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On the Stability of Thallium(I) Transition Metal Carbonyls. Substitution Reactions of Thallous Tetracarbonylcobaltate

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The reactions of $\text{TlCo}(\text{CO})_4$ with a variety of Lewis bases in noncoordinating solvents proceed to completion in several hours at room temperature with gas evolution and formation of either $\text{TlCo}(\text{CO})_3\text{L}$ or $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$ and thallium metal. Thallium(I) compounds stable in solution at room temperature are formed with those Lewis bases which give substituted cobalt carbonyl anions of relatively low basicity ($\text{pK}_a < 5$). In particular, $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ and $\text{TlCo}(\text{CO})_3\text{P}(p\text{-OC}_6\text{H}_4\text{Cl})_3$ result from the reaction of the corresponding Lewis bases with $\text{TlCo}(\text{CO})_4$. With ligands giving more strongly basic anions, thallium(III) derivatives and thallium metal form. Lewis bases including $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{OC}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{Sb}(\text{C}_6\text{H}_5)_3$, and $\text{P}(n\text{-C}_4\text{H}_9)_3$ which give substituted hydridocobaltcarbonyl derivatives with pK_a 's of greater than 5 yield thallium metal and thallium(III) derivatives of $\text{Co}(\text{CO})_3\text{L}^-$. These substitution reactions suggest that a pK_a of about 5 for the hydridocarbonyl is the upper limit of the base strength of the corresponding metal carbonyl anion which is consistent with the formation of thallium(I) derivatives which are stable in noncoordinating solvents.

Introduction

At the beginning of this work, thallium(I) transition metal carbonyls were not well known. Only one such compound, $\text{TlCo}(\text{CO})_4$, had been well characterized^{1,2} although brief reports of $\text{Tl}[\text{C}_5\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3]_3$ and $\text{Tl}[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mo}^4$ and W^5) appeared in the literature. Of these, the molybdenum compound was reported to decompose even in the solid state, and the tungsten derivative had only been mentioned in a patent. Attempts to prepare $\text{TlMn}(\text{C}-\text{O})_5$ ^{6,7} by the metathetical reaction of a thallium(I) salt with the metal carbonyl anion had resulted in the formation of the corresponding thallium(III) derivative. The substitution reaction of $\text{TlCo}(\text{CO})_4$ with triphenylphosphine also gave a thallium(III) compound, $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_3$.²

Toward the end of this study, Burlitch⁸ reported the preparation of $\text{Tl}[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr}$, Mo , and W), $\text{TlMn}(\text{CO})_5$, and $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$. The group 6B derivatives were isolated and characterized, but were only stable in 10% aqueous sodium hydroxide or in the solid state at -65° . In other solvents such as tetrahydrofuran and toluene, these compounds decomposed more or less rapidly to the corresponding thallium(III) derivatives and thallium metal. $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{TlMn}(\text{CO})_5$ were only detected in solution and were characterized by infrared spectroscopy. $\text{TlMn}(\text{CO})_5$ was generated in tetrahydrofuran at -65° and was stable under these conditions. However, at room tem-

perature, it rapidly decomposed to $\text{Tl}[\text{Mn}(\text{CO})_5]_3$ and thallium metal. A similar decomposition took place for $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ in a tetrahydrofuran-methanol solution at room temperature.

From these observations, it appeared with the exception of $\text{TlCo}(\text{CO})_4$ and, perhaps, $\text{Tl}[\text{C}_5\text{H}_4\text{CH}(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3]$ that thallium(I) transition metal carbonyls were unstable with respect to disproportionation to the corresponding thallium(III) derivatives and thallium metal.

We have examined the reactions of a variety of Lewis bases with $\text{TlCo}(\text{CO})_4$ in order to explore the question of the general instability of $\text{TlCo}(\text{CO})_3\text{L}$ and to develop a convenient route for the preparation of the corresponding thallium(III) derivatives. During this study we have prepared several new thallium(I) metal carbonyl derivatives and have determined the conditions under which additional stable thallium(I) derivatives can be prepared.

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 Perkin-Elmer 221 spectrophotometer with NaCl optics. The spectra were calibrated in the carbonyl region using polystyrene and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ in heptane. The CO frequencies of this solution were taken from Adams.⁹ Melting points were determined in sealed capillary tubes under a nitrogen atmosphere. The compounds

Table I. Analytical Data for Thallium Metal Carbonyls and Related Compounds

Compd	Yield, %	Mp, °C	Analysis, %							
			C		H		P		X	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
TlCo(CO) ₄ ^a	95	140-142	12.82	12.61	0	0			54.7 ^g	54.6 ^g
TlCo(CO) ₃ P(<i>p</i> -OC ₆ H ₄ Cl) ₃	90	145-152	33.15	33.19	1.59	1.70	4.07	4.15		
TlCo(CO) ₃ P(OC ₆ H ₅) ₃ ^b	80	118-122	38.35	38.62	2.30	2.58	4.72	4.62	31.1 ^g	32.0 ^g
TlCo(CO) ₃ P(OCH ₂) ₃ CC ₂ H ₅ ^c	60	135 d	21.22	21.43	2.18	2.41				
TlCo(CO) ₃ P(C ₆ H ₅) ₃	95	125 d	41.37	41.46	2.48	2.35				
Tl[Co(CO) ₃ P(<i>p</i> -OC ₆ H ₄ Cl) ₃] ₃	60	88	40.37	40.13	1.94	2.11			17.03 ^h	16.89 ^h
Tl[Co(CO) ₃ P(OC ₆ H ₅) ₃] ₃	70	78	48.37	48.58	2.90	2.67	5.94	6.20		
Tl[Co(CO) ₃ P(OC ₆ H ₅)(OCH ₂) ₂] ₃ ^d	87	128 d	33.43	32.53	2.30	2.43				
Tl[Co(CO) ₃ P(OCH ₃) ₃] ₃	80	116-117	21.50	21.75	2.71	2.70	9.24	9.01		
Tl[Co(CO) ₃ P(C ₆ H ₄ F) ₃] ₃	82	192-196	47.83	48.15	2.29	2.47				
Tl[Co(CO) ₃ P(C ₆ H ₅) ₃] ₃ ·2CH ₂ Cl ₂	68	195-196	49.16	49.57	3.08	3.47	5.85	5.90	8.93 ^h	8.66 ^h
Tl[Co(CO) ₃ As(C ₆ H ₅) ₃] ₃	79	158-162	46.00	46.82	3.06	2.52				
Tl[Co(CO) ₃ Sb(C ₆ H ₅) ₃] ₃	87	160-162	44.71	44.64	2.69	2.97				
Tl[Co(CO) ₃ DPM] ₃ ^e	68	92-94	56.47	55.77	3.73	4.17				
Tl[Co(CO) ₃ P(<i>n</i> -C ₄ H ₉) ₃] ₃	50	102-106	43.57	43.55	6.60	6.43	7.49	7.79		
[Co(CO) ₂ DPE] ₂ ·2CH ₂ Cl ₂ ^f	82	223-228	61.61	61.39	4.53	4.71	11.15	11.07	6.38 ^h	6.10 ^h
[Co(CO) ₂ DPM] ₂ ·CH ₂ Cl ₂ , black-green	70	198-206	60.96	60.58	4.28	4.41	11.43	11.01	6.54 ^h	6.12 ^h
[Co(CO) ₂ DPM] ₂ , yellow	60	198-206	64.94	64.26	4.44	4.37				
[Co(CO) ₂ DPM] ₂ , orange	20	216-224	64.94	63.80	4.44	4.42	12.40	12.14		

^a Mol wt: Calcd, 375; Found, 376, osmometrically in benzene. ^b Mol wt: Calcd, 658; Found, 634, osmometrically in benzene. ^c P(OCH₂)₃CC₂H₅ = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane. ^d P(OC₆H₅)(OCH₂)₂ = phenylethylene phosphite. ^e DPM = bis(diphenylphosphino)methane. ^f DPE = 1,2-bis(diphenylphosphino)ethane. ^g X = Tl. ^h X = Cl.

prepared, melting points, yields, and analyses are reported in Table I.

Preparation of TlCo(CO)₄. Thallous tetracarbonylcobaltate was prepared as described previously^{2,8} by the reaction of excess thallium metal with Co₂(CO)₈ in benzene and by the metathetical reaction of thallous nitrate with NaCo(CO)₄.

Substitution Reactions of TlCo(CO)₄. All substitution reactions were run in essentially the same way. One to one mole ratios of TlCo(CO)₄ and ligand (about 4 mmol in each case) were stirred in 30 ml of 1,2-dichloroethane, dichloromethane, or benzene, usually at 5°, for several hours until gas evolution ceased. The solutions were filtered and reduced in volume until precipitation just began to occur. A large excess of heptane was added as a layer across the top of the solution and allowed to diffuse slowly into the solution. Following formation of the crystalline product, the mother liquor was removed with a syringe, and the product was washed with several 10 ml portions of hexane then dried under vacuum.

With the exception of triphenyl phosphite and tris(*p*-chlorotriphenyl) phosphite, the ligands used in this reaction gave thallium(III) compounds and a metallic lump or mirror. The metal was soluble in dilute nitric acid, and the nitric acid solutions gave a white precipitate upon addition of sodium chloride solutions. No reaction was observed with As(OCH₃)₃ or P(C₆F₅)₃. The reaction of P(C₆H₅)₂Cl gave a product identified as [Co(CO)₃P(C₆H₅)₂]₂ from its infrared spectrum (2030 (w), 1995 (vs), 1970 (sh) cm⁻¹) and melting point (151-153°). The presence of dichloromethane in several of the products was verified by mass spectroscopy which showed CH₂Cl₂ and its fragments in the spectra of these compounds.

Preparation of TlCo(CO)₃P(OCH₂)₃CC₂H₅. Tl[Co(CO)₃P(OCH₂)₃CC₂H₅]₃ (1.3 mmol) in 30 ml of tetrahydrofuran was reduced over 1% sodium amalgam producing NaCo(CO)₃P(OCH₂)₃CC₂H₅. The anion solution was filtered and the tetrahydrofuran was removed in vacuo. The sodium salt was redissolved in 20 ml of water and upon addition of 3.80 mmol of TlNO₃ in 20 ml of water an orange-red precipitate was produced. The water was syringed off and the product was washed with three 20 ml portions of water and dried under vacuum.

Preparation of TlCo(CO)₃P(C₆H₅)₃. NaCo(CO)₃P(C₆H₅)₃ (2.46 mmol) in 20 ml of water was filtered onto 2.5 mmol of TlNO₃ in 20 ml of water producing an orange-red precipitate. The water was syringed off and the product was washed with three 20 ml portions of water and dried under vacuum.

Preparation of Tl[Co(CO)₃P(OC₆H₅)₃]₃ and Tl[Co(CO)₃P(*p*-OC₆H₄Cl)₃]₃. These compounds were prepared by the metathetical reaction of thallic nitrate with the corresponding thallium(I) compounds in a 50-50 water-tetrahydrofuran solution. The tetrahydrofuran was removed under vacuum, and the remaining water was removed from the crystalline product with a syringe. The product

was washed several times with 20 ml portions of water then dried under vacuum.

Preparation of [Co(CO)₂DPE]₂·CH₂Cl₂. A solution of 3.49 mmol of TlCo(CO)₄ and 3.50 mmol of 1,2-bis(diphenylphosphino)ethane in 30 ml of benzene was stirred for 4 hr at 60-80°. After filtration, the solvent was removed in vacuo and the product was dissolved in 30 ml of dichloromethane. After adding 20 ml of acetonitrile, the dichloromethane was slowly removed in vacuo causing red crystals to precipitate. The crystals were washed with two 20 ml portions of acetonitrile.

Preparation of [Co(CO)₂DPM]₂. A solution of 8.18 mmol of TlCo(CO)₄ and 8.20 mmol of DPM in 50 ml of benzene was stirred for 24 hr at 80°. The solution was filtered and the solvent was removed in vacuo. The solid was extracted several times with 20 ml portions of acetone leaving behind a yellow solid. This solid was dissolved in a minimum of dichloromethane, giving a black solution, and filtered. A large excess of hexane was added as a layer and by letting the two layers diffuse together, black-green crystals were obtained. These crystals could be converted to a yellow solid by stirring in acetone for a few minutes. The acetone soluble fraction from the initial extraction, after removal of the acetone in vacuo, was dissolved in a minimum of hot methanol and set aside at 0° for several hours giving orange crystals.

These isomers could also be isolated from a solution of Tl[Co(CO)₃DPM]₃ stirred at 80° in benzene for 24 hr.

Results

Reactions Giving Tl(I) Derivatives. With only a few exceptions, tertiary phosphines, arsines, and stibines react smoothly with TlCo(CO)₄ in solvents of low dielectric constant such as benzene, toluene, dichloromethane, and dichloroethane with the evolution of carbon monoxide and the formation of substituted thallium cobalt carbonyls. With most of the ligands tried, the products isolated from the reaction mixture were derivatives of Tl[Co(CO)₄]₃ and thallium metal (vide infra). However, with P(OC₆H₅)₃ and P(OC₆H₄Cl)₃, Tl(I) derivatives were the final products. In addition to these two compounds, other species appearing to be Tl(I) derivatives were observed in solution (Table II). During the initial stages of the reaction of TlCo(CO)₄ with several Lewis bases, strong bands appeared in the infrared spectra of the reaction mixtures at about 1900 cm⁻¹. This is the region where both TlCo(CO)₃P(OC₆H₅)₃ and TlCo(CO)₃P(OC₆H₄Cl)₃ have a strong band (Table II). These peaks disappeared as the Tl(III) derivatives were formed. We were later able to isolate one of these intermediates, TlCo(CO)₃P(OCH₂)₃CC₂H₅, as well

Table II. Peak Maxima of the Infrared Spectra of $\text{TlCo}(\text{CO})_3\text{L}$ and $\text{NaCo}(\text{CO})_3\text{L}$

	Solvent	$\nu(\text{CO})$, cm^{-1}
$\text{NaCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$	Tetrahydrofuran	1964 (s), 1885 (vs), 1843 (s)
	Dimethyl sulfoxide	1960 (s), 1875 (vs, br)
$\text{NaCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$	Tetrahydrofuran	1969 (s), 1892 (vs), 1859 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$	Dichloromethane	2009 (w), 1973 (m), 1912 (s)
	Tetrahydrofuran	1906 (s)
	Nitromethane	2009 (w), 1970 (m), 1907 (vs), 1881 (s)
	Acetonitrile	1961 (m), 1904 (m, sh), 1881 (vs)
	Dimethyl sulfoxide	1958 (s), 1875 (vs, br)
	Dichloromethane	2011 (w), 1976 (m), 1916 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$	Dichloromethane	1912 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$	Dichloromethane	1902 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3^a$	Dichloromethane	1902 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_4\text{F})_3^a$	Benzene	1896 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)(\text{OCH}_2)_2^a$	Benzene	1911 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OCH}_3)_3^a$	Tetrahydrofuran + water	1900 (s)
$\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_2\text{H}_5)_3^a$	Tetrahydrofuran + water	1898 (s)

^a Observed as reaction intermediates.

as $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, by the metathetical reaction of TlNO_3 with $\text{NaCo}(\text{CO})_3\text{L}$ in water. Similar metathetical reactions carried out in tetrahydrofuran and water gave solutions with infrared spectra characteristic of $\text{TlCo}(\text{CO})_3\text{P}(\text{OCH}_3)_3$ and $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_2\text{H}_5)_3$ although neither of these compounds were isolated. The isolation of $\text{TlCo}(\text{C}-\text{O})_3\text{P}(\text{OCH}_2)_2\text{CC}_2\text{H}_5$ and $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)$ from TlNO_3 and $\text{NaCo}(\text{CO})_3\text{L}$ in water along with the recent work of Burlitch,⁸ who isolated a variety of less stable $\text{Tl}(\text{I})$ derivatives by the same method, seem to indicate that other $\text{Tl}(\text{I})$ compounds might be prepared by this route.

$\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ and $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$ are air sensitive yellow-orange solids which are soluble in all common organic solvents except saturated hydrocarbons giving orange to red solutions. In contrast to $\text{TlCo}(\text{CO})_4$, these complexes are completely insoluble in water. Large crystals of both compounds can be handled in the air for brief periods of time without any significant decomposition, but in solution they are rapidly decomposed upon exposure to the air. The air-sensitive yellow-orange solids $\text{TlCo}(\text{CO})_3\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$ and $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ decompose upon solution in non-donor solvents giving thallium metal and the corresponding thallium(III) derivative.

The infrared spectra of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ are solvent dependent in a fashion similar to that found for $\text{TlCo}(\text{CO})_4$ (Table II). In dimethyl sulfoxide, a solvent of high dielectric constant, the spectrum is indistinguishable from that of $\text{NaCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ in the same solvent. $\text{NaCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ is presumed to dissolve in dimethyl sulfoxide to produce solvent-separated Na^+ ions and $\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3^-$ ions in a fashion analogous to $\text{NaCo}(\text{CO})_4$.¹⁰ Similar species appear to exist in solutions of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ in dimethyl sulfoxide. In solvents of low dielectric constant, such as dichloromethane and tetrahydrofuran, the spectra of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ show three peaks and one peak, respectively, at significantly higher energies than those of the free anion suggesting the same type of $\text{Tl}-\text{Co}$ interaction found for $\text{TlCo}(\text{CO})_4$.^{2,8} is present in these two solvents. In acetonitrile and nitromethane, solvents with dielectric constants intermediate between those of tetrahydrofuran and dimethyl sulfoxide, the spectra show both anion peaks and peaks due to associated species. In acetonitrile the anion peaks predominate while the peaks due to the associated species are of greater intensity than the anion peaks in nitromethane. It appears that equilibrium amounts of both the solvent separated ions and the associated species are present in solution. This equilibrium favors the dissociated species in good donor solvents with high dielectric constants and the associated species in solvents of low dielectric constant.

The infrared and molecular weight data for $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$

Table III. Peak Maxima of the Infrared Spectra of $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$ in Dichloromethane

L	$\nu(\text{CO})$, cm^{-1}
$\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$	2046 (vw), 2009 (m), 1978 (s)
$\text{P}(\text{OC}_6\text{H}_5)_3$	2046 (vw), 2008 (m), 1976 (s)
$\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5^a$	2045 (vw), 2008 (m), 1975 (s)
$\text{P}(\text{OC}_6\text{H}_5)(\text{OCH}_2)_2$	2044 (vw), 2008 (m), 1974 (s)
$\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3^a$	2040 (w), 2000 (m), 1968 (s)
$\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_3^a$	2040 (vw), 2002 (m), 1963 (s)
$\text{P}(\text{OCH}_3)_3$	2038 (w), 1999 (m), 1961 (s)
$\text{P}(\text{OC}_2\text{H}_5)_3^a$	2035 (w), 1997 (m), 1959 (s)
$\text{P}(\text{C}_6\text{H}_4\text{F})_3$	2026 (w), 1993 (m), 1953 (s)
$\text{P}(\text{C}_6\text{H}_5)_3$	2026 (w), 1993 (m), 1953 (s)
$\text{As}(\text{C}_6\text{H}_5)_3$	2024 (w), 1993 (m), 1951 (s)
$\text{Sb}(\text{C}_6\text{H}_5)_3$	2020 (w), 1989 (m), 1951 (s)
$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2(\text{DPM})$	2024 (w), 1990 (m), 1950 (s)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2(\text{DPE})^a$	2025 (w), 1989 (m), 1948 (s)
$\text{P}(\text{C}_4\text{H}_9)_3$	2016 (w), 1979 (m), 1938 (s)

^a Not isolated.

$\text{P}(\text{OC}_6\text{H}_5)_3$ indicate an undissociated species with a covalent $\text{Tl}-\text{Co}$ interaction in solvents of low dielectric constant. An ion pair with a $\text{Tl}-\text{O}$ interaction would be expected to give rise to at least one $\text{C}-\text{O}$ stretching frequency lower than that of the free ion analogous to those observed for metal carbonyl anions O -coordinated to aluminum,¹¹ magnesium,¹² and sodium.¹⁰ This type of interaction is presumably also responsible for the 1843 and 1859 cm^{-1} peaks observed for the $\text{NaCo}(\text{CO})_3\text{L}$ derivatives in tetrahydrofuran (Table II). Since similar low frequency bands are not observed for $\text{TlCo}(\text{C}-\text{O})_3\text{P}(\text{OC}_6\text{H}_5)_3$ in either dichloromethane or tetrahydrofuran, a $\text{Tl}-\text{O}$ interaction can be ruled out.

Although there is a significant shift to higher frequencies in going from the anion to the $\text{Tl}(\text{I})$ compound, the shift is small compared with that observed between the anion and the $\text{Tl}(\text{III})$ derivative (Tables II and III). Considering the more intense band, there is a shift of $\sim 35 \text{ cm}^{-1}$ between the anion and the $\text{Tl}(\text{I})$ derivative but a shift of 100 cm^{-1} between the anion and the $\text{Tl}(\text{III})$ compound. This shift must result from a charge transfer from Co to Tl during bond formation. The charge transfer to $\text{Tl}(\text{I})$ is less than to $\text{Tl}(\text{III})$ which indicates less covalent character in the $\text{Tl}-\text{Co}$ bond in $\text{TlCo}(\text{CO})_3\text{L}$ than in $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$. A similar observation was made for $\text{TlCo}(\text{CO})_4$ and $\text{Tl}[\text{Co}(\text{CO})_4]_3$.^{8,13}

A great variety of $\text{R}_m\text{M}[\text{Co}(\text{CO})_3\text{L}]_n$ species have been reported and structural data are available for a few.¹⁴⁻¹⁸ In all cases the $\text{Co}(\text{CO})_3\text{L}$ group exhibits C_{3v} local symmetry. This type of complex often shows two bands in the carbonyl region, a very strong band and a very weak band at higher frequency. The very weak high-frequency band, which sometimes is not observed, is considered to be due to the totally symmetric equatorial stretching mode (the A_1 mode), while

the intense lower frequency band is due to the E mode.¹⁸ Since in tetrahydrofuran $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ exhibits one very strong band in the carbonyl region, it seems likely that $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ has C_{3v} symmetry in this solvent. The geometry of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ in dichloromethane is much more difficult to determine. The observed three band spectrum is consistent with any of three possible trigonal bipyramidal isomers with axial CO groups, but without additional information the correct structure cannot be ascertained.

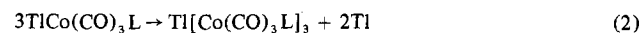
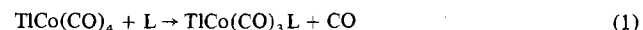
One might speculate as to why there is a change in geometry of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ upon going from tetrahydrofuran to dichloromethane. While tetrahydrofuran is a fair donor solvent which may solvate the thallium atom to some extent increasing its coordination number, dichloromethane is a very poor donor and cannot increase the coordination number. A system in which thallium is coordinated to only one entity is probably not a very stable one, and one way that the thallium might increase its coordination number is to move closer to one or two of the CO groups and interact with the π cloud of the CO. This would result in C_s symmetry and hence three carbonyl bands in the infrared spectrum. This is probably not the case, however, since this association of Tl(I) with one or two CO is not observed for $\text{TlCo}(\text{CO})_4$ in dichloromethane in which it has C_{3v} symmetry.^{8,13}

A second alternative would be a structure in which Tl forms a π complex with the π electron density of the ligand phenyl ring. Two thallium(I)-benzene π complexes have previously been reported,¹⁹ and it has been suggested that $\text{TlCo}(\text{CO})_4$ forms a similar complex with toluene.⁸ Since this toluene- $\text{TlCo}(\text{CO})_4$ complex could not be isolated, the interaction of the thallium with aromatic rings is probably weak and can easily be severed. In a donor solvent such as tetrahydrofuran, this would probably be the case with $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ thus explaining the change in geometry upon going from dichloromethane to tetrahydrofuran.

The spectrum of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$ in dichloromethane is similar to that of $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ in the same solvent which seems to indicate that a similar thallium-phenyl interaction is occurring in this compound.

Reactions Giving Tl(III) Derivatives. In the majority of cases the reaction between $\text{TlCo}(\text{CO})_4$ and Lewis bases results in the formation of thallium(III) derivatives and thallium metal. Table III indicates the thallium(III) derivatives prepared in this manner as well as $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3]_3$ and $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OC}_3\text{H}_5)_3]_3$ which were prepared by reaction of the corresponding Tl(I) compounds with $\text{Tl}(\text{NO}_3)_3$. Since we were primarily interested in the isolation of Tl(I) rather than Tl(III) compounds, no attempts were made to isolate the Tl(III) compounds with some of these ligands. In these cases, the Tl(III) derivatives were only identified by color and infrared spectrum in solution.

Although the final products of these substitution reactions are Tl(III) derivatives and thallium metal, the reactions seem to involve the initial formation of the substituted thallium(I) derivatives followed by disproportionation to the thallium(III) derivatives and thallium metal as shown in reactions 1 and 2.

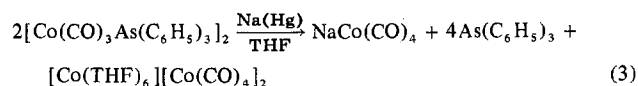


There is ample evidence for this reaction route. First, the isolation of the two previously described $\text{TlCo}(\text{CO})_3\text{L}$ derivatives lends credence to the first step. Furthermore, it was previously mentioned that other $\text{TlCo}(\text{CO})_3\text{L}$ derivatives were detected in the infrared in solution and that spectra due to these species would diminish in intensity with time and eventually disappear completely as those of the Tl(III) derivatives increased. Second, the reaction of thallous nitrate

and $\text{NaCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ in tetrahydrofuran and water² also forms $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_3$ which almost certainly involves the initial formation of $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$. Finally, when $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ or $\text{TlCo}(\text{CO})_3\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$ are dissolved in dichloromethane, they immediately disproportionate to thallium metal and $\text{Tl}[\text{Co}(\text{CO})_3\text{PR}_3]_3$. Thallium(I) derivatives of $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$) and $\text{Mn}(\text{CO})_5^-$ also decompose to the corresponding thallium(III) derivatives and thallium metal.⁸

The $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$ derivatives are air stable dark red or purple solids which sometimes appear to be black when they are isolated as large crystals. Some of these compounds crystallize with 2 mol of dichloromethane when recrystallized from or prepared in this solvent. They are soluble in most common organic solvents except for saturated hydrocarbons in some cases. Although they are air stable in the solid state, the solutions of these compounds must be protected from the air. In contrast to the $\text{TlCo}(\text{CO})_3\text{L}$ derivatives, these compounds are only partially dissociated in good ionizing solvents such as dimethyl sulfoxide as can be ascertained from the weakness or absence of peaks due to the anion in this solvent. This along with a shift of $\sim 100 \text{ cm}^{-1}$ to higher energy in going from the anion to the Tl(III) compound as mentioned above indicate strong covalent thallium-cobalt bonds in the $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$ derivatives.

$\text{Tl}[\text{Co}(\text{CO})_3\text{As}(\text{C}_6\text{H}_5)_3]_3$ is a special case, however. The infrared spectrum of this compound in dimethyl sulfoxide shows only one peak at 1891 cm^{-1} which is what is observed for $\text{NaCo}(\text{CO})_4$ in dimethyl sulfoxide.¹⁰ $\text{Tl}[\text{Co}(\text{CO})_3\text{As}(\text{C}_6\text{H}_5)_3]_3$ is apparently decomposing in dimethyl sulfoxide in a complex fashion which may be similar to the reaction that occurs when $[\text{Co}(\text{CO})_3\text{As}(\text{C}_6\text{H}_5)_3]_2$ is reduced over Na/Hg in tetrahydrofuran as shown in eq 3.²⁰



Reactions Giving $[\text{Co}(\text{CO})_2\text{L}_2]_2$ Dimers. In the previous section, the formations of $\text{Tl}[\text{Co}(\text{CO})_3\text{DPE}]_3$ and $\text{Tl}[\text{Co}(\text{CO})_3\text{DPM}]_3$ were described. From the similarities in color and infrared spectra of these two compounds with other $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$ derivatives, it appears that the bidentate ligands act as monodentate ligands in both cases. With DPE, the thallium(III) derivative is formed only if the substitution reaction is run at or below room temperature with less than a stoichiometric amount of the ligand. With an excess of ligand or at slightly elevated temperatures ($50\text{--}80^\circ$), the previously reported dimer, $[\text{Co}(\text{CO})_2\text{DPE}]_2$,²¹ is formed. This compound is also formed when $\text{Tl}[\text{Co}(\text{CO})_3\text{DPE}]_3$ is stirred for several hours in benzene at $50\text{--}80^\circ$. One might speculate that the formation of this dimer involves the initial formation of the disubstituted thallium(III) compound, $\text{Tl}[\text{Co}(\text{CO})_2\text{DPE}]_3$, followed by disproportionation to the dimer and thallium metal. The latter reaction is presumably analogous to the one in which $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ is formed from the decomposition of $\text{Tl}[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_3$.⁸

$[\text{Co}(\text{CO})_2\text{DPM}]_2$ is prepared by reaction of $\text{TlCo}(\text{CO})_4$ with DPM at 80° in benzene or by decomposition of $\text{Tl}[\text{Co}(\text{CO})_3\text{DPM}]_3$ in benzene at 80° . In contrast to $[\text{Co}(\text{CO})_2\text{DPE}]_2$, which formed only one isomer, three isomers of $[\text{Co}(\text{CO})_2\text{DPM}]_2$ were isolated (Table IV). Only two isomers are present in the reaction mixture, and they can be separated by differences in solubility. One isomer (orange) is soluble in polar solvents while the other (yellow) is not. The yellow isomer is easily converted to a black-green isomer by dissolving it in dichloromethane. Both the yellow and black-green isomers have bridging carbonyls (Table IV). The black-green isomer can be crystallized from dichloromethane and hexane to give large almost black crystals which contain

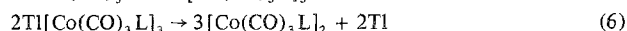
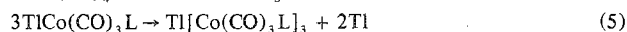
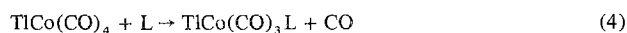
Table IV. Peak Maxima of the Infrared Spectra of Some $[\text{Co}(\text{CO})_2\text{L}_2]_2$ Dimers

Compd	Color	$\nu(\text{CO})$, cm^{-1}	Phase
$[\text{Co}(\text{CO})_2\text{DPE}]_2$	Dark red	1970 (s), 1920 (vs), 1753 (m, sh), 1728 (vs)	CH_2Cl_2
$[\text{Co}(\text{CO})_2\text{DPM}]_2$	Black-green	1978 (m), 1957 (s), 1922 (vs), 1773 (m), 1703 (m)	CH_2Cl_2
$[\text{Co}(\text{CO})_2\text{DPM}]_2$	Yellow	1950 (s), 1910 (vs), 1760 (m), 1696 (w)	KBr
$[\text{Co}(\text{CO})_2\text{DPM}]_2$	Orange	2008 (w), 1948 (m), 1878 (vs, br)	KBr

1 mol of dichloromethane per dimer. It can be converted back to the yellow form by stirring in acetone or acetonitrile which causes the yellow isomer to precipitate out. This behavior is not inconsistent with what has been reported for other $\text{Co}_2(\text{CO})_{8-n}\text{L}_n$ derivatives.^{22,23} The third isomer is orange and has, in contrast to the other two isomers, no bridging carbonyls. It cannot be converted to either of the other two isomers even on refluxing in benzene for several days. This seems to indicate that it has a structure quite different from the other two isomers.

Discussion

The reaction of a Lewis base with a solution of $\text{TlCo}(\text{CO})_4$ in a solvent with a low dielectric constant may proceed through one or more of the following series of reactions.



The basicity of the anion $\text{Co}(\text{CO})_3\text{L}^-$, $\text{Co}(\text{CO})_2\text{DPE}^-$, or $\text{Co}(\text{CO})_2\text{DPM}^-$ can serve as a guide to the stability of the various intermediates in this series.

One index to the relative base strength of transition metal carbonyl anions is provided by the acid dissociation constant of their corresponding hydrides. The position of the carbonyl stretching bands of transition metal carbonyl anion derivatives can also be helpful in assigning relative base strengths to the anions, especially for an isoelectronic series such as $\text{M}(\text{CO})_n\text{L}^-$ where only L is changing. The relative basicity of $\text{M}(\text{CO})_n\text{L}^-$ is presumably related to the π acidity of L. If L is high on the π acidity scale,²³ as is $\text{P}(\text{OC}_6\text{H}_5)_3$, its ability to accept electron density is greater than for some L lower on the same scale such as $\text{P}(\text{C}_6\text{H}_5)_3$. The more electron density L can remove from the metal, the lower the basicity of $\text{M}(\text{CO})_n\text{L}^-$. The carbonyl stretching frequencies are also sensitive to the electron density on the metal. As the π acidity of L decreases so do the frequencies of the CO modes. Lowering of the carbonyl frequency indicates a greater electron density on the metal which suggests that the basicity of the anion, $\text{M}(\text{CO})_3\text{L}^-$, has increased.

In the absence of steric effects, which will be discussed in a separate communication, a $\text{p}K_a$ 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 are stable. In the $\text{Co}(\text{CO})_3\text{L}^-$ series, stable Tl(I) derivatives have been prepared with $\text{L} = \text{CO}$, $\text{P}(\text{OC}_6\text{H}_5)_3$, and $\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$. The $\text{p}K_a$ of $\text{HCo}(\text{CO})_4$ is about 1,²⁴ the $\text{p}K_a$ of $\text{HCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ is 4.95,²⁰ while that of $\text{HCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_4\text{Cl})_3$ is probably somewhat lower. $\text{HCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ has a $\text{p}K_a$ of 6.96 and only the thallium(III) derivative of the corresponding anion is stable in noncoordinating solvents. Tl(I) derivatives of anions whose hydrido derivatives have $\text{p}K_a$ values which fall between $\text{HCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$ and $\text{HCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ as suggested by the relative values of the CO frequencies in $\text{Tl}[\text{Co}(\text{CO})_3\text{L}]_3$ could be detected in solution in noncoordinating solvents but

were not stable enough to be isolated from these solvents. No Tl(I) derivatives of anions whose hydrido derivatives have $\text{p}K_a$ values equal to or greater than $\text{HCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ could be detected in noncoordinating solvents.

Similar results are observed with other transition metal carbonyl anions. We have isolated²⁵ stable Tl(I) derivatives of the relatively weakly basic anions $\text{V}(\text{CO})_6^-$, $\text{Fe}(\text{CO})_3\text{NO}^-$, and $\text{Fe}(\text{CO})_4\text{R}^-$. The Tl(I) derivatives of the moderately basic anions $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Cr}$, Mo , and W) disproportionate rather rapidly in solvents of low dielectric constant,⁸ while Tl(I) derivatives of the strongly basic anions $\text{Mn}(\text{CO})_5^-$ and $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ showed no stability at all in solution at ambient temperatures but immediately disproportionated to the corresponding Tl(III) derivatives.^{6,8}

This seems to indicate that the stability of thallium(I) derivatives of transition metal carbonyl anions decreases gradually with increasing base strength of the anions and presumably the covalent character of the Tl-M bond. Weakly basic anions characterized by hydrido derivatives with $\text{p}K_a$ values of about 5 or less give stable thallium(I) derivatives. Anions whose hydrido derivatives have $\text{p}K_a$ 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 $\text{p}K_a$ values of 7 or greater may be stable in the solid state ($\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$) or at low temperatures ($\text{TlMn}(\text{CO})_5$) but they disproportionate immediately in solvents of low dielectric constant.

The stability of TlR_3 with respect to decomposition to Tl and R_2 might also be related to the base strength of R^- since the very strongly basic anions $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$,⁸ $\text{Co}(\text{CO})_2\text{DPM}^-$, and $\text{Co}(\text{CO})_2\text{DPE}^-$ do not give stable TlR_3 species.

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Registry No. $\text{TlCo}(\text{CO})_4$, 38991-21-8; $\text{TlCo}(\text{CO})_3\text{P}(p\text{-OC}_6\text{H}_4\text{Cl})_3$, 55046-66-7; $\text{TlCo}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$, 55046-65-6; $\text{TlCo}(\text{CO})_3\text{P}(\text{O-CH}_2)_3\text{CC}_2\text{H}_5$, 55871-62-0; $\text{TlCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, 55871-63-1; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(p\text{-OC}_6\text{H}_4\text{Cl})_3]_3$, 55871-64-2; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3]_3$, 55871-65-3; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)(\text{OCH}_2)_2]_3$, 55871-66-4; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OCH}_3)_3]_3$, 55871-67-5; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_4\text{F})_3]_3$, 55925-55-8; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_3$, 55871-68-6; $\text{Tl}[\text{Co}(\text{CO})_3\text{As}(\text{C}_6\text{H}_5)_3]_3$, 55871-69-7; $\text{Tl}[\text{Co}(\text{CO})_3\text{Sb}(\text{C}_6\text{H}_5)_3]_3$, 55871-70-0; $\text{Tl}[\text{Co}(\text{CO})_3\text{DPM}]_3$, 55871-71-1; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(n\text{-C}_4\text{H}_9)_3]_3$, 55871-72-2; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]_3$, 55871-73-3; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3]_3$, 55871-74-4; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OC-H}_2\text{CH}=\text{CH}_2)_3]_3$, 55871-75-5; $\text{Tl}[\text{Co}(\text{CO})_3\text{P}(\text{OC}_2\text{H}_5)_3]_3$, 55871-76-6; $\text{Tl}[\text{Co}(\text{CO})_3(\text{DPE})]_3$, 55871-77-7; $[\text{Co}(\text{CO})_2\text{DPE}]_2$, 18757-99-8; $[\text{Co}(\text{CO})_2\text{DPM}]_2\text{-CH}_2\text{Cl}_2$, black-green, 55871-79-9; $[\text{Co}(\text{CO})_2\text{DPM}]_2$, yellow, 55871-78-8; $[\text{Co}(\text{CO})_2\text{DPM}]_2$, orange, 56172-96-4.

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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, TIR, 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 TIR 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 TIR₃ derivatives. A series of metathetical reactions of TlNO₃ with the relatively weakly basic anions Fe(CO)₃NO⁻ and RFe(CO)₄⁻ (R = CH₂CN, C(=O)C₆H₅, Sn(C₆H₅)₃, and CN) produce stable Tl(I) compounds. TlCr(CO)₃(C₅H₅) 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 TIR 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(OC₆H₄Cl)₃ and P(C₆H₅)₃ react with TlFe(CO)₃NO to give Tl(I) and Tl(III) derivatives, respectively. TlFe(CO)₄Sn(C₆H₅)₃ reacts with Lewis bases in solvents of low dielectric constant to give derivatives of the type TlFe(CO)₃l.Sn(C₆H₅)₃. The stability of these complexes is attributed to the large size of the (C₆H₅)₃SnFe(CO)₃L⁻ 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)₃L or Tl[Co(CO)₃L]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 reported² 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)₃L⁻ 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, Na₂Fe(CO)₄·1.5diglyme, and Na(diglyme)₂V(CO)₆ were obtained from Alfa Inorganics, Beverly, Mass.

Preparation of TlFe(CO)₃NO. Fe(CO)₅ (10.4 mmol) and 10.0 mmol of KNO₂ dissolved in 10 ml of methanol were stirred for 18 hr at 35–40°. After cooling to room temperature, 10.0 mmol of TlNO₃ in 25 ml of water was added and the solvent (CH₃OH + H₂O) 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)₂P(C₆H₅)₃NO]₃. A solution of 1.45 mmol of TlFe(CO)₃NO and 1.45 mmol of P(C₆H₅)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)₂P(C₆H₅)₃NO]₃·2CH₂Cl₂.

Preparation of TlFe(CO)₂P(OC₆H₄Cl)₃NO. Equimolar quantities of TlFe(CO)₃NO and P(OC₆H₄Cl)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)₃C₅H₅. NaCr(CO)₃C₅H₅ (5.00 mmol) in 30 ml of tetrahydrofuran was filtered onto 5.00 mmol of TlNO₃ 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)₃C₅H₅]₃. **Method 1.** A solution of 2.50 mmol of [Cr(CO)₃C₅H₅]₂ dissolved in 20 ml of benzene and a 3 g