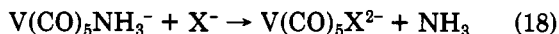


crystal X-ray study will resolve this issue.

**Cyanopentacarbonylvanadate(2-) Ion,  $V(CO)_5CN^{2-}$ .** Addition of excess solid sodium cyanide (10 equiv) and tetraethylammonium bromide to ammoniacal solutions of **1** provides, after an unexceptional workup, 50-60% yields of  $[Et_4N]_2[V(CO)_5CN]$ . This is the only carbonyl dianion prepared thus far from  $V(CO)_5NH_3^-$ . If 20 equiv of NaCN are used, the yield of the product remains essentially unchanged, but when 5 equiv of NaCN are used, the yield of **12** goes down to approximately 35%, so large excesses of  $CN^-$  are required to ensure the formation of reasonable yields of product. In principle, other  $V(CO)_5X^{2-}$  species could be prepared by this general route, provided that  $X^-$  is not so basic that it deprotonates the coordinated or free ammonia.



Attempts to prepare the unknown  $[(OC)_5MnV(CO)_5]^{2-}$  by this procedure were unsuccessful. It appeared that  $Mn(CO)_5^-$  has no tendency to combine with the  $V(CO)_5^-$  fragment in THF.<sup>26</sup> We have also noted that other weakly basic, poor, or non  $\pi$ -acceptor ligands such as  $Ph_2S$  and arenes do not combine with  $V(CO)_5NH_3^-$  to give isolable compounds at room temperature. The only other known substituted pentacarbonylvanadate dianions are  $Ph_3SnV(CO)_5^{2-}$ ,  $Ph_3PbV(CO)_5^{2-}$ ,<sup>27</sup> and an incompletely characterized species thought to be  $HV(CO)_5^{2-}$ .<sup>19</sup>

Infrared solution spectra of  $V(CO)_5CN^{2-}$  in acetonitrile (Table I) are consistent with those expected for a pentacarbonylmetal fragment of  $C_{4v}$  symmetry. Even though compound **12** is a dianion the CO stretching frequencies occur in approximately the same positions as corresponding bands for  $V(CO)_5NH_3^-$ , indicating the cyanide group in  $V(CO)_5CN^{2-}$  is an effective  $\pi$  acceptor. Consistent with this view is the low  $\nu(CN)$  value (2060  $cm^{-1}$ ) for **12** compared to the  $\nu(CN)$  value for uncoordinated  $CN^-$  (2086  $cm^{-1}$ ).<sup>28</sup> An essentially identical infrared spectrum was reported for the previously reported  $[Ph_4P]_2[V(CO)_5CN]$ , prepared in 35% yield by the photolysis of  $V(CO)_6^-$  in liquid ammonia in the presence of excess (ca. 8 equiv) of NaCN. Interestingly, the tetraphenylphosphonium salt

was reported to be a black crystalline solid,<sup>10</sup> while  $[Et_4N]_2[V(CO)_5CN]$  is bright yellow. Both dissolve in  $CH_3CN$  to give red solutions.

**(Acetonitrile)pentacarbonylvanadate(1-),  $V(CO)_5(CH_3CN)^-$ .** When purple  $[Ph_4As][V(CO)_5NH_3]$  is dissolved in acetonitrile at room temperature, an immediate reaction occurs. An orange-yellow solution is formed containing a thermally unstable substance which is formulated as  $V(CO)_5(CH_3CN)^-$  on the basis of its infrared spectrum. Over a period of several minutes at room temperature the  $\nu(CO)$  bands due to  $V(CO)_5(CH_3CN)^-$  (Table I) decay as a band at ca. 1855  $cm^{-1}$  due to  $V(CO)_6^-$  grows. The infrared solution spectrum of this substance is entirely consistent with that expected for a  $V(CO)_5L^-$  species of  $C_{4v}$  symmetry. Wrighton and co-workers have previously reported the preparation of  $V(CO)_5(CH_3CN)^-$  by photolyzing  $V(CO)_6^-$  in neat acetonitrile.<sup>11b</sup> The infrared spectrum of  $V(CO)_5(CH_3CN)^-$  they observe ( $\nu(CO)$  in  $CH_3CN$  1956 (m), 1851 (s), 1811 (m)  $cm^{-1}$ ) is similar to ours except for the strong absorption at 1851  $cm^{-1}$  which is very likely due to  $V(CO)_6^-$ .<sup>11b</sup> The latter forms when  $V(CO)_5(CH_3CN)^-$  decomposes.

As indicated in the Experimental Section, brick-red  $[Ph_4As][V(CO)_5(CH_3CN)]$  was isolated in low yield (30%) at -40 °C from the reaction of **2** with neat acetonitrile, but the solid rapidly decomposed above 15 °C to give a chocolate substance which contained  $[Ph_4As][V(CO)_6]$  as the only metal carbonyl product.

**Concluding Remarks.** In general, it seems likely that any anionic complex containing a metal in a formally negative oxidation state and poor or non  $\pi$ -acceptor ligands will be sufficiently labile to permit thermal-promoted ligand-exchange reactions. This process has obvious advantages over direct photopromoted substitutions when the ligand or the product is photosensitive. Also, in contrast to the photolysis reactions there is generally no need to monitor the course of these thermal reactions to minimize the presence of undesired products, e.g., in the present study, species such as  $V(CO)_6^-$  or  $V(CO)_4L_2^-$ .

**Acknowledgment.** We thank the donors of the petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE79-12159) for support of this research.

**Registry No.** 1, 81831-31-4; 2, 78937-16-3; 3, 36580-51-5; 4, 81831-32-5; 5, 81831-33-6; 6, 78954-04-8; 7, 78953-99-8; 8, 78954-00-4; 9, 78954-02-6; 10, 81831-35-8; 11, 81831-36-9; 12, 81831-38-1; 13, 78969-86-5.

(26) Several attempts to prepare  $VM(CO)_{10}^{2-}$  from the reaction of  $V(CO)_6^{3-}$  and  $M(CO)_6Br$  ( $M = Mn, Re$ ) also failed (Stevens, R. E., unpublished observations).

(27) Ellis, J. E.; Hayes, T. G.; Stevens, R. E. *J. Organomet. Chem.* 1981, 216, 191.

(28) Value from a Nujol mull infrared spectrum of NaCN.

## 1,3-Dithiol-2-ylidene Derivatives of (Arene)chromium Carbonyl Complexes

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The syntheses of (1,3-dithiol-2-ylidene)chromium complexes ( $Cr(\eta^6\text{-arene})(CO)_2CS_2C_2RR'$ ; R, R' = COOMe, COOMe; COH, Ph; COOEt, H) by reaction of  $Cr(\eta^6\text{-arene})(\eta^2\text{-CS}_2)(CO)_2$  complexes with activated acetylenes are reported. Phosphite/phosphonite substitution of CO in the product complexes may be effected by irradiation of the compounds in the presence of excess phosphite/phosphonite ligand. The metal-carbene unit, in contrast, is stable to irradiation in the presence of phosphite/phosphonite or carbon monoxide.

### Introduction

Reaction of  $\eta^2$ -carbon disulfide complexes with activated acetylenes has been shown to result in the formation of

1,3-dithiol-2-ylidene derivatives for iron and manganese complexes and heterocyclic five-membered metallorings for rhodium compounds.<sup>1</sup> We have found that the ad-

dition of acetylenes with electron-withdrawing substituents to  $\text{Cr}(\eta^6\text{-arene})(\eta^2\text{-CS}_2)(\text{CO})_2$  complexes **1** generates 1,3-dithiol-2-ylidene derivatives **2-4**. Solutions of these complexes do not react with oxygen to generate dithiolene complexes as is the case with (1,3-dithiol-2-ylidene)iron compounds.<sup>2</sup>

Continued interest in the reactivity of  $\text{CS}_2$ -transition metal complexes and their derivatives has prompted us to extend our studies of the photochemistry of carbon disulfide complexes to the newly synthesized (1,3-dithiol-2-ylidene)chromium complexes.<sup>3,4</sup> Irradiation of **2** in the presence of phosphite/phosphonite ligand leads to substitution of CO, resulting in the formation of chiral complexes of potential interest as hydrogenation catalysts.

### Experimental Section

$\text{Cr}(\eta^6\text{-arene})(\text{CO})_3$  complexes were prepared essentially in accordance with the procedure outlined in ref 5. Phosphite/phosphonite ligands and  $\text{Cr}(\text{CO})_6$  were obtained from Strem Chemicals, Inc., and were used without additional purification. Solvents were purchased from commercial sources and were bubbled with nitrogen before use. Reactions were performed under a nitrogen atmosphere.

Cyclooctene complex intermediates for carbon disulfide complexes **1** were synthesized in a photochemical reactor with a quartz immersion well and a 450-W Hanovia mercury lamp.<sup>6</sup> Irradiation of solutions of **2** was performed in borosilicate Schlenk tubes using unfiltered light from a 450-W Hanovia lamp.

Infrared spectra were obtained with a Beckman IR12 spectrophotometer. Reported peak positions have been corrected with the assistance of polystyrene calibration peaks. UV-VIS solution spectra were recorded with a Beckman ACTA II spectrophotometer. Varian EM 360 and Nicolet NT-300 spectrometers were employed for recording  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively. Mass spectra were obtained at 70 eV with an AEI MS-30 double-beam mass spectrometer. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected values. Quantitative microanalyses of complexes were performed by Galbraith Laboratories, Inc.

**Synthesis of Complexes 1-4.** A solution of 1 g of  $\text{Cr}(\eta^6\text{-arene})(\text{CO})_3$  (4 mmol) in 400-500 mL of pentane and 6 mL (5 mmol) of cyclooctene was irradiated for 4.5-5 h or until CO evolution stopped. Six milliliters (0.1 mol) of  $\text{CS}_2$  was added to the solution of  $\text{Cr}(\eta^6\text{-arene})(\eta^2\text{-cyclooctene})(\text{CO})_2$ , which rapidly changed from red to brown. After 0.5 h of stirring at ambient temperature, the pentane solution had an appreciable amount of brown precipitate which was allowed to settle at  $-20^\circ\text{C}$ . The solution was carefully filtered to isolate the brown  $\text{Cr}(\eta^6\text{-arene})(\eta^2\text{-CS}_2)(\text{CO})_2$  precipitate to which 0.5 g (4-5 mmol) of activated acetylene in 30-40 mL of tetrahydrofuran was added.<sup>7</sup> After 1-2 h of stirring, the reaction mixture was maintained for several hours at  $-20^\circ\text{C}$  to facilitate precipitation of product. Filtration of the mixture gave crystals, which were sometimes washed with pentane/hexanes before

drying. The tetrahydrofuran filtrate was evaporated and the residue dried under vacuum. Recrystallization of the residue from ether-hexanes gave additional crystals.

Crystals of **2b** and **2c** were obtained by evaporation of solvent from the acetylene-tetrahydrofuran reaction mixture and washing of the resulting residue with ethyl ether. Yields for **4a** are low due to a tendency for this compound to decompose in the acetylene-tetrahydrofuran reaction mixture. The yields for all compounds **2-4** are less than 50% because of incomplete conversion of  $\text{Cr}(\eta^6\text{-arene})(\text{CO})_3$  into  $\text{Cr}(\eta^6\text{-arene})(\eta^2\text{-cyclooctene})(\text{CO})_2$  due to internal filtering by the cyclooctene complex in the latter stages of the irradiation. Infrared spectra of the reaction mixtures confirm that there is efficient conversion of the cyclooctene complexes to  $\text{CS}_2$  complexes. On addition of acetylene, the  $\text{CS}_2$  complexes convert cleanly to the 1,3-dithiol-2-ylidene compounds.

**2a** (Ar = mesitylene; R, R' = COOMe, COOMe): 700 mg (40%); black crystals, mp  $208^\circ\text{C}$  dec; IR (toluene)  $\nu(\text{CO})$  1917, 1874  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.02 ( $\text{CH}_3$ ), 3.87 ( $\text{COOCH}_3$ ), 4.57 (aromatic protons);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.176 ( $\text{CH}_3$ ), 53.191 ( $\text{OCH}_3$ ), 89.623 (mesitylene, CH), 110.478 (mesitylene, CMe), 147.733 ( $\text{SC}=\text{C}$ ), 159.098 ( $\text{C}=\text{O}$ ), 234.060 (metal carbonyls), 279.438 ( $\text{Cr}=\text{C}$ ); mass spectrum (calcd  $M^+$ , 446.45),  $m/e$  446.0 ( $M^+$ ), 389.9 ( $M^+ - 2\text{CO}$ ), 269.9 ( $M^+ - 2\text{CO} - \text{arene}$ ). Anal. Calcd: C, 48.43; H, 4.06; S, 14.36. Found: C, 48.39; H, 4.26; S, 14.21.

**2b** (Ar = *o*-xylene; R, R' = COOMe, COOMe): 550 mg (30%); black crystals; IR (toluene)  $\nu(\text{CO})$  1920, 1875  $\text{cm}^{-1}$ . Anal. Calcd: C, 47.22; H, 3.73; S, 14.83. Found: C, 47.17; H, 3.84; S, 14.64.

**2c** (Ar = *m*-xylene; R, R' = COOMe, COOMe): 500 mg (28%); black crystals; mp  $120^\circ\text{C}$ ; IR (toluene)  $\nu(\text{CO})$  1919, 1875  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.99 ( $\text{CH}_3$ ), 3.87 ( $\text{COOCH}_3$ ), 3.8 (m, aromatic protons). Anal. Calcd: C, 47.22; H, 3.73; S, 14.83. Found: C, 46.95; H, 3.85; S, 14.70.

**2d** (Ar = anisole; R, R' = COOMe, COOMe): 600 mg (34%); black crystals; mp  $98^\circ\text{C}$ ; IR (toluene)  $\nu(\text{CO})$  1921, 1875  $\text{cm}^{-1}$ ; mass spectrum (calcd  $M^+$ , 434.40),  $m/e$  434.0 ( $M^+$ ), 378.0 ( $M^+ - 2\text{CO}$ ), 270.0 ( $M^+ - 2\text{CO} - \text{arene}$ ). Anal. Calcd: C, 44.24; H, 3.25; S, 14.76. Found: C, 44.41; H, 3.16; S, 15.00.

**3a** (Ar = mesitylene; R, R' = COH, Ph): 625 mg (37%); black crystals;  $157-160^\circ\text{C}$  dec; IR (THF)  $\nu(\text{CO})$  1911, 1867  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.210 ( $\text{CH}_3$ ), 90.003 (mesitylene, CH), 110.621 (mesitylene, CMe), 126.870, 129.100, 137.678 (phenyl carbons), 148.961, 168.272 ( $\text{SC}=\text{CS}$ ), 179.691 (COH), 234.633 (metal carbonyls), 281.141 ( $\text{Cr}=\text{C}$ ); mass spectrum (calcd  $M^+$ , 434.49),  $m/e$  433.9 ( $M^+$ ), 378.0 ( $M^+ - 2\text{CO}$ ), 257.9 ( $M^+ - 2\text{CO} - \text{arene}$ ).

**4a** (Ar = mesitylene; R, R' = COOEt, H): 30 mg (2%); black crystals; IR (THF)  $\nu(\text{CO})$  1908, 1861  $\text{cm}^{-1}$ ; mass spectrum (calcd  $M^+$ , 402.44),  $m/e$  401.8 ( $M^+$ ), 345.9 ( $M^+ - 2\text{CO}$ ), 225.9 ( $M^+ - 2\text{CO} - \text{arene}$ ). Anal. Calcd: C, 50.74; H, 4.51; S, 15.93. Found: C, 50.93; H, 4.62; S, 15.72.

**Synthesis of Complexes 5 and 6.** Typically 200 mg (4.5 mmol) of **2a** and 0.2-0.5 mL (2-4 mmol) of  $\text{P}(\text{OMe})_3$  or 0.2-0.5 mL (1-3 mmol) of  $\text{P}(\text{OMe})_2\text{Ph}$  in 15 mL of tetrahydrofuran were irradiated until the carbonyl peaks of **2a** disappeared from the infrared spectrum of the solution. Exhaustive photolysis was used because of the difficulty in separating **5** or **6** from **2a**. Tetrahydrofuran was removed from the irradiated sample under vacuum, and hexanes or ethyl ether was added to the dried residue. A soluble fraction was removed, and one or more recrystallizations from tetrahydrofuran or ether-hexane of the residue from this fraction gave **5** and **6**, respectively.

**5** (Ar = mesitylene; R, R' = COOMe, COOMe; L =  $\text{P}(\text{OMe})_3$ ): 15 mg (6.2%); black crystals,  $146-149^\circ\text{C}$ ; IR (THF)  $\nu(\text{CO})$  1835  $\text{cm}^{-1}$ ; mass spectrum (calcd  $M^+$ , 542.52) 542.5 ( $M^+$ ), 514 ( $M^+ - \text{CO}$ ), 394 ( $M^+ - \text{arene}$ ), 390 ( $M^+ - \text{CO} - \text{P}(\text{OMe})_3$ ), 270 ( $M^+ - \text{arene} - \text{CO} - \text{P}(\text{OMe})_3$ ). Anal. Calcd: C, 44.28; H, 5.02; P, 5.71. Found: C, 43.34; H, 5.17; P, 5.60.

**6** (Ar = mesitylene; R, R' = COOMe, COOMe; L =  $\text{P}(\text{OMe})_2\text{Ph}$ ): 25 mg (9.4%); black crystals; IR (toluene)  $\nu(\text{CO})$  1827  $\text{cm}^{-1}$ ; Anal. Calcd: C, 51.02; H, 4.97; P, 5.26. Found: C, 51.34; H, 5.03; P, 5.51.

### Results and Discussion

Attempted reaction of various substituted acetylenes with **1** has demonstrated that strong electron-withdrawing substituents on the acetylene are required for the forma-

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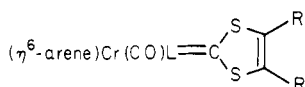
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(7) The carbon disulfide complexes were not dried since this accelerated their decomposition and in some instances produced pyrophoric solids.

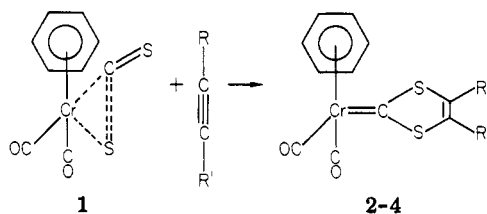
Table I. Spectral Data<sup>a</sup> for

complex	arene	R, R'	L	solvent	bands, cm <sup>-1</sup> (ε)
2a	mesitylene	COOMe, COOMe	CO	isooctane	20 500 30 500
				toluene	20 600 (8800) 30 300 (6700)
				acetonitrile	20 700 (8500) 30 400 (6300)
2d	anisole	COOMe, COOMe	CO	isooctane	20 400 31 000
				toluene	20 400 (8200) 31 000 (6000)
				acetonitrile	20 400 31 100
3a	mesitylene	COH, Ph	CO	toluene	20 600 (7700) 30 900 (6500)
4a	mesitylene	H, COOEt	CO	isooctane	20 500 31 100
5	mesitylene	COOMe, COOMe	P(OMe) <sub>3</sub>	isooctane	21 400 30 100
				toluene	21 300 (9700) 29 900 (7200)

<sup>a</sup> Bands above 34 000 cm<sup>-1</sup> are not listed. All spectra were measured at room temperature.

tion of (1,3-dithiol-2-ylidene)chromium compounds. For example, 2-butyne-1,4-diol, phenylacetylene, and diphenylacetylene either do not react with 1a or only produce small amounts of uncharacterized materials. In contrast, dimethyl acetylenedicarboxylate and phenylpropargylaldehyde react readily and cleanly with 1a to generate 2a and 3a, respectively. Ethyl propiolate forms 4a under similar reaction conditions, but longer reaction times are required and slow decomposition of 4a in the reaction mixture is observed.

Several different arenes were used to synthesize the (η<sup>6</sup>-arene)Cr(CO)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>) intermediates 1 from which complexes 2-4 were prepared. 1a-d reacted equally well with dimethyl acetylenedicarboxylate to give 2a-d. Yields for 2b-d were slightly smaller than the yield for 2a, but this is primarily due to the fact that compounds 2b-d do not crystallize as readily from the reaction mixture as compound 2a.



R, R', 2 (COOMe, COOMe), 3 (COH, Ph), 4 (H, COOEt);  
Ar (arene), a (mesitylene), b (*o*-xylene), c (*m*-xylene),  
d (anisole)

The infrared spectra of complexes 2-4 have two metal carbonyl bands, which are at lower frequencies than the carbonyl peaks of the η<sup>2</sup>-CS<sub>2</sub> precursors 1, e.g., for 2a ν(CO) = 1917 and 1874 and for 1a ν(CO) = 1965 and 1910 in toluene. A similar relationship has been noted for Fe-(η<sup>2</sup>-CS<sub>2</sub>)(CO)<sub>2</sub>[P(OMe)<sub>3</sub>]<sub>2</sub> complexes and (1,3-dithiol-2-ylidene)iron derivatives.<sup>1a</sup> Variation of the arene or acetylene moiety in complexes 2-4 has little effect on the metal carbonyl frequencies.

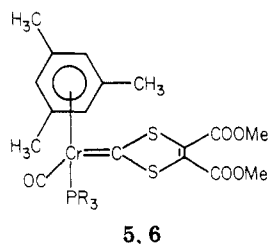
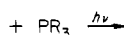
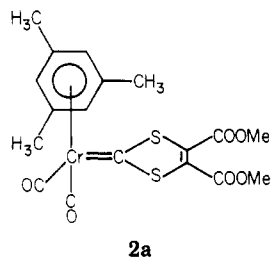
<sup>13</sup>C NMR spectra corroborate that the acetylene adducts are (1,3-dithiol-2-ylidene)chromium complexes. For complex 2a only three peaks are associated with the symmetrical alkyl unit: δ 53.191 (OCH<sub>3</sub>), 147.733 (SC=), 159.098 (C=O). The observation of only one line for each

pair of <sup>13</sup>C nuclei supports the proposed symmetrical structure. The metal carbene <sup>13</sup>C nuclei are observed at 279.438 ppm for 2a and at 281.141 ppm for 3a. These low-field singlets are within the range expected for chromium carbonyl carbene complexes.<sup>8</sup> Proton NMR spectra provide additional verification that the acetylene adducts are (1,3-dithiol-2-ylidene)chromium complexes. The CO<sub>2</sub>Me groups of 2a and 2c are observed as sharp singlets at δ 3.87, indicating a symmetrical arrangement as expected for the proposed structure and in contrast to the splitting which would be observed for a five-membered metallocycle.<sup>1d</sup>

Solutions of 2-4 are not appreciably air sensitive. A tetrahydrofuran solution of 2a exposed to the atmosphere at ambient temperature for 3 days suffered minimal decomposition (less than 5%) with no new metal carbonyl products observed. In contrast, solutions of (1,3-dithiol-2-ylidene)iron complexes exposed to air at room temperature oxidize to dithiolene iron complexes.<sup>1a,b</sup> (1,3-Dithiol-2-ylidene)manganese complexes are also stable to air and do not rearrange to heterometallic compounds. It has been suggested that the stability of the (1,3-dithiol-2-ylidene)metal complexes is enhanced by a weak metal CS<sub>2</sub> electron transfer.<sup>1c</sup> Since Cr(arene)(CO)<sub>2</sub>CS<sub>2</sub> complexes are claimed to have a substantial back-bonding component between chromium and the CS<sub>2</sub> group, the above correlation does not appear to be a satisfactory explanation of the stability of (1,3-dithiol-2-ylidene)chromium complexes.<sup>6a</sup>

Irradiation of tetrahydrofuran or toluene solutions of 2 and excess tertiary phosphite/phosphonite results in the replacement of a CO ligand by phosphite/phosphonite. While only traces of product are observed with some phosphines, e.g., PPh<sub>3</sub>, the formation of a substitution product is readily seen with either P(OMe)<sub>3</sub> or P(OMe)<sub>2</sub>Ph, leading to 5 and 6, respectively. Replacement of the 1,3-dithiolium carbene unit by phosphine to yield the known (arene)dicarbonyl(phosphine)chromium(0) complex and a substituted tetrathiafulvalene was not observed in these photolysis experiments. Indeed, the photochemical

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stability of complexes 2–4 with respect to loss of the carbene moiety is high.<sup>9</sup> For example, irradiation of a CO-saturated solution of 2a failed to generate  $\text{Cr}(\eta^6\text{-mesitylene})(\text{CO})_3$  and tetramethyl [ $\Delta^{2,2'}$ -bi-1,3-dithiole]-4,4',5,5'-tetracarboxylate.<sup>10</sup>

The phosphite/phosphonite substituted complexes 5 and 6 are of interest principally for the following reasons. Compounds of the general type  $\text{Cr}(\eta^6\text{-arene})(\text{CO})\text{LL}'$  are relatively rare due to the fact that loss of more than one CO from  $\text{Cr}(\eta^6\text{-arene})(\text{CO})_3$  complexes on photolysis is uncommon.<sup>11</sup>  $\text{Cr}(\eta^6\text{-arene})(\text{CO})\text{LL}'$  complexes are chiral and have been utilized as catalysts for the 1,4 hydrogenation of methyl sorbate. It is reasonable to assume that centrochiral (arene)chromium carbonyl complexes will be of value as hydrogenation catalysts in asymmetric synthesis.<sup>12</sup> We are currently working to improve the product

(9) The carbene moiety is also reasonably stable in the electron beam of the mass spectrometer. The fragmentation patterns of all of the (1,3-dithiol-2-ylidene)chromium complexes examined to date have shown ions that correspond to species where all ligands except the 1,3-dithiol-2-ylidene unit have been lost from chromium.

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yields and the diversity of chiral derivatives of 2–4 with the intention of exploring the catalytic potential of these complexes.

Table I lists the low-energy electronic transitions of some of the complexes 2–5. Several complexes of the type  $\text{Cr}(\text{arene})(\text{CO})_2\text{L}$  (L = pyridine, *cis*-4-styrylpyridine, *trans*-4-styrylpyridine) have been shown to have a  $\text{Cr} \rightarrow \text{LCT}$  transition as their lowest absorption.<sup>11,13</sup> In these complexes, the low-energy band is significantly red-shifted compared to the parent tricarbonyls and has a relatively large  $\epsilon$  4–10 000. Complexes 2–5 are similarly red-shifted and have reasonably large molar absorptivities. For example, (mesitylene) $\text{Cr}(\text{CO})_2(\text{pyridine})$  in isoctane has a  $\text{M} \rightarrow \text{LCT}$  at 19 230  $\text{cm}^{-1}$  with an  $\epsilon$  of 4900 while the related band of 2a is at 20 500  $\text{cm}^{-1}$  and has an  $\epsilon$  greater than 8000. A  $\text{M} \rightarrow \text{LCT}$  assignment for the low-energy band of complexes 2–5 is suggested by the above correlation and is supported by noting that the lowest absorption of some carbene complexes has been assigned as a probable MLCT transition.<sup>11,14</sup> The carbene nature of the 1,2-dithiol-2-ylidene unit would be expected to exhibit electronic features similar to those associated with simpler metal carbene groups. We are continuing the examination of the spectroscopy of the (1,3-dithiol-2-ylidene)chromium complexes and related compounds in order to establish definitive assignments of the low-energy transitions.

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