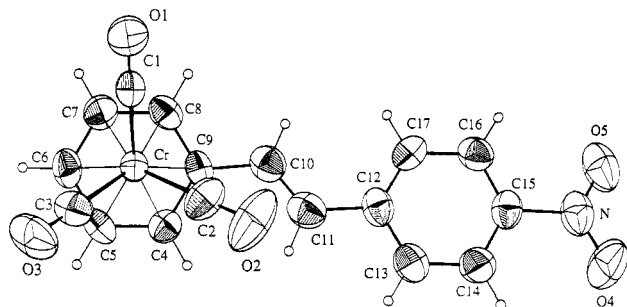
We have had little success separating the isomers chromatographically, in part because it appears that the longer the material is in contact with silica gel, the harder it is to elute. This has forced us to employ short filtration-type columns rather than long ones. Only in the case of dimethylamino complex 13 were we able to elute pure 13Z, and this only in small quantities. Fortunately, in each case the isomers exhibit different solubilities in toluene, so that the E isomer preferentially crystallizes from this solvent. This has allowed us to isolate and fully characterize 13E–16E. We have not yet discovered a way to crystallize the Z isomers preferentially; however, their crystal habits differ sufficiently from those of the E isomers (chunks vs blades) that crystallized mixtures of the two may to some extent be separated manually. As a result, we have characterized some of the Z isomers crystallographically; their structures will provide the subject of a future report.

The two isomers are readily distinguished by <sup>1</sup>H NMR spectroscopy, where distinctive patterns appear for the olefin protons. The E isomer always exhibits an AB quartet, with J<sub>HH</sub> = 16 Hz, downfield of the pair of doublets (J<sub>HH</sub> = 12 Hz) exhibited by the Z isomer. The larger J/(ν<sub>A</sub> – ν<sub>B</sub>) ratio for the E isomer which these observations imply agrees with data reported for free stilbenes and with empirical parameters suitable for prediction of NMR spectra.<sup>40</sup> That the chromium coordinates to the ring to which it was originally bound and not the nitro ring is indicated by the consistency of the resonances in the aromatic region of the spectra: in each of 13E–16E, these appear in a narrow chemical shift range (δ 8.16–8.24 and δ 7.48–7.61) as doublets exhibiting a coupling constant of 8.6–8.9 Hz. The resonances corresponding to the coordinated ring, by contrast, display varying chemical shifts and coupling constants from compound to compound.

The solution infrared spectra of 13E–16E exhibit the expected A<sub>1</sub> and E bands (Table 7). Their energies are



**Figure 1.** ORTEP drawing of **13E** showing the near planarity of the stilbene fragment.

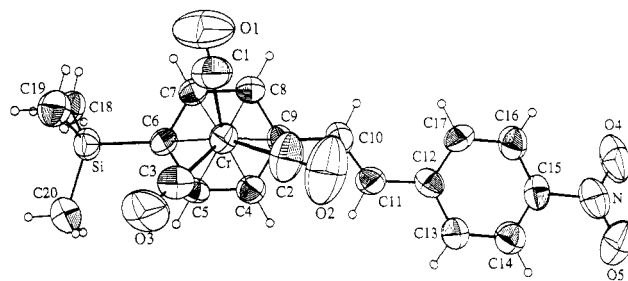


**Figure 2.** ORTEP drawing of **14E** showing the staggered orientation of the carbonyl ligands.

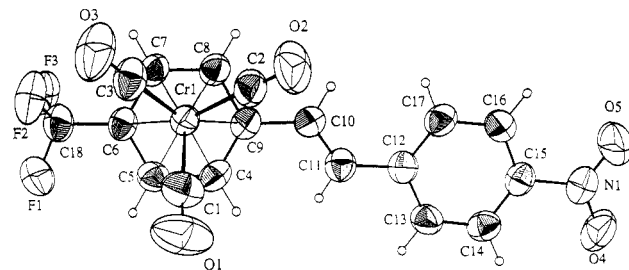
similar to those of the corresponding acetal complexes, and less than those of the benzaldehyde complexes, indicating that an olefin substituent acts as a much better donor than an aldehyde substituent does, despite the fact that in this case the olefin is bound to a strongly electron-withdrawing nitrophenyl group.

One of the motivations for this work was to determine whether the solubility of the stilbene could be enhanced by its coordination to a metal center. The low solubilities of stilbenes and higher  $\alpha,\omega$ -diphenyl polyenes pose a difficult problem in their use as photonic devices.<sup>12,15,41-45</sup> We were therefore pleased to note that **13E-16E** appear considerably more soluble than the free organics. For example,  $8 \times 10^{-2}$  M chloroform solutions of **13E** have been prepared, while the solubility of the free organic DANS in chloroform is  $\sim 10^{-4}$  M.<sup>12</sup> For **14E-16E**, the data are currently qualitative, but they all dissolve more readily than the corresponding organics. Importantly, and somewhat surprisingly, **13E-16E** exhibit unusually high air stability for (arene)chromium tricarbonyl compounds; the solids appear indefinitely stable (no decomposition observed over several months in air), while solutions containing them decompose much more slowly than ones containing **1-12**. We ascribe this observation to increased congestion at the metal center, inhibiting the approach of oxygen.

**Structures of 13E-16E.** It is well-known that the planarity of  $\alpha,\omega$ -diphenyl polyenes plays a key role in their exhibiting sizable hyperpolarizabilities.<sup>41,44</sup> The effect of coordinating a chromium tricarbonyl fragment to one of the arene rings on the overall stilbene planarity is thus of obvious interest. It has been argued, for example, that  $\pi$



**Figure 3.** ORTEP drawing of **15E**.



**Figure 4.** ORTEP drawing of the two independent molecules of **16E** in the asymmetric unit. Note the different carbonyl orientations between the molecules.

donor substituents and their ipso carbon atoms in (donor-substituted arene)chromium tricarbonyls bend up out of the arene plane, away from the metal center, while  $\pi$  acceptor substituents and their ipso carbon atoms either remain in the arene plane or bend slightly toward the metal center;<sup>46,47</sup> such a bend could prove deleterious to the nonlinear optical properties of the molecule. In addition, the olefin function and the noncoordinated ring might twist to avoid steric interactions with the metal moiety. Further, we hoped to determine crystallographically whether the attachment of a metal center affected the bond distances of the conjugated carbon atoms; it has been suggested that  $\alpha$ -phenyl polyenes lie too close to the "alternating bond distances" extreme of conjugated systems to allow the maximization of  $\beta$ .<sup>48,49</sup> We have therefore determined the structures of the (nitrostilbene)chromium tricarbonyl compounds **13E-16E** by single crystal X-ray diffraction.

ORTEP drawings of the molecules appear in Figures 1-4. The data confirm the structural suggestions based on the NMR spectroscopy: the chromium atom coordinates solely to the arene ring to which it was originally bound, the nitroarene ring remains noncoordinated, and the stilbene adopts the *E* orientation.

(41) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

(42) *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N.; Ulrich, D. R., Eds.; Plenum: New York, 1988.

(43) *Materials for Nonlinear Optics*; Marder, S. R.; Sohn, J. E.; Stucky, G. D., Eds.; American Chemical Society: Washington, DC, 1991; Vol. 455.

(44) *Materials for Nonlinear and Electro-Optics*; Lyons, M. H., Ed.; Institute of Physics: Bristol, England, 1989; Vol. 103.

(45) *Organic Materials for Nonlinear Optics*; Hann, R. A.; Bloor, D., Eds.; Royal Society of Chemistry: London, 1989.

(46) Hunter, A. D.; Shilliday, L.; Furey, W. S.; Zaworotko, M. J. *Organometallics* **1992**, *11*, 1550-1560.

(47) Hunter, A. D.; Mozol, V.; Tsai, S. D. *Organometallics* **1992**, *11*, 2251-2262.

(48) Gilmour, S.; Marder, S. R.; Tiemann, B. G.; Cheng, L.-T. *J. Chem. Soc., Chem. Commun.* **1993**, 432-433.

(49) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L.-T. *J. Am. Chem. Soc.* **1993**, *115*, 3006-3007.



The general details of the structures are consistent across the series (Table 6) and are similar to those typically observed in (arene)chromium tricarbonyl compounds.<sup>19</sup> The metal atom lies 1.7 Å from the centroid of the ring, and 1.85 Å from the carbonyl carbons, in a pseudooctahedral environment. The bond distances associated with the carbonyl groups and with the ring substituent appear normal. The steady decrease in the chromium–arene carbon bond length with the decrease in donor ability of the substituent may be real and may have an electronic origin, but since other factors contribute to these bond lengths (see below), we cannot currently state that a correlation exists.

The carbon–carbon distances in the coordinated ring are routinely longer than those in the uncoordinated nitroarene ring. This likely reflects a slight loss in aromaticity upon coordination, owing to back-donation of electron density from the metal into the  $\pi^*$  orbitals of the ring. The differences between rings suggests that this density is localized on the coordinated ring rather than spread out over the entire stilbene fragment. Further evidence for localization derives from inspection of the bond distances involving the olefin carbons (C(9)–C(10), C(10)–C(11), C(11)–C(12)); these fall into short–long–short patterns rather than approaching equivalence. The apparent inability on the part of **13E–16E** to distribute electron density so as to maximize the molecular dipole in the ground state may bode ill for their use as NLO materials.<sup>50</sup>

The overall planarity of the stilbene ring can be expressed in related ways, either by calculating a theoretical plane containing the atoms C(4)–C(17) and examining the deviations of the individual atoms from that plane or by calculating separate planes containing C(4)–C(9) and C(12)–C(17) and determining the angle between them. As applied to **13E–16E**, the former calculation indicates that no individual carbon atom deviates more than 0.22 Å from the calculated plane, while the latter shows a range of angles between 4.45 and 16.34°.

It is evident that the stilbene moieties are therefore largely planar in the solid state, but not perfectly so. Most of the deviations from planarity probably arise from crystal packing forces and thermal motion. Evidence for the former results from the least squares planes data for the two independent molecules in the asymmetric unit of **16E**. In one, the angle between the ring planes is 16.34°, but in the other it is 10.52°. Since these molecules differ only in the orientation of their carbonyl ligands (see below), one concludes that the 6° difference between plane angles stems from packing differences. Further support for this view comes from the data involving the nitroarene ring. Undoubtedly, in solution the NO<sub>2</sub> function and the attached ring are coplanar; this orientation provides maximum orbital overlap and electron delocalization between the two. Here, however, in no case are the nitro group and the attached arene ring coplanar; the nitro group is tipped by values spanning 2–16°. Such a large range occurring for the homologous series **13E–16E** argues for the ability of relatively small effects, such as packing forces, to cause sizable deviations from planarity. That thermal motion also plays a role derives from noting that **13E**, for which data were collected at –100 °C, exhibits the least overall nonplanarity, while the other three compounds,

for which data were collected at room temperature, display larger (and similar) deviations.

However, a detailed inspection of the chromium–arene carbon bond data suggests the presence of sterically and electronically induced nonplanarity within the coordinated rings. As noted above, Hunter and co-workers have provided evidence that the  $\pi$ -donating substituents will cause the coordinated arene ring to bend away from the metal;<sup>46,47</sup> we recently provided confirmatory evidence for this view.<sup>51</sup> Such a bend clearly occurs in **13E**; the substituted carbon C(9) lies 2.351(4) Å from the metal, carbons C(5) and C(7) lie 2.246(4, 16, 2) Å from the metal, and carbons C(4) and C(8) lie 2.198(4, 16, 2) Å from the metal. It appears the distortion caused by the strongly donating Me<sub>2</sub>N group is sufficiently large that the ortho carbons also bend upward. This particular bending seems important only for **13E**, however; none of the other compounds exhibit a similar distortion based on the atom bound to C(6). This accords with Hunter's model: the effect of an acceptor substituent, such as Me<sub>3</sub>Si or F<sub>3</sub>C, is much less than that of a donor.

Another distortion at odds with Hunter's model is clearly present in **13E–16E**. If the donating/accepting characteristics exclusively determine the bending direction, one expects that C(9), the carbon attached to the acceptor olefin group, would lie either in the arene plane or slightly below it. In fact, the data show unequivocally that in each case C(9) lies substantially above the ring, by 0.03–0.06 Å. Since this orientation is inconsistent with the model, it almost certainly arises from steric considerations; the stilbene distorts to minimize interactions between the metal (and the carbonyls, possibly) and the olefin function. The coordinated rings are thus slightly distorted from planarity into either boat (**13E**) or envelope (**14E–16E**) conformations.

Curiously, C(9) appears to “carry” C(8) with it as it bends upward; the Cr–C(8) distance is consistently longer (0.01–0.04 Å) than the Cr–C(4) distance. This might be related to the fact that C(8) is trans to the olefin double bond, while C(4) is cis to the double bond, but the importance of this observation is unclear. The effect apparently does not lie with the coordinated arene ring tipping toward the metal to minimize the interaction between the olefin hydrogen atoms and the hydrogen atoms bonded to C(4) and C(8), since the Cr–C(5) and Cr–C(7) distances, which should mimic the behavior of the Cr–C(4) and Cr–C(8) distances, are essentially identical in each molecule.

It is thus evident that coordination of the metal does induce nonplanarity of the stilbene fragment, at least in the solid state. However, as the deviations are quite small, and will likely be overcome by atomic motion in solution or in a glass, **13E–16E** may still exhibit useful NLO characteristics.

A final note of interest concerns the orientation of the carbonyl groups with respect to the substituents on the coordinated arene ring. Considerable theoretical and experimental work has indicated that a [mono(donor)-substituted arene]chromium tricarbonyl complex should adopt an eclipsed conformation, while a [mono(acceptor)-substituted arene]chromium tricarbonyl complex should adopt an inverted eclipsed (staggered) orientation.<sup>19,46,47,52,53</sup> Attempts have been made to extend this analysis to

(50) Although, as a reviewer commented, materials exhibiting bond localized behavior in the ground state may still act as good NLO materials if a bond delocalized excited state can be accessed.

(51) Gilbert, T. M.; Bond, A. H.; Rogers, R. D. *J. Organomet. Chem.*, in press.

(disubstituted arene)metal systems, but few experimental data exist to address the question.<sup>51</sup>

Intriguingly, only the (dimethylamino)nitrostilbene compound **13E** crystallizes with the carbonyls in the anticipated eclipsed positions. The parent nitrostilbene **14E**, the (trimethylsilyl)nitrostilbene **15E**, and the (trifluoromethyl)nitrostilbene **16E** adopt staggered-gauche conformations between the eclipsed extremes. If we define the torsional angle  $\tau$  as containing C(6), the ring centroid, Cr, and the carbonyl carbon closest to C(6),  $\tau$  will lie between 0° (one eclipsed extreme) and 60° (the other eclipsed extreme). The data give  $\tau = 11.9^\circ$  for **13E**, 35.8° for **14E**, 41.6° for **15E**, and 35.0 and 33.9° for the two molecules of **16E**. It seems clear that only the very strong donor Me<sub>2</sub>N can dictate the carbonyl orientation in these molecules; the other substituents, including the olefin group, do not exert sufficient electronic pressure to accomplish this. The observations here accord with our previous work<sup>51</sup> in arguing that only a very few strong donor groups can force the carbonyl ligands to a particular arrangement, that the potential surface for carbonyl rotation in these systems is nearly flat, and that steric/crystal packing effects, rather than the nature of the ring substituents, may determine the observed orientations.

**Absorption Spectra of 13E–16E.** Intense colors are a general feature of organic nonlinear optical materials, reflecting their low-energy charge transfer characteristics.<sup>41,43–45</sup> We were therefore pleased when **13E–16E** proved to be deep red-orange compounds, as nearly all (arene)chromium tricarbonyl complexes are yellow or yellow-orange.<sup>19</sup> This appeared an indication that the lowest energy transitions would prove metal–ligand (MLCT), ligand–metal (LMCT), or intraligand charge transfer (ILCT) in nature. As long as the ligand involved in the charge transfer is the stilbene, such transitions should enhance the NLO characteristics of the molecules.

Recent theoretical work from Kanis, Ratner, and Marks (KRM)<sup>18</sup> compared the calculated electronic makeup and spectra of (arene)chromium tricarbonyl compounds vs ( $\alpha,\omega$ -diphenyl polyene)chromium tricarbonyls. The data suggest that, while the lowest energy transition in a model (arene)chromium tricarbonyl should prove mostly ligand field (LF) in nature, (stilbene)- and higher order (diphenyl polyene)chromium complexes will exhibit MLCT/ILCT bands at the lowest energy. Thus one expects the latter to be more highly colored. Intriguingly, KRM predicted that band energies of (stilbene)chromium tricarbonyls will differ only slightly (ca. 2400 cm<sup>-1</sup>) regardless of whether the electron-poor chromium tricarbonyl fragment is bound to an electron-rich arene ring or an electron-poor one.

Complexes **13E–16E** provide a good set of compounds with which to test the model, since they incorporate donor–acceptor, neutral–acceptor, and acceptor–acceptor stilbenes, and appear structurally identical. Furthermore, we felt the absorption spectra would assist us in evaluating the question of how well “matched” the electronic behavior of the chromium tricarbonyl center was to that of the arene ring substituent in each compound. It seemed likely, for example, that **13E**, where the donor-substituted ring of the stilbene is coordinated to the acceptor metal moiety, would prove mismatched and would exhibit a different absorption spectrum than that of **15E** and **16E**, where the

**Table 8.** Absorption Spectral Data for **13E–16E** in CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon$  in M<sup>-1</sup> cm<sup>-1</sup>)

	$\lambda_{\max}$	$\lambda_{\text{next}}$
<b>13E</b>	471 (5700)	342 (25 000)
<b>14E</b>	453 (6600)	317 (25 000)
<b>15E</b>	453 (4800)	319 (24 000)
<b>16E</b>	446 (3100)	316 (12 500)

acceptor chromium fragment coordinates a ring containing an acceptor substituent, and the systems are better matched.

The absorption data we obtained appear in Table 8. As is obvious, the spectra are quite similar despite the variations in substituent donating ability and in matching. The (dimethylamino)nitrostilbene **13E** clearly represents the most extreme case; its absorption bands appear at distinctly lower energies than those of **14E–16E**, which exhibit nearly identical spectra. Still, in accordance with KRM theory, the range of band energies for the lowest energy band spans only 1200 cm<sup>-1</sup>.

The fairly large molar absorptivities of the two observable bands of **13E–16E** suggest that, as KRM proposed, these both correspond to charge transfer transitions. We tentatively assign the lower energy band to an MLCT transition on the basis of its smaller  $\epsilon$  and KRM's results, although the value of  $\epsilon$  suggests that this transition may contain considerable LF character. It is evident that the experimental and calculated band energies differ significantly. For example, KRM computed  $\lambda_{\max}$  ( $=\lambda_{\text{MLCT}}$ ) to be 368 nm for **14E** and 376 nm for (4-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH=CH-4'-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)Cr(CO)<sub>3</sub>, a close fit inexact model for **13E**. These values lie 100 nm (5200 cm<sup>-1</sup>) higher in energy than the experimental values. It is not unusual for calculated and experimental transition energy values to disagree, but it is curious here because the calculated and experimental transition energies for the (arene)chromium tricarbonyl compounds in the KRM work proved very similar. The variations do not appear to arise from differences between the experimental structures and those idealized structures used in the computations; KRM used distances and angles similar to the experimentally determined values.<sup>54</sup> It may be that the computational model breaks down when applied to diphenyl polyene systems. It should be noted, however, that rough calculations<sup>55</sup> of the oscillator strength  $f$  give values (0.12 for **13E** and 0.15 for **14E**) which accord acceptably with the computed ones.

The large molar absorptivities observed for the higher energy bands in the spectra of **13E–16E** argue for assignment of these bands to ILCT transitions within the stilbene moiety. This assignment is extremely tentative, but evidence for it arises from noting that the band occurs at lowest energy in **13E**, which contains the stilbene with the greatest charge transfer ability owing to its donor–acceptor substitution.<sup>56</sup>

(54) For example, KRM set the Cr–C(arene) distances to 2.20 Å, the C(arene)–C(arene) distances to 1.40 Å, and the bridging polyene distances to alternating values of 1.44–1.36–1.44 Å. These are all reasonably close to the experimental values, although values of 1.47–1.31–1.47 Å for the bridging polyenes would better model the experimental structures.

(55) Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: New York, 1992.

(56) A reviewer suggested that solvatochromic experiments might prove useful in predicting the magnitudes of  $\Delta\mu$  and  $\beta$  for **13E–16E**; possibly, they would assist band assignments as well. While such experiments would provide qualitative data, we feel that the EFISH experiments in progress will provide more exact values of the NLO parameters. Further, experiments have demonstrated that halocarbon solvents are the most appropriate for NLO measurements; other solvents, such as dioxane, can give spurious data since their ground and excited state dipoles differ greatly.

(52) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499–525.

(53) Solladie-Cavallo, A. *Polyhedron* **1985**, *4*, 901–927.

### Conclusion

We have synthesized a new class of potential organometallic NLO materials which may maintain the stilbene planarity necessary for conjugation and good NLO response in solution and which exhibit the intense electronic absorptions characteristic of charge-transfer capability. EFISH measurements of the first and second hyperpolarizabilities ( $\beta$  and  $\gamma$ ) are in progress.

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Chemical Society, and to the Graduate School Research and Artistry Fund, Northern Illinois University, for partial support of this research.

**Supplementary Material Available:** Tables of calculated positional parameters for hydrogen atoms, anisotropic thermal parameters, least squares planes, and complete bond distances and angles for 13E–16E (26 pages). Ordering information is given on any current masthead page. Tables of  $F_o$  and  $F_c$  are available upon request from the authors.

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