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On the Stability of Thallium(I) Transition Metal Carbonyls. Derivatives Containing Iron, Chromium, and Vanadium

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The stability of Tl(I) derivatives of transition metal carbonyl anions, TlR, has been shown to depend on at least two factors: (1) the percent covalent character of the Tl–M bond and (2) the size of R. Only those compounds with weak covalency in the Tl–M bond are stable in solvents in which they are not dissociated except when R is bulky. In the absence of steric effects the base strength of R can be used as a guide to the stability of the TlR derivatives. With weakly basic anions, Tl(I) derivatives are stable as associated species and may be isolated at room temperature. Tl(I) derivatives of more strongly basic anions are not stable and attempts to prepare these compounds in noncoordinating solvents result in the formation of thallium metal and TlR$_3$ derivatives. A series of metathetical reactions of TlNO$_3$ with the relatively weakly basic anions Fe(CO)$_3$NO$^-$ and RFe(CO)$_4^-$ (R = CH$_2$CN, C(=O)C$_6$H$_5$, Sn(C$_6$H$_5$)$_3$, and CN) produce stable Tl(I) compounds. TlCr(CO)$_3$(C$_5$H$_5$) can be isolated by the same method but is only stable in the solid state. The reaction of elemental thallium with V(CO)$_6$ gives the Tl(I) derivative of the weakly basic V(CO)$_6^-$ anion. All of these Tl(I) derivatives contain a weak Tl–M bond in solvents in which they are not dissociated. Although this bond is weak, some of the TlR derivatives undergo substitution reactions with Lewis bases. The products of the substitution reactions are either Tl(I) or Tl(III) derivatives depending on factors 1 and 2 above. Thus P(OC$_6$H$_4$Cl)$_3$ and P(C$_6$H$_5$)$_3$ react with TlFe(CO)$_3$NO to give Tl(I) and Tl(III) derivatives, respectively. TlFe(CO)$_4$Sn(C$_6$H$_5$)$_3$ reacts with Lewis bases in solvents of low dielectric constant to give derivatives of the type TlFe(CO)$_3$LSn(C$_6$H$_5$)$_3$. The stability of these complexes is attributed to the large size of the (C$_6$H$_5$)$_3$SnFe(CO)$_3$L$^-$ anion which prevents the formation of the corresponding Tl(III) derivatives.

Introduction

The reactions of TlCo(CO)$_4$ with a variety of Lewis bases in noncoordinating solvents have been shown to proceed with formation of either TlCo(CO)$_3$L or Tl[Co(CO)$_3$L]$_3$ and thallium metal.[1] Thallium(I) compounds were formed with Lewis bases which give substituted cobalt carbonyl anions of relatively low basicity while with ligands giving more strongly basic anions, thallium(III) derivatives and thallium metal formed. These substitution reactions suggested that a pK_a of about 5 for the hydridocarbonyl is the upper limit of the base strength which is consistent with the formation of stable thallium(I) derivatives of the corresponding metal carbonyl anions.

It has been reported[2] that thallium(I) derivatives of other strongly basic anions disproportionate readily to the thallium(III) derivatives and thallium metal. However, no stable thallium derivatives of weakly basic anions other than those of Co(CO)$_3$L$^-$ noted above have been reported. We set out to determine if thallium(I) derivatives of weakly basic transition metal carbonyl anions were stable in general and have prepared such derivatives containing vanadium, chromium, and iron. From the results of this work it is apparent that the stability of these thallium(I) compounds is related to the base strength of the metal carbonyl anion as well as to the size of this anion. A note describing portions of this work has appeared.[3]

Experimental Section

All operations were conducted under nitrogen using Schlenk-type equipment with deoxygenated solvents. Tetrahydrofuran was distilled from lithium aluminum hydride and stored over molecular sieves. All spectra were recorded on a Beckman IR-12 spectrophotometer. The spectra were calibrated in the carbonyl region using polystyrene and Hg[Co(CO)$_4$]$_2$ in heptane. The CO frequencies of this solution were taken from Adams.[4] Melting points were determined in sealed capillary tubes under a nitrogen atmosphere. The compounds prepared, melting points, yields, and analyses are reported in Table I. Molecular weights were determined under nitrogen by vapor pressure osmometry in benzene. Fe(CO)$_5$, Na$_2$Fe(CO)$_4$·1.5diglyme, and Na(diglyme)$_2$V(CO)$_6$ were obtained from Alfa Inorganics, Beverly, Mass.

Preparation of TlFe(CO)$_3$NO. Fe(CO)$_5$ (10.4 mmol) and 10.0 mmol of KNO$_2$ dissolved in 10 ml of methanol were stirred for 18 hr at 35–40°.[5] After cooling to room temperature, 10.0 mmol of TlNO$_3$ in 25 ml of water was added and the solvent (CH$_3$OH + H$_2$O) was removed in vacuo. The remaining solid was extracted with four 20 ml portions of benzene and the resulting solution was reduced in volume to ca. 10 ml. Heptane (60 ml) was carefully placed on top of the benzene solution and the two layers were allowed to diffuse together giving red crystals.

Preparation of Tl[Fe(CO)$_2$P(C$_6$H$_5$)$_3$NO]$_3$. A solution of 1.45 mmol of TlFe(CO)$_3$NO and 1.45 mmol of P(C$_6$H$_5$)$_3$ in 20 ml of dichloromethane was stirred at 20° for 8 hr. The solution was filtered and concentrated to ca. 5 ml. A layer of 50 ml of hexane was added and the two layers were allowed to diffuse together producing black crystals. By this method the product was Tl[Fe(CO)$_2$P(C$_6$H$_5$)$_3$-NO]$_3$·2CH$_2$Cl$_2$.

Preparation of TlFe(CO)$_2$P(OC$_6$H$_4$Cl)$_3$NO. Equimolar quantities of TlFe(CO)$_3$NO and P(OC$_6$H$_4$Cl)$_3$ were dissolved in toluene and stirred for several hours at 0°. After filtration, the solvent was removed in vacuo and the residue was dissolved in a minimum of dichloromethane. A large excess of hexane was added and when the two layers had diffused together golden yellow needles were recovered by filtration.

Preparation of TlCr(CO)$_3$C$_5$H$_5$. NaCr(CO)$_3$C$_5$H$_5$ (5.00 mmol) in 30 ml of tetrahydrofuran was filtered onto 5.00 mmol of TlNO$_3$ in 30 ml of water producing an orange solution. The tetrahydrofuran was removed in vacuo with the precipitation of a yellow solid. The water was syringed off and the product was washed with three 20 ml portions of water and dried in vacuo.

Preparation of Tl[Cr(CO)$_3$C$_5$H$_5$]$_3$. Method 1. A solution of 2.50 mmol of [Cr(CO)$_3$C$_5$H$_5$]$_2$ dissolved in 20 ml of benzene and a 3 g

Table I. Analytical Data for Thallium Metal Carbonyls

| Compd | Yield, % | Mp, °C | Analysis, % | | | | | |
| | | | C | | H | | X | |
			Calcd	Found	Calcd	Found	Calcd	Found
TlFe(CO)₃NO^a	40	171–176	9.63	9.73	0	0	3.74^d	3.72^d
Tl[Fe(CO)₂NOP(p-OC₆H₄Cl)₃]	85	118–123	31.61	31.36	1.59	1.79		
Tl[Fe(CO)₂NOP(C₆H₅)₃]₃·2CH₂Cl₂	95	135 d	46.93	47.03	3.13	2.99	2.65^d 8.94^e	2.78^d 8.74^e
TlFe(CO)₄CH₂CN^b	40	105 d	17.48	17.51	0.49	0.49	3.40^d	3.35^d
TlFe(CO)₄C(=O)C₆H₅	42	105–108	27.68	27.57	1.06	1.18		
TlFe(CO)₄CN^c	68	150 d	15.08	15.10	0	0	3.52^d	3.53^d
TlFe(CO)₄Sn(C₆H₅)₃	90	215–218	36.59	36.35	2.09	2.22		
TlFe(CO)₃P(p-OC₆H₅Cl)₃Sn(C₆H₅)₃	95	145–155	42.28	42.34	2.46	2.60	9.60^e	9.79^e
TlFe(CO)₃P(C₆H₅)₃Sn(C₆H₅)₃	60	247–251	48.97	49.16	3.16	3.30		
TlFe(CO)₃P(n-C₄H₉)₃Sn(C₆H₅)₃	79	148 d	44.21	43.95	4.72	4.76		
TlV(CO)₆	95	115 d			0	0	48.27^f	47.99^f
Tl[C₅H₅Cr(CO)₃]		213–214	23.70	23.20	1.24	1.70		
Tl[C₅H₅Cr(CO)₃]₃	97	194–196	35.69	35.50	1.87	1.89		

^{a} Mol wt: Calcd, 374; Found, 393. ^{b} Mol wt: Calcd, 412; Found, 409. ^{c} Mol wt: Calcd, 398; Found, 391. ^{d} X = N. ^{e} X = Cl. ^{f} X = Tl.

piece of thallium metal (cleaned in concentrated nitric acid) were stirred for 2 hr at room temperature. The solution was filtered and the benzene removed in vacuo. The product was dissolved in a minimum of dichloromethane and precipitated with hexane. **Method 2.** TlCr(CO)₃C₅H₅ (2.50 mmol) was dissolved in 20 ml of dichloromethane and stirred for 2 hr. After filtration the product was isolated as in method 1.

Preparation of TlFe(CO)₄CH₂CN. To 3.67 mmol of Na₂Fe(CO)₄·1.5C₄H₈O₂ in 20 ml of tetrahydrofuran was added dropwise 3.39 mmol of ClCH₂CN, dissolved in 10 ml of tetrahydrofuran. After the addition was completed, the solution was stirred for 30 min and filtered onto 3.7 mmol of TlNO₃ dissolved in 30 ml of water. The solvent was removed in vacuo and the residue was extracted with three 20 ml portions of benzene. The benzene was removed in vacuo and the product was recrystallized from dichloromethane and hexane giving red crystals of the product.

Preparation of TlFe(CO)₄C(=O)C₆H₅. To 5.14 mmol of Na₂Fe(CO)₄·1.5C₄H₈O₂ in 20 ml of tetrahydrofuran was added dropwise 4.70 mmol of C₆H₅C(=O)Cl dissolved in 10 ml of tetrahydrofuran. After stirring for 30 min, the solution was filtered onto 5.1 mmol of TlNO₃ dissolved in 30 ml of water. The method of isolation and purification of the product was the same as that used for TlFe(CO)₄CH₂CN.

Preparation of TlFe(CO)₄CN. Method 1. Fe₂(CO)₉ (5.5 mmol) and ~20 g of KCN were stirred in 180 ml of acetonitrile at 50–60° for 5–6 hr. After cooling, the solution was filtered onto 11.2 mmol of TlNO₃ dissolved in 40 ml of water and the solvent was removed in vacuo. The residue was extracted with four 20 ml portions of benzene and the resulting solution was concentrated to ca. 20 ml. A 60 ml layer of heptane was added which resulted in the deposition of red-brown crystals in 2 days. **Method 2.** Fe(CO)₅ (5.0 mmol) and 10.0 mmol of KCN in 50 ml of methanol were stirred for 24 hr at 50–60°. Following addition of 5.2 mmol of TlNO₃ in 40 ml of water the isolation and purification was done as above.

Preparation of TlFe(CO)₄Sn(C₆H₅)₃. To 2.95 mmol of Na₂-Fe(CO)₄·1.5C₄H₈O₂ in 20 ml of tetrahydrofuran was added dropwise 2.90 mmol of ClSn(C₆H₅)₃ dissolved in 10 ml of tetrahydrofuran. After stirring for 30 min, the solution was filtered onto 2.95 mmol of TlNO₃ in 25 ml of water. The solvent was removed in vacuo and the residue was extracted with six 30 ml portions of benzene. Because of the product's low solubility in benzene, it was recrystallized from tetrahydrofuran and heptane to give yellow fluffy needles.

Preparation of TlFe(CO)₃P(OC₆H₄Cl)₃Sn(C₆H₅)₃. P(OC₆H₄Cl)₃ (0.70 mmol) was added to 0.70 mmol of TlFe(CO)₄Sn(C₆H₅)₃ suspended in 30 ml of benzene and the resulting solution was stirred for 3 hr at room temperature at which time everything had dissolved giving an orange solution. After filtration, the solvent was removed in vacuo and the product was recrystallized from dichloromethane and hexane giving yellow crystals.

Preparation of TlFe(CO)₃P(C₆H₅)₃Sn(C₆H₅)₃. TlFe(CO)₄-Sn(C₆H₅)₃ (0.70 mmol) and 0.72 mmol of P(C₆H₅)₃ in 30 ml of dichloroethane were stirred 6–8 hr at room temperature producing a pale yellow precipitate which was recrystallized from dimethylformamide and toluene.

Preparation of TlFe(CO)₃P(C₄H₉)₃Sn(C₆H₅)₃. TlFe(CO)₄-Sn(C₆H₅)₃ (0.70 mmol) and 0.70 mmol of P(C₄H₉)₃ in 30 ml of dichloroethane were stirred for 4 hr at room temperature at which time everything had dissolved producing a red solution. The solution was filtered and reduced in volume to ca. 10 ml. Addition of heptane resulted in the production of red crystals.

Preparation of TlV(CO)₆. Na(diglyme)₂V(CO)₆ (0.01 mol) was added to a 100-ml three-necked flask which was connected to another 100-ml three-necked flask with a glass joint. To the flask containing the Na(diglyme)₂V(CO)₆ 30 ml of 85% H₃PO₄ was added and the mixture was stirred for 30 min with the evolution of H₂. The empty flask was cooled to −78° and partially evacuated. After all the V(CO)₆ had been sublimed over, the two flasks were disconnected, and to the flask containing the V(CO)₆ was added a piece of clean thallium metal and 50 ml of dichloroethane. The solution was stirred for several hours at room temperature changing the color from yellow-green to reddish-orange. After filtration, the solvent was removed in vacuo leaving behind an orange-red pyrophoric solid.

Results

TlFe(CO)₃NO. In contrast to Hg[Fe(CO)₃NO]₂,[6] Tl-Fe(CO)₃NO is stable indefinitely under nitrogen at room temperature. TlFe(CO)₃NO is soluble in aromatic and most polar solvents giving air-sensitive dark yellow to red solutions; it is only very slightly soluble in chlorinated hydrocarbons and insoluble in saturated hydrocarbons. In benzene, molecular weight measurements showed TlFe(CO)₃NO to be monomeric.

Peak maxima of the infrared spectra of TlFe(CO)₃NO in various solvents are listed in Table II. The infrared spectrum in dimethyl sulfoxide is essentially indistinguishable from the spectrum of (C₆H₅)₄AsFe(CO)₃NO in tetrahydrofuran, prepared by adding an excess of (C₆H₅)₄AsCl to TlFe(CO)₃NO. Since (C₆H₅)₄AsFe(CO)₃NO is presumed to dissolve in tetrahydrofuran forming solvent separated (C₆H₅)₄As⁺ and Fe(CO)₃NO⁻ ions, the spectral analogies suggest solvent separated ions in dimethyl sulfoxide solutions of TlFe(CO)₃NO. In solvents of low dielectric constant such as benzene, dichloromethane, and dichloroethane, the spectra contain three principal absorption bands in the carbonyl region and one in the nitrosyl region due to an associated species. This same pattern of bands is also present in tetrahydrofuran but at significantly lower energy. The infrared spectrum of Tl-Fe(CO)₃NO in acetonitrile is more complex. The broad, assymmetric band with its maximum at 1886 cm⁻¹ is probably made up of three bands, a weak band at ca. 1920 cm⁻¹, a medium band at ca. 1900 cm⁻¹, and a strong band at the maximum of 1886 cm⁻¹. The spectrum is consistent with the presence of an associated species as found in tetrahydrofuran (2000, 1920, and 1900 cm⁻¹) and solvent separated ions as found in dimethyl sulfoxide (1989, 1886 cm⁻¹). Such an equilibrium mixture has been shown to exist for TlCo(CO)₄[2]

Table II. CO and NO Spectra of Thallium Metal Carbonyls and Related Compounds

Compd	Solvent	Peak maxima, cm⁻¹
$TlFe(CO)_3NO$	Benzene	2014 (s), 1934 (s), 1903 (s), 1674 (m)[a]
	CH_2Cl_2	2019 (vs), 1946 (s), 1915 (s), 1678 (m)[a]
	$(CH_2Cl)_2$	2013 (s), 2041 (s), 1913 (s), 1679 (m)[a]
	THF	2000 (s), 1919 (s), 1899 (s), 1661 (m)[a]
	CH_3CN	2000 (w), 1989 (m), 1886 (vs, b),[b] 1653 (m)[a]
	$(CH_3)_2SO$	1985 (m), 1881 (s), 1651 (s)[a]
$(C_6H_5)_4AsFe(CO)_3NO$	THF	1983 (m), 1882 (s), 1652 (s)[a]
$TlFe(CO)_2NOP(OC_6H_4Cl)_3$	CH_2Cl_2	1953 (m), 1894 (s), 1674 (m)[a]
$TlFe(CO)_2NOP(OC_6H_5)_3$[c]	CH_2Cl_2	~1950 (m),[d] 1892 (s), 1670 (m)[a]
$Tl[Fe(CO)_2NOP(OC_6H_5)_3]_3$[c]	CH_2Cl_2	2015 (m), 1985 (s), 1950 (vs), 1795 (vw), 1745 (s)[a]
$Tl[Fe(CO)_2NOP(C_6H_5)_3]_3$	CH_2Cl_2	1990 (m), 1960 (s), 1927 (vs), 1767 (vw),[a] 1729 (s, sh),[a] 1720 (s)[a]
$TlFe(CO)_4CH_2CN$	CH_2Cl_2	2165 (w),[e] 2040 (s), 1970 (s), 1925 (s)
	THF	2188 (w),[e] 2014 (m), 1917 (m, sh), 1900 (vs)
$NaFe(CO)_4CH_2CN$	THF	2190 (w),[e] 2012 (m), 1915 (m, sh), 1895 (vs)
$TlFe(CO)_4Sn(C_6H_5)_3$	$C_6H_5CH_3$	2011 (s), 1954 (m), 1911 (m, sh), 1891 (s)
	CH_2Cl_2	2016 (s), 1954 (m), 1912 (m, sh), 1892 (s)
	THF	2000 (s), 1910 (m, sh), 1881 (vs), 1865 (s, sh)
	$(CH_3)_2SO$	1995 (m), 1907 (m), 1879 (vs)
$NaFe(CO)_4Sn(C_6H_5)_3$	THF	1995 (s), 1907 (m, sh), 1879 (vs), 1865 (s, sh)
$TlFe(CO)_4CN$	C_6H_6	2035 (m), 2024 (s), 1975 (s), 1942 (vs)
	CH_2Cl_2	2036 (s), 2023 (m, sh), 1996 (s, sh), 1941 (vs)
	THF	2106 (w),[e] 2037 (s), 1957 (s), 1936 (vs)
	CH_3CN	2107 (w),[e] 2039 (s), 1954 (s, sh), 1934 (vs)
	$(CH_3)_2SO$	2108 (w),[e] 2036 (m), 1946 (s, sh), 1928 (vs)
$NaFe(CO)_4CN$	CH_3CN	2108 (w),[e] 2034 (m), 1946 (s, sh), 1927 (vs)
$TlFe(CO)_3P(OC_6H_4Cl)_3Sn(C_6H_5)_3$	CH_2Cl_2	1963 (m), 1884 (s), 1860 (vs)
	CH_3CN	1855 (s)
$TlFe(CO)_3P(OC_2H_5)_3Sn(C_6H_5)_3$	CH_2Cl_2	1953 (m), 1882 (s), 1854 (vs)
$TlFe(CO)_3P(C_6H_5)_3Sn(C_6H_5)_3$	Nujol	1924 (w), 1858 (m), 1841 (m), 1828 (s)
	CH_3CN	1828 (s)
	$(CH_3)_2SO$	1826 (s)
$TlFe(CO)_3P(C_4H_9)_3Sn(C_6H_5)$	CH_2Cl_2	1938 (m), 1864 (s), 1841 (vs)
	CH_3CN	1815 (s)
$TlV(CO)_6$	$(CH_2Cl)_2$	2029 (m), 1939 (m), 1880 (vs), 1862 (vs)
	C_6H_6	2031 (m), 1940 (m), 1884 (s), 1863 (s)
	THF	1896 (w), 1860 (vs)
	$(CH_3)_2SO$	1895 (vw), 1857 (vs)
$Tl[Cr(CO)_3(C_5H_5)]$	CH_2Cl_2	1935 (s), 1845 (m), 1810 (s)
	THF	1923 (s), 1840 (m), 1808 (s)
$Na[Cr(CO)_3C_5H_5]$	THF	1900 (s), 1795 (s), 1750 (s)
$Tl[Cr(CO)_3C_5H_5]_3$	CH_2Cl_2	1990 (w), 1952 (s), 1901 (s)

[a] ν(NO). [b] Broad and complex; see text. [c] Not isolated. [d] Exact position masked by $Tl[Fe(CO)_2NOP(OC_6H_5)_3]_3$ peak. [e] ν(CN).

in acetonitrile and $TlCo(CO)_3P(OC_6H_5)_3$[1] in acetonitrile and nitromethane.

As was the case for $TlCo(CO)_4$ and $TlCo(CO)_3L$, the infrared data for $TlFe(CO)_3NO$ indicate the presence of a metal–metal bond in solvents of low dielectric constant. The evidence for the presence of a thallium–iron bond is as follows: (1) in these solvents the bands in the infrared spectra appear at significantly higher energy than is observed for the free $Fe(CO)_3NO^-$ anion; (2) the pattern in the infrared spectrum in these solvents is similar to what has been observed for other covalent $MFe(CO)_3NO$ derivatives[7,8] as well as for $Mn(CO)_3(NO)P(C_6H_5)_3$;[9,10] (3) as with $TlCo(CO)_3L$,[1] a Tl–O interaction can be ruled out in view of the absence of bands at lower frequencies than the anion bands.

Analogous spectra have been observed for other $MFe(CO)_3NO$ derivatives which are believed to have trigonal bipyramidal structures with a metal occupying an axial position and the nitrosyl an equatorial position in the coordination sphere.[7,8] In addition, $Mn(CO)_3(NO)P(C_6H_5)_3$, which is known to have a trigonal bipyramidal structure with $P(C_6H_5)_3$ in an axial position and NO in the equatorial plane,[9] has a similar infrared spectrum.[10] These similarities led us to conclude that in solvents of low dielectric constant $TlFe(CO)_3NO$ has a trigonal bipyramidal structure with thallium in an axial position and NO in an equatorial position.

A comparison of the infrared spectrum of $TlFe(CO)_3NO$ with the spectrum of other $MFe(CO)_3NO$ derivatives clearly indicates the weakness of the Tl–Fe interaction in $TlFe(CO)_3NO$. For brevity we shall consider the relative position of the nitrosyl peaks only although a comparable shift occurs for the carbonyl bands. The nitrosyl band of $TlFe(CO)_3NO$ appears at ca. 1677 cm⁻¹, but the same bands of $(C_6H_5)_3PAuFe(CO)_3NO$[7] and $(C_6H_5)_3SnFe(CO)_3NO$[8] appear at 1745 and 1773 cm⁻¹, respectively. Since the nitrosyl band for the $Fe(CO)_3NO^-$ anion occurs at 1651 cm⁻¹, it is apparent that only a small amount of electron density has been transferred to the thallium in $TlFe(CO)_3NO$ and that a much larger charge transfer has taken place to the main group metals in $(C_6H_5)_3PAuFe(CO)_3NO$ and $(C_6H_5)_3SnFe(CO)_3NO$. Assuming that the amount of charge transfer reflects the covalent character of the metal–metal bond, the covalent character of the thallium–iron bond in $TlFe(CO)_3NO$ is small. Similar weak Tl–M bonds are observed in thallium(I) metal carbonyl derivatives with Co,[1,2] Cr,[2] Mo,[2] W,[2] and Mn.[2]

It has been postulated that $TlCo(CO)_4$ forms π complexes with aromatic solvents,[2] and we proposed[1] that thallium may interact with one of the phenyl rings of $P(OC_6H_5)_3$ in $TlCo(CO)_3P(OC_6H_5)_3$. In view of the great solubility of $TlFe(CO)_3NO$ in benzene compared to its insolubility in chlorinated hydrocarbons, $TlFe(CO)_3NO$ may also form a π complex with benzene. Such a thallium–benzene complex should increase the electron density on the thallium which in turn should accept less electron density from the iron. This should shift the carbonyl and nitrosyl bands to lower energy from what is observed in nonaromatic, nondonor solvents. This appears to be the case for $TlFe(CO)_3NO$ since the carbonyl and nitrosyl bands appear at 4–12 cm⁻¹ lower in benzene than in dichloromethane and dichloroethane. Analogous shifts

suggesting thallium–aromatic charge transfer are observed with TlCo(CO)₄.[2]

Reactions of TlFe(CO)₃NO. TlFe(CO)₃NO will undergo substitution reactions with Lewis bases in low dielectric solvents. As with TlCo(CO)₄,[1] the substitution products are either thallium(I) or thallium(III) derivatives depending on the ligand used. With P(C₆H₅)₃, the substitution reaction produced the Tl(III) derivative, Tl[Fe(CO)₂(NO)P(C₆H₅)₃]₃, while the stable thallium(I) derivative, TlFe(CO)₂(NO)-P(OC₆H₄Cl)₃, could be isolated from the reaction mixture of TlFe(CO)₃NO and P(OC₆H₄Cl)₃. The corresponding TlFe(CO)₂(NO)P(OC₆H₅)₃ derivative could not be isolated, although the initial product in the reaction between Tl-Fe(CO)₃NO and P(OC₆H₅)₃ appeared to be TlFe(C-O)₂(NO)P(OC₆H₅)₃ as judged from the appearance of peaks at 1892 and 1670 cm⁻¹, which almost coincide with the peak positions of TlFe(CO)₂(NO)P(OC₆H₄Cl)₃ in the infrared. During work-up the peaks assumed to be due to the Tl(I) derivative diminished in intensity with time and new peaks, presumably due to the Tl(III) derivative, would appear along with thallium metal. Since we were mainly interested in Tl(I) derivatives, we did not fully characterize this product. The infrared data for the substitution products are listed in Table II.

The different behavior of TlCo(CO)₄ and TlFe(CO)₃NO with P(OC₆H₅)₃ probably reflects a slight difference in the basicity of the two anions, Co(CO)₃P(OC₆H₅)₃⁻ and Fe(C-O)₂(NO)P(OC₆H₅)₃⁻. If the stability of thallium(I) derivatives is dependent on the base strength of the anion as we have postulated, then Fe(CO)₂(NO)P(OC₆H₅)₃⁻ must be a slightly stronger base than Co(CO)₃P(OC₆H₅)₃⁻. This in turn would suggest that Fe(CO)₃NO⁻ is a stronger base than Co(CO)₄⁻.

TlFe(CO)₄R (R = CH₂CN, C(=O)C₆H₅, Sn(C₆H₅)₃, and CN). HFe(CO)₄⁻ is a weakly basic anion; the first acid dissociation constant of the dihydride is 3.6×10^{-5} (pK_a = 4.44).[11] This value is slightly less than the value of 4.95 which was obtained for HCo(CO)₃P(OC₆H₅)₃[12] indicating that HFe(CO)₄⁻ has the required base strength to stabilize thallium in its lower oxidation state. However, the metathetical reaction of TlNO₃ with NaFe(CO)₄H produces Tl₂Fe₃(CO)₁₂.[13] The replacement of H with other groups stabilizes the system, and we have isolated several stable thallium(I) complexes of the general formula TlFe(CO)₄R. The R group has to be rather special since the complexes are stable only if R is capable of accepting electron density from the iron either through induction or via π back-bonding. Successful results were obtained with four such groups, CH₂CN, C(=O)C₆H₅, Sn(C₆H₅)₃, and CN. Groups which failed to give the desired complexes included CH₃ and CH₂C₆H₅ as well as H. There are undoubtedly a number of other groups which might stabilize the TlFe(CO)₄R system besides the four groups already mentioned, but for expediency we chose to look at only those four since they are fairly representative of the kinds of groups available.

The TlFe(CO)₄R complexes were prepared by adding an equivalent of TlNO₃ in water to tetrahydrofuran or methanol solutions of Fe(CO)₄R⁻. These compounds are dark red to yellow crystalline solids. All can be handled in the air for short periods of time without any significant decomposition. TlFe(CO)₄Sn(C₆H₅)₃ appears to be stable indefinitely in the air. All four complexes are soluble in polar organic solvent giving yellowish air-sensitive solutions. TlFe(CO)₄Sn(C₆H₅)₃ is only slightly soluble in nonpolar solvents, but the remaining three show good solubility in benzene. Molecular weight measurements of TlFe(CO)₄CH₂CN and TlFe(CO)₄CN showed these two complexes to be monomeric in benzene. Although TlFe(CO)₄CH₂CN and TlFe(CO)₄C(=O)C₆H₅ are stable in the solid state, they slowly decompose in solution.

One of the decomposition products appears to be Tl₂Fe₃(CO)₁₂ based on solubility and color.

Two structures are possible for complexes of the type TlFe(CO)₄R, a cis form and a trans form. The cis form has C_s symmetry and would from symmetry considerations be expected to show four infrared-allowed C–O stretching vibrations one of which might be so weak as to be unobserved.[14-17] The trans form, on the other hand, would have C_{4v} symmetry and only two infrared-allowed C–O stretching vibrations would be predicted.[17-20] The appearance of three and four bands in the spectra of these complexes (Table II) seems to rule out the trans structure.

Like the other thallium(I) compounds studied, the spectra of the TlFe(CO)₄R complexes are solvent dependent. Except for TlFe(CO)₄CN, the spectra in polar solvents such as tetrahydrofuran, acetonitrile, and dimethyl sulfoxide are similar to the spectra of the NaFe(CO)₄R salts. Only in dimethyl sulfoxide does the spectrum of TlFe(CO)₄CN approach that of NaFe(CO)₄CN. Since the NaFe(CO)₄R compounds presumably dissolve in polar solvents to give solvent separated Na⁺ and Fe(CO)₄R⁻ ions, similar species are evidently present in the solutions of the TlFe(CO)₄R complexes when their spectra are similar to those of NaFe(CO)₄R. In solvents of low dielectric constant the spectra of the TlFe-(CO)₄R complexes show three or four bands at significantly higher energy than those of the anions. This suggests the presence of covalent thallium–iron bonds if one uses the same arguments presented in the discussion of a covalent thallium–iron bond in TlFe(CO)₃NO. Evidently the thallium–iron bond in the TlFe(CO)₄CN complex is significantly stronger than in the other three complexes. The latter three are completely dissociated in tetrahydrofuran while a much more polar solvent such as dimethyl sulfoxide is needed to accomplish complete dissociation of TlFe(CO)₄CN.

TlFe(CO)₄CN also exhibits another interesting feature. Its high frequency carbonyl band, which in similar complexes has been attributed to the symmetric stretch of the two trans carbonyls,[14,17] is split into two bands in dichloroethane or benzene accompanied by the disappearance of the weak cyanide band. Not only is this CO band split into two new bands, but the intensity of these two bands varies with solvent. We have no satisfactory explanation for this behavior, but it seems reasonable to believe that coupling is occurring between the two trans carbonyls and the cyanide since no cyanide stretch is observed in the cyanide region of ~2100 cm⁻¹ in these two solvents.

Reactions of TlFe(CO)₄R. To complete our study of the TlFe(CO)₄R complexes, we examined the reactions of these compounds with Lewis bases. Other six-coordinated carbonyl complexes with metal–metal bonds such as (C₆H₅)₃PAu-Mn(CO)₅ and (C₆H₅)₃SnMn(CO)₅ are known to undergo substitution reaction with Lewis bases but only at elevated temperatures.[14,21]

The instability of TlFe(CO)₄CH₂CN and TlFe(CO)₄-C(=O)C₆H₅ in solution made them unsuitable for substitution reactions. Attempts to prepare substituted derivatives of these two complexes invariably resulted in decomposition, and no substituted derivative could be isolated. TlFe(CO)₄CN, which is stable in solution, turned out to be almost inert to substitution up to the temperature (80°) at which decomposition began. TlFe(CO)₄Sn(C₆H₅)₃, however, readily underwent substitution reactions with a number of ligands at room temperature to give derivatives of the type TlFe(CO)₃L-Sn(C₆H₅)₃ which are listed in Table II.

The TlFe(CO)₃LSn(C₆H₅)₃ derivatives are yellow to red crystalline solids with only limited air stability. With the exception of TlFe(CO)₃P(C₆H₅)₃Sn(C₆H₅)₃, they are soluble in all common organic solvents except saturated hydrocarbons.

In nonpolar solvents, three carbonyl bands are observed in the infrared spectra as were found for the similar complexes X₃SnFe(CO)₃XP(C₆H₅)₃ (X = Cl and I).[17] In polar solvents such as acetonitrile and dimethyl sulfoxide only one peak is observed. This is consistent with the presence of the (C₆H₅)₃SnFe(CO)₃L⁻ anion. (C₆H₅)₃SnFe(CO)₃L⁻ is isoelectronic with (C₆H₅)₃SnCo(CO)₃L which also generally exhibits only one band in the carbonyl region.[22] These cobalt complexes are reported to have a trigonal bipyramidal structure with a linear Sn–Co–P unit; consequently, an isostructural trigonal bipyramidal (C₆H₅)₃SnFe(CO)₃L⁻ ion is the most likely species present in acetonitrile and dimethyl sulfoxide solutions of TlFe(CO)₃LSn(C₆H₅)₃.

Assuming that these substituted TlFe(CO)₄R complexes have a thallium–iron bond in nonpolar solvents, four isomers are possible each with three infrared-active carbonyl stretching modes. The observed pattern (Table II) for the TlFe(CO)₃LSn(C₆H₅)₃ complexes would favor a mer isomer[17] but does not make possible an unambiguous choice. However, since the thallium and the R group are invariably cis in the TlFe(CO)₄R complexes, we tend to prefer a structure containing this configuration. This type structure was also suggested for (CO)₃LXFeMX₃.[17]

TlV(CO)₆. The hexacarbonylvandate anion, V(CO)₆⁻, has been reported to be a weak base[23] with a pK_a value of about 1. As a weak base, V(CO)₆⁻ should stabilize thallium in its lower oxidation state, and we set out to prepare such a complex. V(CO)₆ was readily reduced by thallium metal in dichloromethane giving orange, pyrophoric TlV(CO)₆. This compound is soluble in all common organic solvents except saturated hydrocarbons. Solutions of TlV(CO)₆ are not very stable and become noticeably cloudy after a few hours. The decomposition products are not soluble and eventually precipitate out. TlV(CO)₆ is, however, reasonably stable in an inert atmosphere in the solid state at room temperature, and no noticeable change had taken place after 4 months.

The peak maxima of the infrared spectra of TlV(CO)₆ in various solvents are listed in Table II. The spectra in tetrahydrofuran and dimethyl sulfoxide are essentially indistinguishable from the spectrum of V(CO)₆⁻ in tetrahydrofuran[24] suggesting that solvent separated Tl⁺ and V(CO)₆⁻ ions are present in these two solvents. The general shift to higher energies and the increase in the number of CO frequencies in nondonor solvents is consistent with the formation of an associated species with a weak Tl–V bond analogous to the species observed in other thallium(I) systems. However, it is not possible to assign a structure for this species from the information available.

Attempts were made to substitute TlV(CO)₆ with Lewis bases. Although such substitution reactions may occur, attempts to isolate the desired TlV(CO)₅L derivatives failed because of rapid decomposition of TlV(CO)₆ in solution. The substituted TlV(CO)₆ derivatives might be obtained by the metathetical reaction of TlNO₃ with NaV(CO)₅L derivatives,[25] but such reactions were not attempted.

Tl[Cr(CO)₃C₅H₅]. At the time this study was begun, thallium(I) derivatives of M(CO)₃(C₅H₅)⁻ (M = Mo[26] and W[27]) had only briefly been mentioned in the literature. The substituted chromium compound, Tl[C₅H₄CH(C₆H₅)₂Cr(CO)₃,[28] was reported, and we decided to try to prepare Tl[Cr(CO)₃(C₅H₅)]. While this work was in progress, a paper describing the preparation and stability of Tl[M(CO)₃(C₅H₅)] (M = Cr, Mo, and W) appeared,[2] and the findings of this paper are basically in agreement with our results on Tl[Cr(CO)₃(C₅H₅)].

The infrared spectra of Tl[Cr(CO)₃(C₅H₅)] in both dichloromethane and tetrahydrofuran (Table II) consist of three carbonyl bands at significantly higher energy than those of

the anion but at lower energy than those of Tl[Cr(CO)₃(C₅H₅)]₃ which is consistent with the presence of a weak chromium–thallium bond. The pattern is consistent with C_s symmetry and is similar to the spectra of R₃M'[M(CO)₃(C₅H₅)] (M' = Ge, Sn, and Pb; M = Cr, Mo, and W; R is an alkyl or aryl) compounds.[29]

An attempt to prepare Tl[Mo(CO)₃(C₅H₅)] under conditions similar to the ones used to prepare Tl[Cr(CO)₃(C₅H₅)] resulted in the formation of the corresponding thallium(III) derivative, Tl[Mo(CO)₃(C₅H₅)]₃, and thallium metal. This seems to indicate that (C₅H₅)Cr(CO)₃⁻ is a somewhat weaker base than (C₅H₅)Mo(CO)₃⁻. Burlitch[2] reported that the stability with respect to disproportionation of the Tl[M(CO)₃(C₅H₅)] (M = Cr, Mo, and W) compounds went in the order W > Mo > Cr. We did not attempt to prepare Tl[W(CO)₃(C₅H₅)], but since Tl[Mo(CO)₃(C₅H₅)] disproportionates in a mixture of water and tetrahydrofuran and since Tl[Cr(CO)₃(C₅H₅)] is stable in the same solvent mixture, we must conclude that with respect to disproportionation in solution Tl[Cr(CO)₃(C₅H₅)] is more stable than Tl[Mo(CO)₃(C₅H₅)].

We also attempted to prepared Tl[Cr(CO)₃(C₅H₅)] by the reaction of thallium metal with the [(C₅H₅)Cr(CO)₃]₂ dimer in benzene. While the thallium(I) compound could not be prepared by this route, it proved to be an especially covenient way to prepare the thallium(III) derivative, Tl[Cr(CO)₃(C₅H₅)]₃.

Discussion

The stability of thallium(I) transition metal carbonyls with respect to disproportionation according to eq 1 appears to be

$$3TlR \rightarrow TlR_3 + 2Tl \tag{1}$$

related to at least two factors: (1) the percent covalent character of the Tl–M interaction and (2) the size of the R group. The unassociated free ions Tl⁺ and R⁻ appear to be stable in solution indefinitely. TlCr(CO)₃(C₅H₅) which disproportionates in low dielectric solvents is stable in a water–tetrahydrofuran mixture in which it exists as free Tl⁺ and (C₅H₅)Cr(CO)₃⁻ ions. Similarly, TlM(CO)₃(C₅H₅) (M = Mo, W) can be crystallized from a 10% aqueous sodium hydroxide solution[2] presumably because of complete dissociation in this solvent system. Solution of TlM(CO)₃(C₅H₅) in dichloromethane results in rapid disproportionation. In addition, these same compounds, TlCo(CO)₃P(OCH₂)₃CC₂H₅ and TlCo(CO)₃P(C₆H₅)₃[1,2] which all disproportionate in noncoordinating solvents, are much more stable in the solid state, presumably because of the existence of ionic lattices such as was found in TlCo(CO)₄.[30] Those Tl(I) compounds which are stable in solution as undissociated species have apparently little covalency in the Tl–M bond as can be inferred from a relatively small shift in the carbonyl stretching frequency on going from the anions to the Tl(I) derivatives.

As a guide to those anions which will give weakly covalent Tl–M bonds and hence stable Tl(I) derivatives, it appears that the basicity of the anion is suitable. It has been shown[1] that a pK_a of about 5 for the hydridocarbonyls is the upper limit of base strength for which thallium(I) derivatives of the corresponding transition metal carbonyl anions Co(CO)₃L⁻ are stable as undissociated species in solution. It was also observed that the Tl(I) derivatives of anions whose hydrido derivatives have pK_a values between about 5 and 7 could be detected in solution as nondissociated species but were not stable enough to be isolated from these solutions. No Tl(I) derivatives of anions whose hydrido derivatives have pK_a values greater than about 7 could be detected in noncoordinating solvents at room temperature.

Similar results are observed with other transition metal carbonyl anions. We have isolated stable Tl(I) derivatives of

the relatively weakly basic anions $V(CO)_6^-$, $Fe(CO)_3NO^-$, and $Fe(CO)_4R^-$, while the Tl(I) derivatives of the moderately basic anions $(C_5H_5)M(CO)_3^-$ (M = Cr, Mo, and W) disproportionate rapidly.[2] Finally, it has been observed that Tl(I) derivatives of the strongly basic ions $Mn(CO)_5^-$ and $(C_5H_5)Fe(CO)_2^-$ showed no stability at all in solution at ambient temperatures but immediately disproportionated to the corresponding Tl(III) derivatives.[2,31,32]

This seems to indicate that, in general, the stability of thallium(I) derivatives of transition metal carbonyl anions decreases gradually with increasing base strength of the anions and, presumably, increasing covalent character of the Tl–M bond. Weakly basic anions characterized by hydrido derivatives with pK_a values of about 5 or less give stable thallium(I) derivatives. Anions whose hydrido derivatives have pK_a values between 5 and 7 form thallium(I) derivatives of marginal stability. Such derivatives are usually stable in the solid state but disproportionate more or less rapidly in solvents of low dielectric constant. Anions whose hydrides have pK_a values of 7 or greater may be stable in the solid state for a few days at room temperature or in solution at low temperatures, but they disproportionate immediately in solvents of low dielectric constant.

A second factor which may influence the stability of TlR is the size of the R group. For bulky R groups TlR_3 may be so unstable that reaction 1 will not go. This size effect may be significant in the stability of the derivatives of $Fe(CO)_3LSn(C_6H_5)_3^-$. While the pK_a values of the hydrido derivatives of these anions have not been measured, there is evidence to suggest that they are considerably greater than 5. Although the pK_a value of the unsubstituted hydride $HFe(CO)_4Sn(C_6H_5)_3$ is not known, the related hydrido species $H_2Fe(CO)_4$ has a pK_a value of 4.4.[11] A comparison of the infrared spectra of the two anions $HFe(CO)_4^-$ and $(C_6H_5)_3SnFe(CO)_4^-$ in the carbonyl region shows that they are similar, both in the positions and intensity of their corresponding bands. This suggests that the electron density of the iron does not change significantly from one anion to the other and that the basicities of the two anions are approximately the same.

It is well known that the replacement of a carbonyl group with poorer π acceptors such as triphenylphosphine or cyclopentadienyl increases the negative charge on the central metal atom and hence its basicity.[33] A significant increase in basicity is expected upon going from $(C_6H_5)_3SnFe(CO)_4^-$ to $(C_6H_5)_3SnFe(CO)_3L^-$. That such an increase has actually taken place is evident from the shift to lower frequencies of the carbonyl bands of the $TlFe(CO)_3LSn(C_6H_5)_3$ derivatives relative to those of $TlFe(CO)_4Sn(C_6H_5)_3$. Shifts of a similar magnitude[1] accompany the substitution of a CO group in $Co(CO)_4^-$, and the substitution of CO by $P(OC_6H_5)_3$ increases the pK_a value of the corresponding hydride from about 1 to 4.95 while substitution with $P(C_6H_5)_3$ increases the pK_a to 6.96. A corresponding increase of 4 to 6 units resulting from substitution of a CO in $HFe(CO)_4Sn(C_6H_5)_3$ by a phosphite or phosphine should increase the basicity of $HFe(CO)_3LSn(C_6H_5)_3$ to such an extent that the thallium(I) derivative of these hydrides should not be stable.

We feel that steric effects are responsible for the stability of the thallium(I) derivatives of $Fe(CO)_3LSn(C_6H_5)_3^-$. Any $Tl[Fe(CO)_3LSn(C_6H_5)_3]_3$ derivative must have the thallium cis to either L or the $Sn(C_6H_5)_3$ group. The steric requirements of such a system are such that it would be sterically unfavorable to situate three such anions around one thallium atom. Indeed, attempts to prepare $Tl[Fe(CO)_3LSn(C_6H_5)_3]_3$ with L = CO, $P(OC_6H_5)_3$, and $P(OC_6H_4Cl)_3$ by the metathetical reactions of thallium(III) salts with salts of the corresponding anions were not successful. The usual de-

composition route of thallium(I) derivatives of strongly basic anions is disproportionation to the corresponding thallium(III) derivatives and thallium metal as shown in eq 1. If this route is blocked because the Tl(III) derivatives cannot be formed, this would add extra stability to the Tl(I) compounds.

It appears that the behavior of thallium transition metal carbonyl derivatives is consistent with the behavior of other thallium systems. In its chemistry, the thallous ion resembles either the potassium or silver ions, forming ionic salts and generally not forming systems with any significant covalent character. For instance, Tl(I) alkyls and aryls are not stable. Monoalkyl- and monoarylthallium(I) derivatives have been postulated as reaction intermediates, but they have never been isolated. The reaction of thallous iodide and methyllithium in the presence of methyl iodide has been postulated[34] to proceed via methylthallium(I), although only trimethylthallium is isolated. A similar reaction between TlCl and phenyllithium gives triphenylthallium and thallium metal even at $-70°$.[35] On the other hand, groups such as $C_5H_5^-$ and $C(SO_2CH_3)_3^-$ form stable derivatives with Tl(I)[36,37] which are presumably ionic. It would seem that "stable" anions such as $C_5H_5^-$ and $C(SO_2CH_3)_3^-$ form stable derivatives with Tl(I) whereas those groups (CH_3^- and $C_6H_5^-$) that are strongly basic or nucleophilic and form strong covalent bonds lead to Tl(III) derivatives.

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Matrix Isolation and Computer Simulation Spectra of Cr(CO)₆ and Mo(CO)₆

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The low-frequency infrared spectra of Cr(CO)₆ and Mo(CO)₆ have been obtained in argon, nitrogen, and oxygen matrices. The ν_7 bands of Cr(CO)₆ and Mo(CO)₆ at about 670 and 600 cm⁻¹, respectively, both show metal isotopic structure in nitrogen matrix experiments. This isotopic structure has been reproduced by a computer simulation. The new isotopic frequencies allow a more complete force field calculation for the F_{1u} symmetry species. This calculation has been performed for Cr(CO)₆ and is in good agreement with earlier results.

Introduction

Many papers have appeared in the last 20 years on the infrared spectra of Cr(CO)₆ and Mo(CO)₆. In one of the first, Hawkins et al.[1] observed metal carbonyl gas infrared bands using a hot cell to increase the vapor pressure of these compounds. Subsequently, Danti and Cotton[2] reported the Raman spectra of chromium, molybdenum, and tungsten carbonyls in CHCl₃ solution. Kawai and Murata[3] calculated a very simple Urey–Bradley force field for Cr(CO)₆ and Mo(CO)₆ which was in fair agreement with the observed spectra. Jones et al.[4–10] have carried out a rather complete survey of the Cr(CO)₆, Mo(CO)₆, and W(CO)₆ species. In their most recent paper, they prepared ¹³C and ¹⁸O derivatives of these carbonyls and calculated complete sets of symmetry and valence force constants. Turner et al.[11,12] have recently studied the matrix isolation infrared spectrum of Cr(CO)₆ in the CO stretching region and the ultraviolet photolysis behavior of this compound.

Experimental Section

Cr(CO)₆ and Mo(CO)₆ highly diluted in argon, nitrogen, or oxygen were slowly deposited for infrared spectral investigation onto a cesium iodide window held at 15 K. The respective gas samples were prepared by adding approximately 300 mm of the diluent gases to the room-temperature vapor pressure of the carbonyls in a glass bulb using standard vacuum-line techniques.

After 6 hr of sample deposition, spectra were recorded on a Beckman IR-12 infrared spectrophotometer using a 10 cm⁻¹/in. chart expansion and a 3.2 cm⁻¹/min scan speed. Spectra were calibrated using the vibration–rotation bands of standard molecules.

Results

Since the matrix isolation spectrum of the CO stretching region of Cr(CO)₆ has been previously reported,[11,12] no further discussion of this region is necessary except to mention that the present results are in complete agreement with the earlier results.

The room-temperature vapor pressure of solid Cr(CO)₆ is approximately 150 μ;[13] this produces a matrix to Cr(CO)₆ ratio of approximately 2000:1. The frequencies of the ν_7 bands of Cr(CO)₆ in the various matrices are listed in Table I along with the assignments and the percentage natural abundances of the chromium isotopes. The nitrogen matrix spectra of ν_7 and ν_8 are shown in Figure 1B. Four bands were observed in the 670-cm⁻¹ (ν_7) region which closely correspond to the expected chromium isotopic pattern, and the isotopic shift was measured to be 2.5 cm⁻¹/amu. Using these data and a

Table I. Observed Frequencies (cm⁻¹) and Assignments of the ν_7 Band of Cr(CO)₆ in Various Matrices

Ar matrix	O₂ matrix	N₂ matrix	Isotope	% natural abundance
		Freq		
675.6	677.0	676.5	⁵⁰Cr	4.31
678.1			⁵⁰Crᵃ	
670.5	672.0	671.4	⁵²Cr	83.76
672.5	673.9		⁵²Crᵃ	
668.5	670.0	669.5	⁵³Cr	9.55
			⁵³Crᵃ	·
665.7	667.2	666.4	⁵⁴Cr	2.38
668.5			⁵⁴Crᵃ	

ᵃ As discussed in the text, two matrix sites were detected in Ar and O₂ matrices.

1.2-cm⁻¹ half-bandwidth, the computer-simulated spectrum shown in Figure 1B (bottom) was reproduced. The ν_8 band at about 450 cm⁻¹ also appeared to have some structure; a shoulder band was observed at 451.6 cm⁻¹ in addition to the main peak at 447.4 cm⁻¹ (⁵²Cr). If we assume that the former is due to the ⁵⁰Cr species, the isotope separation of ν_8 is about 2.1 cm⁻¹/amu. An attempted computer simulation using this separation and 2.0-cm⁻¹ half-bandwidth produces the spectrum shown in the bottom of Figure 1B; the computed spectrum for the ν_8 band does not match the observed spectrum. Therefore, the observed fine structure was not attributed to metal isotopes.

Figure 1A shows the argon matrix spectrum of the ν_7 band of Cr(CO)₆ at about 670 cm⁻¹. As the spectrum shows, there are at least six bands clearly resolved in this spectral region, and it can most easily be understood as being due to the four isotopic chromium species in two slightly different matrix sites. Using the assumptions that (1) the chromium isotopic shift is 2.5 cm⁻¹/amu, (2) the matrix shift for the second site is +2 cm⁻¹, (3) the half-bandwidth of all the bands is 1.2 cm⁻¹, and (4) the relative population of the molecules in the two sites is 2:1, a computer-simulated spectrum shown in the bottom of Figure 1A was obtained. The agreement is excellent.

Two distinct sites were also observed in the oxygen matrix. In this case, only five bands were observed, and a ratio of about 5:1 could be inferred for the relative populations of molecules in these sites. Only the ⁵²Cr isotopic species in the less populated matrix site was intense enough to be observed in our experiment.

The isotope frequencies of the ν_7 bands of Mo(CO)₆ are listed in Table II along with the natural abundances of molybdenum isotopes. The two top traces of Figure 2 show