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## Complexes of Trivalent Phosphorus Derivatives. XV. A Comparative Study of Analogous Metal Carbonyl Complexes of Tris(dimethylamino)phosphine and Tris(dimethylamino)arsine<sup>1</sup>

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Thermal reactions of the metal hexacarbonyls  $M(\text{CO})_6$  ( $M = \text{Cr}$  and  $\text{Mo}$  but not  $\text{W}$ ) with tris(dimethylamino)arsine (Tdas) give the yellow monosubstituted derivatives  $\text{Tdas}M(\text{CO})_5$  ( $M = \text{Cr}$  and  $\text{Mo}$ ). Photochemical reactions of  $\text{W}(\text{CO})_6$  with the ligands  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}$  and  $\text{As}$ ) give the monosubstituted derivatives  $\text{LW}(\text{CO})_5$  ( $\text{L} = \text{Tdp}$  (white) and  $\text{Tdas}$  (yellow)). Reactions of  $\text{Fe}_2(\text{CO})_9$  with the ligands  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}$  and  $\text{As}$ ) at room temperature give the monosubstituted derivatives  $\text{LFe}(\text{CO})_4$  ( $\text{L} = \text{Tdp}$  and  $\text{Tdas}$ ). Reaction of the norbornadiene complex  $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_4$  with tris(dimethylamino)arsine at room temperature gives the yellow disubstituted derivative *trans*- $(\text{Tdas})_2\text{Cr}(\text{CO})_4$ , the only disubstituted derivative of tris(dimethylamino)arsine that was isolated in the pure state. Reactions of the disubstituted derivatives *trans*- $\text{L}_2\text{Cr}(\text{CO})_4$  ( $\text{L} = \text{Tdp}$  and  $\text{Tdas}$ ) with carbon monoxide at atmospheric pressure give the monosubstituted derivatives  $\text{LCr}(\text{CO})_5$ . The reactions of tris(dimethylamino)phosphine and tris(dimethylamino)arsine with the olefinmetal carbonyls  $\text{C}_7\text{H}_8\text{M}(\text{CO})_4$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{C}_7\text{H}_8 = \text{norbornadiene}$ ),  $\text{C}_7\text{H}_8\text{M}(\text{CO})_3$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{C}_7\text{H}_8 = \text{cycloheptatriene}$ ), and *cis*- $(\text{C}_6\text{H}_8)_2\text{M}(\text{CO})_2$  ( $M = \text{Mo}, \text{W}$ ;  $\text{C}_6\text{H}_8 = 1,3\text{-cyclohexadiene}$ ) in hydrocarbon solvents have been investigated using the infrared spectra in the  $\nu(\text{CO})$  region for analysis of the reaction mixtures. In all cases the first step(s) in these reactions appear to be the complete displacement of the coordinated olefin(s) with the  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) ligands. However, products with two  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) ligands in *cis* positions are unstable and undergo further change by the following two processes: (1) rearrangement of a *cis* derivative to a *trans* derivative; (2) removal of a  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) ligand by reaction with decomposition-generated carbon monoxide. The following reaction sequences have been identified: (1) *cis*- $(\text{Tdp})_4\text{M}(\text{CO})_2$  ( $M = \text{Mo}, \text{W}$ )  $\rightarrow$  *mer*- $(\text{Tdp})_3\text{M}(\text{CO})_3$   $\rightarrow$  *trans*- $(\text{Tdp})_2\text{M}(\text{CO})_4$ ; (2) *fac*- $(\text{Tdp})_3\text{M}(\text{CO})_3$  ( $M = \text{Mo}, \text{W}$ )  $\rightarrow$  *cis*- $(\text{Tdp})_2\text{M}(\text{CO})_4$   $\rightarrow$  *trans*- $(\text{Tdp})_2\text{M}(\text{CO})_4$ ; (3) *fac*- $(\text{Tdp})_3\text{Cr}(\text{CO})_3$   $\rightarrow$  *mer*- $(\text{Tdp})_2\text{Cr}(\text{CO})_4$   $\rightarrow$  *trans*- $(\text{Tdp})_2\text{Cr}(\text{CO})_4$ ; (4) *trans*- $(\text{Tdas})_2\text{Cr}(\text{CO})_4$   $\rightarrow$   $\text{TdasCr}(\text{CO})_5$ ; (5) *cis*- $(\text{Tdas})_2\text{M}(\text{CO})_4$  ( $M = \text{Mo}, \text{W}$ )  $\rightarrow$   $\text{TdasM}(\text{CO})_5$ .

### Introduction

In 1963 numerous metal carbonyl complexes of tris(dimethylamino)phosphine (abbreviated as Tdp) were first reported.<sup>4,5</sup> Subsequent papers on tris(dimethylamino)phosphinometal carbonyl complexes have discussed more specifically its manganese carbonyl complexes<sup>6</sup> and phosphorus-phosphorus coupling in disubstituted tris(dimethylamino)phosphine complexes.<sup>7</sup>

The variety of stable and readily characterized tris(dimethylamino)phosphine complexes of metal carbonyls makes of interest the preparation and study of related metal carbonyl complexes of tris(dimethylamino)arsine. The same considerations which make tris(dimethylamino)phosphine an attractive<sup>4</sup> ligand for study of its metal carbonyl complexes also apply to tris(dimethylamino)arsine. This paper describes the preparation and properties of some metal carbonyl complexes of tris(dimethylamino)arsine.

One apparent peculiarity which was noted in the earlier work<sup>4</sup> with tris(dimethylamino)phosphine complexes was the inability to bond more than two tris(dimethylamino)phosphine ligands to a single metal atom. This paper also reports further studies on the ability for three or more tris(dimethylamino)phosphine ligands to bond to a single metal atom. The presently reported work takes advantage both of increased understanding<sup>8</sup> of the use of the  $\nu(\text{CO})$  frequencies in octa-

hedral metal carbonyl derivatives for the detection of labile intermediates in reaction mixtures and of the availability for use as starting materials of certain olefinmetal carbonyls prepared by synthetic techniques based on  $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$  derivatives developed since 1965.<sup>9,10</sup>

### Experimental Section

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, and (c) admission to evacuated vessels.

**Materials.**—The ligands tris(dimethylamino)phosphine<sup>11</sup> and tris(dimethylamino)arsine<sup>12</sup> were prepared from the corresponding trihalides and excess dimethylamine by the cited published procedures. The metal hexacarbonyls were purchased from Pressure Chemical Co., Pittsburgh, Pa. The norbornadiene complexes  $\text{C}_7\text{H}_8\text{M}(\text{CO})_4$  ( $M = \text{Cr}, \text{Mo}$ ) and the cycloheptatriene complexes  $\text{C}_7\text{H}_8\text{M}(\text{CO})_3$  ( $M = \text{Cr}, \text{Mo}$ ) were prepared by heating the corresponding metal hexacarbonyl with the appropriate olefin using published procedures.<sup>13</sup> The tungsten complexes  $\text{C}_7\text{H}_8\text{W}(\text{CO})_4$ ,  $\text{C}_7\text{H}_8\text{W}(\text{CO})_3$ , and  $(\text{C}_6\text{H}_8)_2\text{W}(\text{CO})_2$  as well as the molybdenum complex  $(\text{C}_6\text{H}_8)_2\text{Mo}(\text{CO})_2$  were prepared from the corresponding  $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$  ( $M = \text{Mo}, \text{W}$ ) derivative and the appropriate olefin.<sup>9,10</sup>

Analytical, melting point, and proton nmr data on the new tris(dimethylamino)arsine complexes are presented in Table I. The infrared  $\nu(\text{CO})$  frequencies of the tris(dimethylamino)phosphine- and tris(dimethylamino)arsinometal carbonyl complexes discussed in this paper are listed in Table II.

**Preparation of  $\text{TdasCr}(\text{CO})_5$ .**—A mixture of 2.20 g (10 mmol) of hexacarbonylchromium, 2.48 g (12 mmol) of tris(dimethylamino)arsine, and 50 ml of 2,2,5-trimethylhexane was boiled under reflux for 26 hr. Solvent was removed from the cooled and filtered reaction mixture at 25° (0.1 mm). The residue was extracted with 50 ml of pentane in several portions. The filtered pentane extracts were cooled several hours in a  $-78^\circ$  bath. The

(1) (a) Part XIV: R. B. King and A. Efraty, *Inorg. Chim. Acta*, **4**, 319 (1970). (b) Portions of this work were presented at the 11th International Conference on Coordination Chemistry, Haifa, Israel, Sept 1968.

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TABLE I  
 SOME METAL CARBONYL COMPLEXES OF TRIS(DIMETHYLAMINO)ARSINE

Compound <sup>a</sup>	Mp, <sup>b</sup> °C	Anal., %								Proton nmr spectrum <sup>d</sup>	
		C		H		N		O		$\tau(\text{CH}_3)$	$\Delta\tau^e$
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
TdasCr(CO) <sub>5</sub> <sup>f</sup>	131-133	33.1	33.2	4.5	4.6	10.5	10.5	20.0	20.6	7.57	+0.17 (+0.18)
TdasMo(CO) <sub>5</sub>	112-113	29.8	29.9	4.1	3.9	9.5	9.4	18.1	18.3	7.60	+0.20 (+0.19)
TdasW(CO) <sub>5</sub>	104-107	24.9	24.6	3.4	3.2	7.9	7.8	15.1	15.3	7.66	+0.26 (+0.25)
<i>trans</i> -(Tdas) <sub>2</sub> Cr(CO) <sub>4</sub> <sup>g</sup>	115-116 dec	33.2	33.3	6.3	6.2	14.5	14.1	11.1	11.2	7.26	-0.14 (-0.14)
TdasFe(CO) <sub>4</sub>	84.5-85.5	32.0	31.9	4.8	5.1	11.2	11.2	17.1	17.1	7.55	+0.15 (+0.10)

<sup>a</sup> Tdas = tris(dimethylamino)arsine. All compounds are yellow. <sup>b</sup> Melting points were taken in capillaries and are uncorrected. <sup>c</sup> The C, H, N, and O analyses listed here were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, using normal combustion procedures. The analyses given in footnotes *f* and *g* were performed by Professor D. E. Leyden and Mr. J. M. McCall of this department using a new unpublished X-ray fluorescence method. <sup>d</sup> The proton nmr spectra were taken in benzene solutions at 100 Mc using a Varian HA-100 nmr spectrometer. All methyl resonances were the expected singlets. Free tris(dimethylamino)arsine exhibits a singlet nmr methyl resonance at  $\tau$  7.40. <sup>e</sup> The parameter  $\Delta\tau$  for a given complex of tris(dimethylamino)phosphine or tris(dimethylamino)arsine is the change in  $\tau(\text{CH}_3)$  in going from the free ligand to the complex in question. The  $\Delta\tau$  values for the corresponding tris(dimethylamino)phosphine complex are given in parentheses. All  $\Delta\tau$  values listed in this table were obtained in benzene solution. <sup>f</sup> Calcd: Cr, 13.0; As, 18.8. Found: Cr, 12.9; As, 19.9 (X-ray fluorescence). <sup>g</sup> Calcd: As/Cr = 2.00. Found: As/Cr = 1.93 (X-ray fluorescence).

 TABLE II  
 INFRARED SPECTRA OF ANALOGOUS METAL CARBONYL COMPLEXES OF TRIS(DIMETHYLAMINO)PHOSPHINE AND TRIS(DIMETHYLAMINO)ARSINE IN THE 2000-CM<sup>-1</sup> REGION<sup>a</sup>

Compound <sup>b</sup>	$\nu(\text{CO})$ freq, cm <sup>-1</sup>						
(A) Compounds Isolated in the Pure State							
TdpCr(CO) <sub>5</sub>	2064 w	1943 s	1934 s				
TdasCr(CO) <sub>5</sub>	2074 w	1956 s	1945 s				
TdpMo(CO) <sub>5</sub>	2073 w	1949 s	1942 s				
TdasMo(CO) <sub>5</sub>	2082 w	1960 s	1951 s				
TdpW(CO) <sub>5</sub>	2074 w	1940 s	1932 s				
TdasW(CO) <sub>5</sub>	2081 w	1950 s	1943 s				
<i>trans</i> -(Tdp) <sub>2</sub> Cr(CO) <sub>4</sub>		1880 vs					
<i>trans</i> -(Tdas) <sub>2</sub> Cr(CO) <sub>4</sub>	1902 vs	1894 s					
<i>trans</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub>		1891 vs					
<i>trans</i> -(Tdp) <sub>2</sub> W(CO) <sub>4</sub>		1884 vs					
TdpFe(CO) <sub>4</sub>	2053 m	1975 m	1937 s				
TdasFe(CO) <sub>4</sub>	2060 m	1979 m	1949 s				
(B) Intermediates Detected in Solution but Not Isolated and Analogous Model Compounds <sup>c</sup>							
<i>cis</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub> <sup>d</sup>	2022 m		1917 s	1903 vs	1900 vs	1890 vs	1883 vs
<i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub>	2030 m		1938 (sh)		1922 vs	1907 s	
<i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub>	2037 m	2029 m	1931 s	1920 s	1911 vs	1905 vs	
<i>mer</i> -(Tdp) <sub>3</sub> Cr(CO) <sub>3</sub>				1851 s <sup>e</sup>			
<i>mer</i> -(Tdp) <sub>3</sub> Mo(CO) <sub>3</sub>			1970 vw			1865 m	
<i>mer</i> -(Tdp) <sub>3</sub> W(CO) <sub>3</sub>			1960 w			1860 s	
<i>mer</i> -[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P] <sub>2</sub> Mo(CO) <sub>3</sub> <sup>f</sup>			1952 w			1846 s	
<i>mer</i> -(Pf—Pf)Mo(CO) <sub>3</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> <sup>g</sup>	1971 w		1945 m			1864 vs	
<i>cis</i> -(Tdp) <sub>4</sub> Mo(CO) <sub>2</sub>			1821 m <sup>e</sup>				
<i>cis</i> -(Tdp) <sub>4</sub> W(CO) <sub>2</sub>	1876 s		1815 s				
<i>cis</i> -(cPf=PF) <sub>2</sub> Mo(CO) <sub>2</sub> <sup>h</sup>	1878 s		1810 s				
<i>cis</i> -C <sub>6</sub> H <sub>5</sub> W(CO) <sub>2</sub> (Tdp) <sub>2</sub>	1895 s		1839 s				
<i>cis</i> -(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub>	1997 s		1947 s				
C <sub>7</sub> H <sub>3</sub> W(CO) <sub>3</sub> Tdas	1982 s		1932 m	1875 s			
C <sub>7</sub> H <sub>3</sub> W(CO) <sub>3</sub> Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	1980 s		1916 s	1873 s			

<sup>a</sup> These spectra were run on a Perkin-Elmer Model 621 spectrometer with grating optics. Cyclohexane solutions were used for the pure compounds. Each spectrum was calibrated against the 1601.4-cm<sup>-1</sup> band of polystyrene. <sup>b</sup> The following abbreviations were used: Tdp, tris(dimethylamino)phosphine; Tdas, tris(dimethylamino)arsine; Pf—Pf, 1,2-bis(diphenylphosphino)ethane; cPf=PF, *cis*-1,2-bis(diphenylphosphino)ethylene. <sup>c</sup> These spectra were taken in the saturated hydrocarbon solvents used for the reactions (hexane, methylcyclohexane, or 2,2,5-trimethylhexane). <sup>d</sup> The following  $\nu(\text{CO})$  frequencies for *cis*-(Tdp)<sub>2</sub>Mo(CO)<sub>4</sub> were obtained in chloroform solution by F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 92, 1916 (1970): 2012 (m), 1908 (sh), and 1894 cm<sup>-1</sup> (s). <sup>e</sup> The higher  $\nu(\text{CO})$  frequencies expected for these compounds were obscured by  $\nu(\text{CO})$  frequencies of other components of the reaction mixtures. <sup>f</sup> Data of R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962). <sup>g</sup> Data of G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, 1, 287 (1967), obtained in chloroform solution. <sup>h</sup> Data of R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, 8, 1042 (1969), obtained in dichloromethane solution.

yellow crystals which separated were removed by filtration and sublimed twice at 85° (0.8 mm) to give 0.9 g (23% yield) of yellow TdasCr(CO)<sub>5</sub>, mp 131-133°.

**Preparation of TdasMo(CO)<sub>5</sub>.**—A mixture of 2.64 g (10 mmol) of hexacarbonylmolybdenum, 2.48 g (12 mmol) of tris(dimethylamino)arsine, and 50 ml of methylcyclohexane was boiled under reflux for 10 hr. From the resulting reaction mixture 1.76 g (40% yield) of yellow TdasMo(CO)<sub>5</sub>, mp 112-113°, was isolated by a procedure essentially identical with that given above for the isolation of TdasCr(CO)<sub>5</sub>.

**Preparation of TdasW(CO)<sub>5</sub>.**—A mixture of 3.52 g (10 mmol)

of hexacarbonyltungsten, 2.48 g (12 mmol) of tris(dimethylamino)arsine, and 70 ml of hexane was exposed to the ultraviolet irradiation from a General Electric GBL-100C lamp for 41 hr. Solvent was then removed from the reaction mixture at 25° (30 mm). The tarry residue was dried for several hours at 25° (0.1 mm) and then extracted with 25 ml of hexane in several portions. The filtered hexane extracts were cooled to -78° for several hours. The crystals which separated were sublimed at 25-40° (0.1 mm) for 24 hr to give a sublimate of 0.924 g (26% recovery) of unreacted hexacarbonyltungsten. After removal of this sublimate, the residue was sublimed further at 50-55°

(0.1 mm) to give 0.412 g (7.8% conversion, 10% yield) of yellow  $\text{TdasW}(\text{CO})_5$ , mp 104–107°.

Attempts to prepare  $\text{TdasW}(\text{CO})_5$  by reaction of hexacarbonyl tungsten with tris(dimethylamino)arsine in boiling methylcyclohexane or 2,2,5-trimethylhexane were unsuccessful.

**Preparation of  $\text{TdasFe}(\text{CO})_4$ .**—A mixture of 1.82 g (5 mmol) of  $\text{Fe}_2(\text{CO})_9$ , 4.15 g (20 mmol) of tris(dimethylamino)arsine, and 70 ml of pentane was stirred for 30 hr at room temperature. The reaction mixture was filtered in the air three times; this hydrolyzed much of the unreacted tris(dimethylamino)arsine to a white slime. The pentane filtrate was cooled in a  $-78^\circ$  bath for 14 hr. The resulting yellow-brown crystals were removed by filtration and sublimed at 60° (0.1 mm) to give 0.761 g (41% yield) of yellow  $\text{TdasFe}(\text{CO})_4$ , mp 84.5–85.5°.

A similar reaction of  $\text{Fe}_2(\text{CO})_9$  with tris(dimethylamino)phosphine in pentane at room temperature gave  $\text{TdpFe}(\text{CO})_4$  free from  $(\text{Tdp})_2\text{Fe}(\text{CO})_3$  in contrast to the previously described reactions of  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  with tris(dimethylamino)phosphine.

**Preparation of  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$ .**—A mixture of 1.70 g (6.63 mmol) of norbornadienetetracarbonylchromium, 6.5 ml (7.0 g, 33.8 mmol) of tris(dimethylamino)arsine, and 60 ml of hexane was stirred for 127 hr at room temperature. Solvent was then removed at  $\sim 25^\circ$  (20 mm). The residue was washed quickly with 15 ml of hexane and the residue was then extracted with 30 ml of hexane in three portions. The filtered hexane extracts were concentrated to 20 ml and then cooled for 7 hr in a  $-78^\circ$  bath. The resulting yellow crystals were filtered, dried, and recrystallized from hexane below room temperature to give 0.479 g (12.5% yield) of pale yellow  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$ , mp 115–116° dec.

**Unsuccessful Attempts to Prepare Tris(dimethylamino)arsine Complexes.**—The following metal carbonyl derivatives failed to give identifiable tris(dimethylamino)arsine metal carbonyl complexes when treated with the tris(dimethylamino)arsine in the indicated solvents. The techniques tried for product isolations utilized procedures successful for the preparation and isolation of corresponding tris(dimethylamino)phosphine complexes:<sup>4</sup> (a)  $\text{C}_3\text{H}_5\text{V}(\text{CO})_4$  in boiling methylcyclohexane (complete decomposition occurred); (b)  $\text{C}_3\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$  in boiling benzene; (c)  $\{(\text{C}_2\text{H}_5)_4\text{N}\}[\text{W}(\text{CO})_5\text{I}]$  in tetrahydrofuran at room temperature (no reaction took place); (d)  $\text{Mn}_2(\text{CO})_{10}$  in boiling toluene or in toluene at room temperature with ultraviolet irradiation (partial decomposition occurred; unchanged  $\text{Mn}_2(\text{CO})_{10}$  found); (e)  $[\text{C}_3\text{H}_5\text{Mn}(\text{CO})_2\text{NO}][\text{PF}_6]$  in methanol at room temperature (apparent decomposition); (f)  $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  in boiling benzene (no reaction); (g)  $\text{Co}_2(\text{CO})_8$  in benzene at room temperature (complete decomposition observed); (h)  $\text{Ni}(\text{CO})_4$  in hexane at room temperature (rapid gas evolution took place but no products could be isolated from the reaction mixture apparently because of their instability).

**Preparation of  $\text{TdpW}(\text{CO})_5$ .**—A mixture of 3.52 g (10 mmol) of hexacarbonyl tungsten, 2.0 g (12.4 mmol) of tris(dimethylamino)phosphine, and 70 ml of hexane was irradiated with a General Electric GBL-100C ultraviolet lamp for 27 hr. Solvent was removed from the filtered reaction mixture at  $\sim 25^\circ$  (30 mm). The residue was subjected to fractional sublimation at 0.1 mm. A small amount of unreacted hexacarbonyl tungsten was removed at 25–50° (0.1 mm). Then 0.147 g (3% yield) of white  $\text{TdpW}(\text{CO})_5$  was collected at 55–60° (0.1 mm). The residue was then sublimed exhaustively at 60–70° (0.1 mm) to give a mixture of  $\text{TdpW}(\text{CO})_5$  and  $\text{trans}-(\text{Tdp})_2\text{W}(\text{CO})_4$ . After removal of this sublimate further sublimation at 110° (0.1 mm) gave 1.016 g (26% yield) of pure  $\text{trans}-(\text{Tdp})_2\text{W}(\text{CO})_4$ , identified by comparison of its infrared spectrum with that of authentic material.<sup>4</sup>

The sample of  $\text{TdpW}(\text{CO})_5$  was purified by further sublimation at 40° (0.05 mm) for 33 hr after prior removal of oily impurities by heating at 25–30° (0.1 mm) for 16 hr. In this manner 0.10 g (2.1% yield) of pure  $\text{TdpW}(\text{CO})_5$ , mp 176–178°, was obtained. *Anal.* Calcd for  $\text{C}_{11}\text{H}_{18}\text{N}_3\text{O}_5\text{PW}$ : C, 27.1; H, 3.7; N, 8.6; O, 16.4. Found: C, 27.1; H, 3.6; N, 8.6; O, 16.3.

The proton nmr spectrum of  $\text{TdpW}(\text{CO})_5$  in benzene solution exhibited a doublet ( $J = 11$  cps) at  $\tau$  7.81.

**Ultraviolet Irradiation of  $\text{Cr}(\text{CO})_6$  with Tris(dimethylamino)phosphine.**—A mixture of 2.2 g (10 mmol) of hexacarbonylchromium, 2.0 g (12.4 mmol) of tris(dimethylamino)phosphine, and 70 ml of hexane was irradiated for 48 hr with a General Electric GBL-100C ultraviolet lamp. From this reaction mixture 1.724 g (49% yield) of  $\text{TdpCr}(\text{CO})_5$  and 0.343 g (11.3% yield) of  $\text{trans}-(\text{Tdp})_2\text{Cr}(\text{CO})_4$  were obtained by a procedure similar to the

isolation of  $\text{TdpW}(\text{CO})_5$  described above including fractional sublimation with collection of the  $\text{TdpCr}(\text{CO})_5$  at 72° (0.1 mm) for 36 hr and then the  $\text{trans}-(\text{Tdp})_2\text{Cr}(\text{CO})_4$  at 105° (0.1 mm) for 16 hr.

**Ultraviolet Irradiation of  $\text{Cr}(\text{CO})_6$  with Tris(dimethylamino)arsine.**—A mixture of 2.2 g (10 mmol) of hexacarbonylchromium, 2.4 g (11.6 mmol) of tris(dimethylamino)arsine, and 70 ml of hexane was irradiated for 42 hr with a General Electric GBL-100C ultraviolet lamp. From this reaction mixture 0.991 g (45% recovery) of unreacted  $\text{Cr}(\text{CO})_6$  and 0.389 g (9.8% conversion, 18% yield) of  $\text{TdasCr}(\text{CO})_5$  were obtained by a procedure similar to the isolation of  $\text{TdpW}(\text{CO})_5$  described above including fractional sublimation with collection of the  $\text{Cr}(\text{CO})_6$  at 40° (0.03 mm) and the  $\text{TdasCr}(\text{CO})_5$  at 80° (0.03 mm).

**Reaction of  $\text{trans}-(\text{Tdp})_2\text{Cr}(\text{CO})_4$  with Carbon Monoxide.**—A solution of 0.20 g (0.41 mmol) of  $\text{trans}-(\text{Tdp})_2\text{Cr}(\text{CO})_4$  in 70 ml of hexane was treated for 6 hr with carbon monoxide at atmospheric pressure and room temperature. The infrared  $\nu(\text{CO})$  frequencies of the resulting solution were identical with those of the  $\text{trans}-(\text{Tdp})_2\text{Cr}(\text{CO})_4$  starting material indicating that no reaction had taken place. Therefore the hexane solution of  $\text{trans}-(\text{Tdp})_2\text{Cr}(\text{CO})_4$  was boiled under reflux in a stream of carbon monoxide. After 16 hr the infrared  $\nu(\text{CO})$  frequencies of the resulting solution showed  $\text{TdpCr}(\text{CO})_5$  as the only chromium carbonyl derivative present. Solvent was then removed from the reaction mixture at 25° (30 mm) and the residue was extracted with 7 ml of hexane. The hexane extracts were cooled to  $-78^\circ$  to precipitate 0.028 mg (19% yield) of white  $\text{TdpCr}(\text{CO})_5$  which was removed by filtration and identified by comparison of its melting point and infrared spectrum with those of authentic material<sup>4</sup> prepared from hexacarbonylchromium and tris(dimethylamino)phosphine.

**Reaction of  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$  with Carbon Monoxide.**—A solution of 0.20 g (0.35 mmol) of  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$  in 70 ml of hexane was treated for 60 hr with carbon monoxide at room temperature and atmospheric pressure. The infrared spectrum in the  $\nu(\text{CO})$  region indicated partial conversion of the  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$  to  $\text{TdasCr}(\text{CO})_5$  and even a small amount of further conversion to  $\text{Cr}(\text{CO})_6$ . Removal of solvent from the final reaction mixture at 25° (30 mm) followed by sublimation of the residue at 80° (0.1 mm) gave 0.089 g (61% yield if pure) of  $\text{TdasCr}(\text{CO})_5$  slightly contaminated with some  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$ .

A similar reaction of 0.10 g (0.17 mmol) of  $\text{trans}-(\text{Tdas})_2\text{Cr}(\text{CO})_4$  with carbon monoxide in hexane solution (70 ml) at its boiling point (68°) resulted in complete conversion to  $\text{TdasCr}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  after only 1 hr. After treatment of the boiling hexane solution with carbon monoxide for 52 hr, 0.01 g (15% yield) of  $\text{TdasCr}(\text{CO})_5$  was isolated from the reaction mixture by a procedure similar to that given above.

**Reactions of Olefinmetal Carbonyls with Tris(dimethylamino)phosphine and Tris(dimethylamino)arsine (Table III).**—A mixture of the olefinmetal carbonyl complex (0.1–1.2 g), tris(dimethylamino)phosphine or tris(dimethylamino)arsine, and 35–70 ml of the indicated saturated hydrocarbon solvent was stirred at the temperature indicated in Table III. The mole ratios of tris(dimethylamino)phosphine or tris(dimethylamino)arsine to olefinmetal complex varied from 3:1 to 8:1 but always provided at least enough ligand to displace all of the coordinated olefins. Aliquots were withdrawn periodically for examination of their infrared spectra in the 2000- $\text{cm}^{-1}$   $\nu(\text{CO})$  region. All infrared spectra were calibrated against the 1601.4- $\text{cm}^{-1}$  band of polystyrene film. The metal carbonyl derivatives present in the reaction solutions were identified by comparison of the observed  $\nu(\text{CO})$  frequencies with those found for pure tris(dimethylamino)phosphine and tris(dimethylamino)arsine derivatives (Table II). The known compounds *mer*- $[(\text{C}_2\text{H}_5)_3\text{P}]_3\text{Mo}(\text{CO})_3$ <sup>14</sup> and *cis*- $[(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2]_2\text{Mo}(\text{CO})_2$ <sup>15</sup> served as model compounds for tris(dimethylamino)phosphine complexes of the types *mer*- $(\text{Tdp})_3\text{M}(\text{CO})_3$  and *cis*- $(\text{Tdp})_2\text{M}(\text{CO})_2$  which could not be obtained in the pure state for characterization (see Table II).

## Discussion

**(A) Preparation and Properties of the Tris(dimethylamino)arsine Complexes.**—The initial attempts to prepare tris(dimethylamino)arsine metal carbonyl

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(15) R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969).

TABLE III  
 REACTIONS OF OLEFINMETAL CARBONYLS WITH TRIS(DIMETHYLAMINO)PHOSPHINE AND TRIS(DIMETHYLAMINO)ARSINE

Reactants <sup>a</sup>	Solvent <sup>b</sup>	Temp, °C	Time, ° hr	Products <sup>a</sup>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>4</sub> + Tdp	Hexane	25	78	<i>trans</i> -(Tdp) <sub>2</sub> Cr(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>4</sub> + Tdp	MCH	100	8	<i>trans</i> -(Tdp) <sub>2</sub> Cr(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>4</sub> + Tdas	Hexane	25	120	<i>trans</i> -(Tdas) <sub>2</sub> Cr(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>4</sub> + Tdas	Hexane	68	24	TdasCr(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>4</sub> + Tdp	Hexane	25	4	<i>cis</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>4</sub> + Tdp	Hexane	25	24	<i>trans</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>4</sub> + Tdas	Hexane	25	8	<i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub> + TdasMo(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>4</sub> + Tdas	Hexane	68	4	<i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub> + TdasMo(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>4</sub> + Tdas	TMH	124	22	<i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub> + TdasMo(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdp	TMH	25	6	C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + <i>trans</i> -(Tdp) <sub>2</sub> W(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdp	TMH	25	12	<i>trans</i> -(Tdp) <sub>2</sub> W(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdas	Hexane	25	24	C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + <i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdas	Hexane	25	192	<i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub> + TdasW(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdas	Hexane	25 (uv) <sup>d</sup>	2	C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> Tdas
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdas	Hexane	25 (uv) <sup>d</sup>	24	C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> Tdas + <i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub> + TdasW(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + Tdas	TMH	124	9	<i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub> + TdasW(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + CH <sub>3</sub> CN	Hexane	25 (uv) <sup>d</sup>	6	<i>fac</i> -(CH <sub>3</sub> CN) <sub>3</sub> W(CO) <sub>3</sub> <sup>e</sup>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb	Hexane	25 (uv) <sup>d</sup>	49	C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>4</sub> + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb	Hexane	68	49	<i>cis</i> -[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb] <sub>2</sub> W(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> + Tdp	Hexane	68	132	C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> + <i>trans</i> -(Tdp) <sub>2</sub> Cr(CO) <sub>4</sub> + <i>mer</i> -(Tdp) <sub>3</sub> Cr(CO) <sub>3</sub>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> + Tdas	Hexane	68	193	C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> (no reaction)
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> + Tdas	TMH	124	24	C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> + TdasCr(CO) <sub>5</sub> + (arene)Cr(CO) <sub>3</sub> <sup>f</sup>
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>3</sub> + Tdas	TMH	124	104	(Arene)Cr(CO) <sub>3</sub> <sup>f</sup>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>3</sub> + Tdp	Hexane	25	0.1	<i>cis</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>3</sub> + Tdp	Hexane	25	127	<i>trans</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>3</sub> + Tdas	Hexane	25	19	C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>3</sub> + <i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub>
C <sub>7</sub> H <sub>8</sub> Mo(CO) <sub>3</sub> + Tdas	Hexane	25	309	<i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub> + TdasMo(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> + Tdp	TMH	124	27	<i>trans</i> -(Tdp) <sub>2</sub> W(CO) <sub>4</sub> + trace <i>mer</i> -(Tdp) <sub>3</sub> -W(CO) <sub>3</sub> (?)
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> + Tdas	TMH	25	42	C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> (no reaction)
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> + Tdas	TMH	124	19	<i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub> + TdasW(CO) <sub>5</sub>
C <sub>7</sub> H <sub>8</sub> W(CO) <sub>3</sub> + Tdas	TMH	124	90	TdasW(CO) <sub>5</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Mo(CO) <sub>2</sub> + Tdp	MCH	100	3	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Mo(CO) <sub>2</sub> + <i>cis</i> -(Tdp) <sub>4</sub> Mo(CO) <sub>2</sub> + <i>mer</i> -(Tdp) <sub>3</sub> Mo(CO) <sub>3</sub> + <i>trans</i> -(Tdp) <sub>2</sub> -Mo(CO) <sub>4</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Mo(CO) <sub>2</sub> + Tdp	MCH	100	46	<i>trans</i> -(Tdp) <sub>2</sub> Mo(CO) <sub>4</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Mo(CO) <sub>2</sub> + Tdas	TMH	124	17	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Mo(CO) <sub>2</sub> + <i>cis</i> -(Tdas) <sub>2</sub> Mo(CO) <sub>4</sub> + TdasMo(CO) <sub>5</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Mo(CO) <sub>2</sub> + Tdas	TMH	124	46	TdasMo(CO) <sub>5</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> + Tdp	MCH	100	72	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> + <i>cis</i> -(Tdp) <sub>4</sub> W(CO) <sub>2</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> + Tdp	TMH	124	5	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> + <i>cis</i> -(Tdp) <sub>4</sub> W(CO) <sub>2</sub> + <i>mer</i> -(Tdp) <sub>3</sub> W(CO) <sub>3</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> + Tdp	TMH	124	68	Trace <i>cis</i> -(Tdp) <sub>4</sub> W(CO) <sub>2</sub> + <i>mer</i> -(Tdp) <sub>3</sub> -W(CO) <sub>3</sub> + <i>trans</i> -(Tdp) <sub>2</sub> W(CO) <sub>4</sub>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> + Tdas	TMH	124	112	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> W(CO) <sub>2</sub> (no reaction)
(CH <sub>3</sub> CN) <sub>3</sub> W(CO) <sub>3</sub> + Tdas	Hexane	68	27	<i>cis</i> -(Tdas) <sub>2</sub> W(CO) <sub>4</sub> + TdasW(CO) <sub>5</sub>

<sup>a</sup> The following abbreviations are used: Tdp, tris(dimethylamino)phosphine; Tdas, tris(dimethylamino)arsine; C<sub>7</sub>H<sub>8</sub>M(CO)<sub>4</sub>, norbornadienemetal tetracarbonyl; C<sub>7</sub>H<sub>8</sub>M(CO)<sub>3</sub>, cycloheptatrienemetal tricarbonyl. <sup>b</sup> MCH = methylcyclohexane; TMH = 2,2,5-trimethylhexane. <sup>c</sup> The infrared spectra of the reaction mixtures were checked at times other than those shown specifically in this table. For brevity only the times at which significant changes occurred are listed. <sup>d</sup> A Nester-Faust 125-W mercury lamp (7 mm argon pressure) was immersed in the center neck of the reaction vessel while this reaction was carried out. <sup>e</sup> This compound is completely insoluble in the reaction mixture and thus formed a pale yellow precipitate. <sup>f</sup> This chromium carbonyl derivative exhibited ν(CO) frequencies at 1970, 1907, and 1894 cm<sup>-1</sup> and hence was identified as an (arene)Cr(CO)<sub>3</sub> derivative. (C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> is reported<sup>g</sup> to exhibit ν(CO) frequencies at 1987 and 1917 cm<sup>-1</sup>.) However, the exact nature of the arene was not identified. <sup>g</sup> R. D. Fischer, *Ber.*, 93, 165 (1960).

complexes utilized reactions previously demonstrated<sup>4</sup> to be successful for the preparation of tris(dimethylamino)phosphine complexes. The metal hexacarbonyls M(CO)<sub>6</sub> (M = Cr, Mo) thus reacted with tris(dimethylamino)arsine to give the corresponding TdasM(CO)<sub>5</sub> (M = Cr, Mo) derivatives analogous to their reactions with tris(dimethylamino)phosphine to give the corresponding TdpM(CO)<sub>5</sub> (M = Cr, Mo) derivatives.<sup>4</sup> However, the tris(dimethylamino)arsine complexes C<sub>5</sub>H<sub>5</sub>V(CO)<sub>2</sub>Tdas, *trans*-(Tdas)<sub>2</sub>Mo(CO)<sub>4</sub>, *trans*-(Tdas)<sub>2</sub>W(CO)<sub>4</sub>, *trans*-(Tdas)<sub>2</sub>Fe(CO)<sub>3</sub>, [C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>-Tdas]I, [(Tdas)<sub>2</sub>(CO)<sub>3</sub>][Co(CO)<sub>4</sub>], and (Tdas)<sub>2</sub>Ni(CO)<sub>2</sub> could not be prepared by methods analogous to successful methods for the preparation of corresponding tris-

(dimethylamino)phosphine complexes. Preparation of complexes with two or more tris(dimethylamino)arsine ligands attached to a single metal atom appeared to be particularly difficult. Thus the reactions of the cycloheptatriene complexes C<sub>7</sub>H<sub>8</sub>M(CO)<sub>3</sub> (M = Cr, Mo) and the norbornadiene complexes C<sub>7</sub>H<sub>8</sub>M(CO)<sub>4</sub> (M = Cr, Mo) with tris(dimethylamino)arsine when carried out under conditions reported<sup>4</sup> for the preparation of *trans*-(Tdp)<sub>2</sub>M(CO)<sub>4</sub> (M = Cr, Mo) derivatives either gave no isolable products or gave only small quantities of the TdasM(CO)<sub>5</sub> (M = Cr, Mo) derivatives. Eventually the disubstituted derivative *trans*-(Tdas)<sub>2</sub>Cr(CO)<sub>4</sub> was prepared from norbornadienetetracarbonylchromium and tris(dimethylamino)arsine by carrying out the

reaction at a lower temperature and for a longer time than reported<sup>4</sup> for the preparation of the tris(dimethylamino)phosphine analog.

These preparative studies indicate that the preparation of metal carbonyl derivatives with two tris(dimethylamino)arsine ligands bonded to a single metal atom is much more difficult than the preparation of metal carbonyl derivatives with two tris(dimethylamino)phosphine ligands bonded to a single metal atom even when preparative methods are used which generate two or more free coordination sites on the metal atom. This suggests a certain instability of two tris(dimethylamino)arsine ligands bonded to the same metal atom. In order to determine further the relative stabilities of two tris(dimethylamino)phosphine and two tris(dimethylamino)arsine ligands when bonded to the same metal atom, the reactions of the complexes *trans*-(Tdp)<sub>2</sub>Cr(CO)<sub>4</sub> and *trans*-(Tdas)<sub>2</sub>Cr(CO)<sub>4</sub> with carbon monoxide were investigated using the infrared  $\nu(\text{CO})$  frequencies for analysis of the reaction mixtures. The tris(dimethylamino)phosphine complex *trans*-(Tdp)<sub>2</sub>Cr(CO)<sub>4</sub> remained unchanged when treated with carbon monoxide at atmospheric pressure and room temperature for 6 hr although it was smoothly carbonylated to TdpCr(CO)<sub>5</sub> when treated with carbon monoxide at atmospheric pressure and 68° (boiling hexane). However, the tris(dimethylamino)arsine complex *trans*-(Tdas)<sub>2</sub>Cr(CO)<sub>4</sub> was partially converted to TdasCr(CO)<sub>5</sub> and even some Cr(CO)<sub>5</sub> when treated with carbon monoxide at atmospheric pressure and room temperature. These observations indicate that carbon monoxide removes the tris(dimethylamino)arsine ligands in *trans*-(Tdas)<sub>2</sub>Cr(CO)<sub>4</sub> much more readily than it removes the tris(dimethylamino)phosphine ligands in *trans*-(Tdp)<sub>2</sub>Cr(CO)<sub>4</sub>. Attempts to prepare a mixed chromium carbonyl complex of tris(dimethylamino)phosphine and trifluorophosphine by treatment of *trans*-(Tdp)<sub>2</sub>Cr(CO)<sub>4</sub> with phosphorus trifluoride in hexane solution at atmospheric pressure analogous to the carbon monoxide reaction were unsuccessful; infrared spectra showed that no reaction took place.

The preparations of the tungsten compound TdasW(CO)<sub>5</sub> and the iron compound TdasFe(CO)<sub>4</sub> both employed reactions not used in the previous work with tris(dimethylamino)phosphine.<sup>4</sup> The tungsten compound TdasW(CO)<sub>5</sub> was prepared by the photochemical reaction of W(CO)<sub>6</sub> with tris(dimethylamino)arsine similar to numerous other reported<sup>16</sup> photochemical reactions of metal hexacarbonyls with donor ligands. Attempts to prepare a tungsten carbonyl derivative of tris(dimethylamino)arsine by heating hexacarbonyltungsten with tris(dimethylamino)arsine failed. The corresponding thermal reaction of hexacarbonyltungsten with tris(dimethylamino)phosphine gave the disubstituted derivative *trans*-(Tdp)<sub>2</sub>W(CO)<sub>4</sub> rather than the monosubstituted derivative TdpW(CO)<sub>5</sub>.<sup>4</sup> The compound TdpW(CO)<sub>5</sub> was prepared in this work by the photochemical reaction of W(CO)<sub>6</sub> with tris(dimethylamino)phosphine as described in the Experimental Section.

The photochemical reactions of Cr(CO)<sub>6</sub> with both tris(dimethylamino)phosphine and tris(dimethylamino)arsine were also investigated in this work. The photochemical reaction between Cr(CO)<sub>6</sub> and tris(di-

methylamino)phosphine gave a mixture of the monosubstituted derivative TdpCr(CO)<sub>5</sub> and the disubstituted derivative *trans*-(Tdp)<sub>2</sub>Cr(CO)<sub>4</sub>. However, the corresponding photochemical reaction between Cr(CO)<sub>6</sub> and tris(dimethylamino)arsine gave only the monosubstituted derivative TdasCr(CO)<sub>5</sub>.

The previously<sup>4</sup> reported preparation of TdpFe(CO)<sub>4</sub> from tris(dimethylamino)phosphine and Fe<sub>3</sub>(CO)<sub>12</sub> or Fe(CO)<sub>5</sub> gave a mixture of TdpFe(CO)<sub>4</sub> and *trans*-(Tdp)<sub>2</sub>Fe(CO)<sub>3</sub> which required fractional vacuum sublimation for separation. The reaction of Fe<sub>2</sub>(CO)<sub>9</sub> with tris(dimethylamino)phosphine at room temperature has now been found to be a facile method for preparing TdpFe(CO)<sub>4</sub> free from *trans*-(Tdp)<sub>2</sub>Fe(CO)<sub>3</sub>; this reaction takes advantage of the facile dissociation of Fe<sub>2</sub>(CO)<sub>9</sub> into Fe(CO)<sub>3</sub> and a reactive Fe(CO)<sub>4</sub> fragment under mild conditions.<sup>17</sup> A similar reaction between Fe<sub>2</sub>(CO)<sub>9</sub> and tris(dimethylamino)arsine at room temperature gives TdasFe(CO)<sub>4</sub>. No evidence for the existence of *trans*-(Tdas)<sub>2</sub>Fe(CO)<sub>3</sub> was observed in this work; even the reaction of C<sub>2</sub>H<sub>5</sub>Fe(CO)<sub>3</sub> with tris(dimethylamino)arsine analogous to a successful synthesis of *trans*-(Tdp)<sub>2</sub>Fe(CO)<sub>3</sub> failed to yield any *trans*-(Tdas)<sub>2</sub>Fe(CO)<sub>3</sub>. On the other hand, infrared and mass spectral data on samples of TdpFe(CO)<sub>4</sub> which had been stored at -15° or higher for several months or longer invariably demonstrated the presence of some *trans*-(Tdp)<sub>2</sub>Fe(CO)<sub>3</sub>. All of these observations on iron carbonyl derivatives of tris(dimethylamino)phosphine and tris(dimethylamino)arsine suggest that *trans*-(Tdp)<sub>2</sub>Fe(CO)<sub>3</sub> and TdasFe(CO)<sub>4</sub> are the most readily formed iron carbonyl derivatives of these two ligands and indicate further the reluctance of two tris(dimethylamino)arsine ligands to bond to the same metal atom.

All of the tris(dimethylamino)arsine derivatives prepared in this work are yellow solids readily soluble in nonpolar organic solvents and moderately stable to air oxidation and/or hydrolysis. The monosubstituted derivatives TdasM(CO)<sub>5</sub> (M = Cr, Mo, W) and TdasFe(CO)<sub>4</sub> are readily purified by vacuum sublimation like their tris(dimethylamino)phosphine analogs. Vacuum sublimation was avoided with *trans*-(Tdas)<sub>2</sub>Cr(CO)<sub>4</sub> because of its thermal instability with respect to formation of TdasCr(CO)<sub>5</sub>.

The  $\nu(\text{CO})$  frequencies in the infrared spectra of the new tris(dimethylamino)arsinemetal carbonyl complexes (Table II) corresponded completely to those found in other similarly substituted metal carbonyls<sup>8,18</sup> and, in particular, to those in the analogous tris(dimethylamino)phosphine complexes. Substituting a tris(dimethylamino)arsine ligand for a tris(dimethylamino)phosphine ligand in a complex results in an increase in the  $\nu(\text{CO})$  frequencies by about 10 cm<sup>-1</sup>. This indicates that the metal atom has less negative charge in tris(dimethylamino)arsine complexes than in tris(dimethylamino)phosphine complexes. This can arise either from decreased  $\sigma$ -donor ability (forward bonding) or increased  $\pi$ -acceptor ability (retrodonative or "back-bonding") of tris(dimethylamino)arsine relative to tris(dimethylamino)phosphine. For a given triad of complexes the  $\nu(\text{CO})$  frequencies decrease in the follow-

(17) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

(18) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

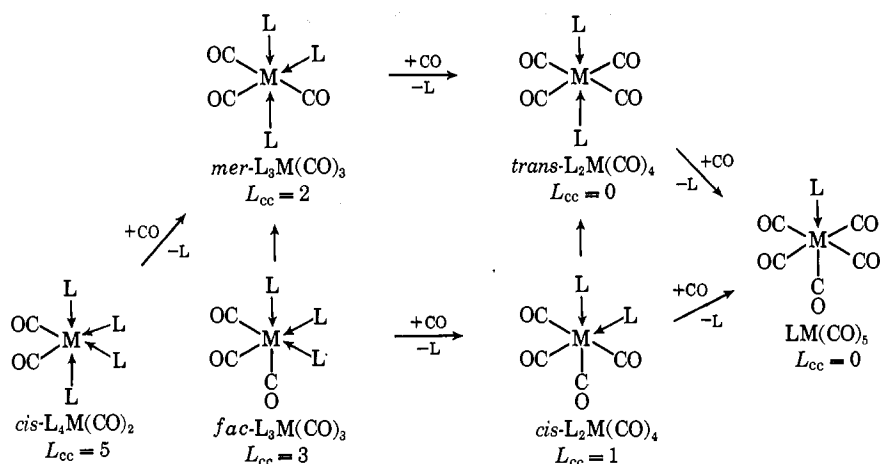


Figure 1.—Some interconversions between substituted octahedral metal carbonyl complexes.

ing sequence: Mo (greatest) > Cr > W (least). This is in accord with previously discussed observations on the  $\nu(\text{CO})$  frequencies of the metal hexacarbonyls themselves<sup>19</sup> as well as kinetic studies on octahedral metal carbonyl derivatives which indicate that the retrodonative bonding of the metal atom to the carbonyl groups in the metal hexacarbonyls increases in the sequence  $\text{Mo}(\text{CO})_6$  (least) <  $\text{Cr}(\text{CO})_6$  <  $\text{W}(\text{CO})_6$  (greatest).

The proton nmr spectra of the tris(dimethylamino)arsinemetal carbonyl complexes all exhibit the expected singlets arising from the 18 equivalent methyl protons in each tris(dimethylamino)arsine ligand (Table I). This indicates unequivocally that the tris(dimethylamino)arsine ligand is bonded to the metal atom through arsenic in all of the complexes discussed in this paper. The change in chemical shift in going from the free ligand to a given type of metal carbonyl complex ( $\Delta\tau$  in Table I) is the same for tris(dimethylamino)arsine as for tris(dimethylamino)phosphine. For the monosubstituted metal carbonyl complexes of the type  $\text{LM}(\text{CO})_5$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $\text{LFe}(\text{CO})_4$  the chemical shifts of the methyl protons increase from the free  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ligand to the metal complex but for the disubstituted metal carbonyl complexes the chemical shifts of the methyl protons decrease from the free ligand to the metal complex. This is consistent with previous results<sup>4</sup> on tris(dimethylamino)phosphine complexes except for halide derivatives such as  $\text{C}_7\text{H}_7\text{Mo}(\text{CO})\text{TdpI}$  unlike any of the tris(dimethylamino)arsine complexes discussed in this paper where other effects can occur.

**(B) Reactions of Olefinmetal Carbonyls with Tris(dimethylamino)phosphine and Tris(dimethylamino)arsine.**—One of the most striking observations in the chemistry of metal complexes of tris(dimethylamino)phosphine and tris(dimethylamino)arsine is the apparent inability to isolate metal complexes with more than two tris(dimethylamino)phosphine ligands bonded to a single metal atom<sup>4</sup> and the difficulty in isolating metal complexes with even two tris(dimethylamino)arsine ligands bonded to a single metal atom. In order to explore more extensively the possibilities for preparation of less favored types of metal carbonyl complexes of tris(dimethylamino)phosphine and tris(dimethylamino)arsine, some reactions of olefinmetal complexes derived from the octahedral metal carbonyls with the ligands

$[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}, \text{As}$ ) were investigated in saturated hydrocarbon solvents under various conditions (Table III) utilizing the infrared  $\nu(\text{CO})$  frequencies for analysis of the resulting reaction mixtures.

These reactions of octahedral olefinmetal carbonyl complexes with tris(dimethylamino)phosphine and tris(dimethylamino)arsine summarized in Table III demonstrate repeatedly the instability of two  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}, \text{As}$ ) ligands in cis positions of an octahedron. This instability apparently arises by steric interference between the dimethylamino groups attached to the donor atoms of the mutually cis ligands possibly enhanced by electrostatic repulsion between the lone pairs of the nitrogen atoms. This instability of mutually cis  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}, \text{As}$ ) ligands is greater for derivatives containing the relatively small chromium and/or phosphorus atoms than for those containing the larger molybdenum or tungsten and/or arsenic atoms. An increase in the number of different pairs of mutually cis  $[(\text{CH}_3)_2\text{N}]_3\text{E}$  ( $\text{E} = \text{P}, \text{As}$ ) ligands in a substituted octahedral complex (this number of cis ligand pairs is conveniently designated as  $L_{cc}$ ) will result in increased instability from the cis ligand interconversions. Table IV lists the number of cis ligand pairs

TABLE IV  
NUMBER OF CIS LIGAND PAIRS IN SUBSTITUTED  
OCTAHEDRAL METAL CARBONYLS

Type	Point group	No. of cis ligand pairs, $L_{cc}$	Type	Point group	No. of cis ligand pairs, $L_{cc}$
$\text{M}(\text{CO})_6$	$O_h$	0	$fac\text{-L}_3\text{M}(\text{CO})_3$	$C_{3v}$	3
$\text{LM}(\text{CO})_5$	$C_{4v}$	0	$trans\text{-L}_4\text{M}(\text{CO})_2$	$D_{4h}$	4
$trans\text{-L}_2\text{M}(\text{CO})_4$	$D_{4h}$	0	$cis\text{-L}_4\text{M}(\text{CO})_2$	$C_{2v}$	5
$cis\text{-L}_2\text{M}(\text{CO})_4$	$C_{2v}$	1	$\text{L}_5\text{M}(\text{CO})$	$C_{4v}$	8
$mer\text{-L}_3\text{M}(\text{CO})_3$	$C_{2v}$	2	$\text{L}_6\text{M}$	$O_h$	12

( $L_{cc}$ ) for all of the possible types of substituted octahedral metal carbonyls.

The interconversions of octahedral metal carbonyl derivatives of tris(dimethylamino)phosphine and tris(dimethylamino)arsine observed in this paper (Table III) are all of types which reduce the number of cis ligand pairs ( $L_{cc}$ ). The relevant pathways for interconversions among the systems encountered in this work are illustrated in Figure 1. The processes for going from one system to another are of two types, as follow.

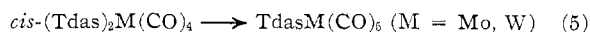
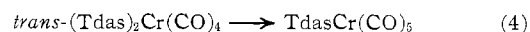
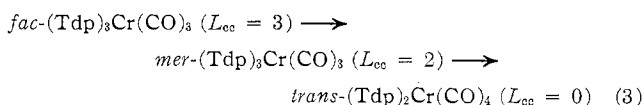
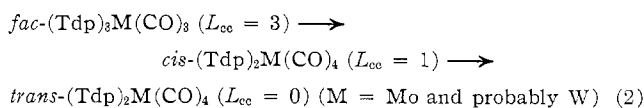
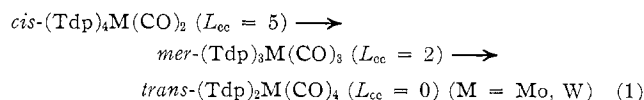
**1. Rearrangement of a Cis Isomer into the Corresponding Trans Isomer.**—This process can reduce the number of cis ligand pairs ( $L_{cc}$ ) by 1 in the case of the disubstituted, trisubstituted, and tetrasubstituted derivatives (Table IV). In this work this process has been observed for the disubstituted and trisubstituted derivatives and is favored for chromium derivatives relative to analogous molybdenum and tungsten derivatives because of the smaller size of the chromium atom.

**2. Removal of a  $[(CH_3)_2N]_3E$  ( $E = P, As$ ) Ligand by Reaction with Carbon Monoxide Produced from Decomposition of the Metal Carbonyl Derivatives.**—

The process reduces the number of cis ligand pairs by reducing the number of ligands in question (*i.e.*,  $[(C-H_3)_2N]_3E$  ( $E = P, As$ )) attached to the central metal atom. It can only occur under conditions where some of the metal carbonyl derivatives are unstable with respect to complete decomposition with liberation of carbon monoxide. For this reason reaction with decomposition-generated carbon monoxide occurs most readily with the molybdenum carbonyl derivatives since molybdenum-carbon bonds are weaker than analogous chromium-carbon and tungsten-carbon bonds.<sup>19</sup> Furthermore, these reactions of octahedral metal carbonyl complexes with decomposition-generated carbon monoxide are also more likely to occur with molybdenum and tungsten derivatives than with chromium derivatives because of the possibility for both  $SN_1$  and  $SN_2$  carbon monoxide substitution processes to occur with the derivatives of the larger molybdenum and tungsten atoms but not with the derivatives of the smaller chromium atom.<sup>20</sup> The reaction mixtures where reaction with decomposition-generated carbon monoxide has taken place contain varying amounts of dark (generally brown), insoluble, and intractable materials, apparently the decomposition products from the metal carbonyl derivative serving as the source of the carbon monoxide. The relative weakness of the bonds between the donor phosphorus or arsenic atom and the nitrogen atoms in tris(dimethylamino)phosphine and tris(dimethylamino)arsine complexes coupled with the tendency for amine and related nitrogen derivatives produced as decomposition products to coordinate to transition metals may account for the greater apparent tendency for complexes of the  $[(C-H_3)_2N]_3E$  ( $E = P, As$ ) ligands to undergo reaction with decomposition-generated carbon monoxide than that of complexes of other organophosphorus or organoarsenic ligands such as tertiary phosphines with phosphorus-carbon bonds, tertiary arsines with arsenic-carbon bonds, trialkyl and triaryl phosphites with phosphorus-oxygen bonds, and phosphorus trihalides with phosphorus-halogen bonds. In this manner the dimethylamino substituents on the tris(dimethylamino)phosphine ligand appear to be responsible for the previously discussed<sup>4</sup> inability to prepare and isolate tris(dimethylamino)phosphine derivatives with three or more tris(dimethylamino)phosphine ligands bonded to the same metal atom. The greater tendency for tris(dimethylamino)arsinemetal carbonyl complexes than corresponding tris(dimethylamino)phosphine complexes to undergo reaction with decomposition-generated carbon monoxide may be attributed to the follow-

ing two factors: (1) the lower stability of arsenic-metal bonds than that of analogous phosphorus-metal bonds making tris(dimethylamino)arsine a more readily displaced ligand than tris(dimethylamino)phosphine; (2) the lower stability of arsenic-nitrogen bonds than that of analogous phosphorus-nitrogen bonds making tris(dimethylamino)arsinemetal carbonyl complexes more susceptible to decomposition with liberation of carbon monoxide than corresponding tris(dimethylamino)phosphine complexes.

Figure 1 summarizes the interconversions of substituted octahedral metal carbonyl complexes observed in this work. Actual processes have been observed which proceed along the following pathways in Figure 1



Of particular interest are the different pathways for conversion of the chromium derivative  $fac-(Tdp)_3Cr(CO)_3$  to  $trans-(Tdp)_2Cr(CO)_4$  through  $mer-(Tdp)_3Cr(CO)_3$  and for conversion of the molybdenum derivative  $fac-(Tdp)_3Mo(CO)_3$  to  $trans-(Tdp)_2Mo(CO)_4$  through  $cis-(Tdp)_2Mo(CO)_4$ . This difference is an apparent consequence of the tendency for chromium derivatives to undergo cis-trans (or fac-mer) rearrangements and for molybdenum derivatives to undergo reactions with decomposition-generated carbon monoxide.

This work also provides the first clear indication of the relative reactivities toward Lewis base ligands of different olefin derivatives of the same metal carbonyl. For a given central metal atom the reactivities of the olefinmetal carbonyl complexes were found to decrease with decreasing numbers of carbonyl groups, *i.e.*,  $C_7H_8M(CO)_4$  ( $C_7H_8 =$  norbornadiene; most reactive)  $> C_7H_8M(CO)_3$  ( $C_7H_8 =$  cycloheptatriene)  $> cis-(1,3-C_6H_8)_2M(CO)_2$  (least reactive). This difference in reactivity is most clearly illustrated by the reactions of the tungsten carbonyl derivatives with tris(dimethylamino)arsine. Thus the norbornadiene complex  $C_7H_8W(CO)_4$  and tris(dimethylamino)arsine react at room temperature over a period of hours. However, the cycloheptatriene complex  $C_7H_8W(CO)_3$  and tris(dimethylamino)arsine fail to react at room temperature but react in boiling 2,2,5-trimethylhexane ( $\sim 124^\circ$ ). The 1,3-cyclohexadiene complex  $(C_6H_8)_2W(CO)_2$  and tris(dimethylamino)arsine fail to react in boiling 2,2,5-trimethylhexane even after 112 hr. This increasing difficulty of displacement of coordinated olefin ligands by Lewis bases upon successive replacement of carbonyl groups with additional olefin ligands, which are weaker  $\pi$  acceptors than carbonyl groups, may be attributed to

(20) R. J. Angelici and J. R. Graham, *J. Amer. Chem. Soc.*, **87**, 5586 (1965); J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).

the strengthening of the metal-olefin bonds by additional retrodonative bonding to the coordinated olefins. This is a consequence of greater electron density on the metal atom arising from the presence of fewer strongly  $\pi$ -accepting (*i.e.*, electron-withdrawing) carbonyl groups.

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## Chelates of Iron(III), Cobalt(III), Copper(II), and Zinc(II) with 2-(Trifluoroacetyl)picolinate Ion and Copper(II) with 2-(Acetyl)picolinate Ion

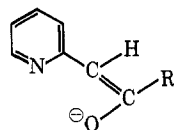
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The Co(III), Fe(III), Zn(II), and Cu(II) complexes of trifluoroacetylpicolinate ion, TFAP, and the Cu(II) complex of acetylpicolinate ion, AP, are prepared and characterized. All the complexes are monomeric and neutral. Molecular weights, magnetic moments, electronic spectra, and  $^1\text{H}$  and  $^{19}\text{F}$  magnetic resonance data are reported. Particular attention is given to the structure of  $\text{Co}(\text{TFAP})_3$ . Chemical shift differences of the three olefinic chelate ring proton resonances and of the three uniquely oriented  $\text{CF}_3$  groups and analysis of the electronic spectrum indicate the synthesis of  $\text{Co}(\text{TFAP})_3$  to be highly specific for the meridional isomer.

Chelates of anions derived from 2-(trifluoroacetyl)picoline<sup>1</sup> and 2-(acetyl)picoline were first reported by McGrath and Levine<sup>2</sup> and by Beckett, Kerridge, Clark, and Smith.<sup>3</sup> McGrath and Levine developed a new synthesis of perfluoroacetylpicolines and found that these compounds react with copper(II) to give brown precipitates, mp 219.5–220°. They assumed that these compounds were copper chelates of the newly synthesized ligand. Beckett, Kerridge, Clark, and Smith studied the antibacterial activity of 2-phenacylpyridine and related compounds and found that it reacted with copper(II), iron(II), iron(III), and cobalt(II).<sup>3</sup> The resulting complexes were not characterized.

We report here the synthesis and characterization of Zn(II), Fe(III), Co(III), and Cu(II) complexes of the enolate derived from 2-(trifluoroacetyl)picoline, TFAP, and the copper(II) complex of 2-(acetyl)picolinate ion (AP). A discussion of the isomeric forms of  $\text{Co}(\text{TFAP})_3$  is included.



AP, R =  $\text{CH}_3$   
TFAP, R =  $\text{CF}_3$

### Experimental Section

**Preparation of the Ligands.**—2-(Trifluoroacetyl)picoline was synthesized according to the method described by McGrath and Levine,<sup>2</sup> and 2-(acetyl)picoline was prepared by the procedure of Burger and Allyot.<sup>4</sup>

(1) The anionic ligands derived by enolization of 2-(trifluoroacetyl)picoline and 2-(acetyl)picoline are abbreviated TFAP and AP, respectively, in this paper.

(2) T. F. McGrath and R. Levine, *J. Amer. Chem. Soc.*, **77**, 3656 (1955).

(3) A. H. Beckett, K. A. Kerridge, P. M. Clark, and W. G. Smith, *J. Pharm. Pharmacol.*, **7**, 717 (1955).

(4) A. Burger and G. E. Allyot, *J. Org. Chem.*, **12**, 345 (1947).

**Preparation of the Chelates. Tris(trifluoroacetylpicolinate)-iron(III).**—To 0.27 g (0.0010 mol) of ferric chloride, dissolved in water, was added 0.57 g (0.0030 mol) of trifluoroacetylpicoline dissolved in 25 ml of 95% ethanol. The mixture immediately turned purple and more water was added to decrease the solubility of the complex. The fine purple precipitate was filtered and recrystallized from a 1:4 benzene-petroleum ether mixture; mp 205°; yield 34%. *Anal.* Calcd for  $\text{C}_{24}\text{H}_{15}\text{O}_3\text{N}_3\text{F}_9\text{Fe}$ : C, 46.48; H, 2.44; N, 6.77; F, 27.57; Fe, 9.00. Found: C, 46.46; H, 2.54; N, 6.67; F, 27.42; Fe, 9.53.

**Tris(trifluoroacetylpicolinate)cobalt(III).**—An aqueous solution containing 0.24 g (0.0010 mol) of cobaltous chloride was added to 0.57 g (0.0030 mol) of trifluoroacetylpicoline dissolved in 25 ml of 95% ethanol. The mixture was heated to 50° while being stirred. Oxidation was effected by the addition of 1.2 ml of 10% hydrogen peroxide solution. The pink solution turned green and a brownish green precipitate formed quickly. The mixture was cooled and filtered and the resulting product was recrystallized several times from 1:1 benzene-petroleum ether; mp 205–208° dec; yield 64%. *Anal.* Calcd for  $\text{C}_{24}\text{H}_{15}\text{O}_3\text{N}_3\text{F}_9\text{Co}$ : C, 46.25; H, 2.43; N, 6.74; F, 27.43; Co, 9.45. Found: C, 45.66; H, 2.41; N, 6.52; F, 27.15; Co, 9.44.

**Bis(trifluoroacetylpicolinate)copper(II).**—Twenty-five milliliters of an absolute ethanol solution containing 0.20 g (0.0010 mol) of copper(II) acetate was treated with 0.38 g of trifluoroacetylpicoline (0.0020 mol) dissolved in 10 ml of absolute ethanol. The mixture was heated, and a dark brown precipitate formed immediately. After cooling, the solution was filtered and the brown crystals were recrystallized twice from ethanol; yield 85%; mp 218–220°. *Anal.* Calcd for  $\text{C}_{18}\text{H}_{10}\text{O}_2\text{N}_2\text{F}_6\text{Cu}$ : C, 43.70; H, 2.29; N, 6.37; F, 25.92; Cu, 14.45. Found: C, 43.83; H, 2.40; N, 6.32; F, 26.09; Cu, 14.58.

**Bis(trifluoroacetylpicolinate)zinc(II).**—A solution containing 0.38 g (0.0020 mol) of trifluoroacetylpicoline, dissolved in 95% ethanol, was added to a warm aqueous solution containing 0.29 g (0.0010 mol) of zinc(II) sulfate. The mixture was stirred and heated a few minutes on a hot plate. Upon cooling, white needles were formed and these were filtered and recrystallized from ethanol or chloroform; yield 55%; mp 215°. *Anal.* Calcd for  $\text{C}_{18}\text{H}_{10}\text{O}_2\text{N}_2\text{F}_6\text{Zn}$ : C, 43.51; H, 2.28; N, 6.34; F, 25.81; Zn, 14.80. Found: C, 43.59; H, 2.30; N, 6.18; F, 25.59; Zn, 14.64.

**Bis(acetylpicolinate)copper(II).**—Twenty-five milliliters of a 95% ethanol solution containing 0.27 g (0.0020 mol) of acetylpicoline was heated and mixed with 15 ml of an ethanolic solution containing 0.20 g (0.0010 mol) of copper(II) acetate. Complexation occurred immediately with the formation of a dark brown