

Journal of The Chemical Society, Chemical Communications

NUMBER 20/1974

23 OCTOBER

Stability of Thallium(I) Transition Metal Carbonyls

By S. ERIK PEDERSEN, WILLIAM R. ROBINSON,* and DAVID P. SCHUSSLER
(Department of Chemistry, Purdue University, West Lafayette, Indiana 47907)

Summary Thallium(I) derivatives of metal carbonyl anions are generally stable with weakly basic anions whereas disproportionation to thallium(III) derivatives occurs with more strongly basic anions.

A NUMBER of recent reports¹⁻⁴ have indicated that with the exception of $\text{TlCo}(\text{CO})_4$ ^{5,6} and $\text{Tl}(\text{C}_6\text{H}_4\text{CHPh}_2)\text{Cr}(\text{CO})_3$,⁷ thallium(I) transition metal carbonyl derivatives, TlR , are unstable in solvents of low dielectric constant with respect to disproportionation to thallium metal and the corresponding thallium(III) derivative TlR_3 . Recent work in our laboratory indicates that the stability of thallium(I) derivatives is a function of the base strength of the transition metal carbonyl anions and that many such derivatives are generally stable.

The reaction of $\text{TlCo}(\text{CO})_4$ (I) in CH_2Cl_2 with a variety of Lewis bases proceeds to completion in 1-2 h 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. Stable thallium(I) compounds are formed with those Lewis bases which give substituted cobalt carbonyl anions of relatively low basicity. In particular, $\text{TlCo}(\text{CO})_3\text{P}(\text{OPh})_3$ † 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 (I). The pK_a of $\text{HCo}(\text{CO})_3\text{P}(\text{OPh}_3)$ is 4.95 while that of $\text{HCo}(\text{CO})_3\text{P}(p\text{-OC}_6\text{H}_4\text{Cl})_3$ is somewhat lower.⁸ The pK_a of $\text{HCo}(\text{CO})_4$ is ca. 1.⁹ With ligands giving more strongly basic anions, thallium(III) derivatives and thallium metal form. $\text{Tl}[\text{Co}(\text{CO})_3\text{PPh}_3]_3$ results from the reaction of PPh_3 with (I). The pK_a of $\text{HCo}(\text{CO})_3\text{PPh}_3$ is 6.96.⁸ Other Lewis bases including $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, AsPh_3 , SbPh_3 , and $\text{P}(\text{Bu}^n)_3$ which

give substituted hydridocobaltcarbonyl derivatives with pK_a 's > 5 also react with (I) in CH_2Cl_2 to give thallium metal and thallium(III) derivatives of $\text{Co}(\text{CO})_3\text{L}^-$. These substitutions suggest that a pK_a of ca. 5 for the hydrido-carbonyl 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.

A variety of other reactions also indicate that this value of the pK_a is of about the correct magnitude. Metathetical reactions of thallium(I) salts with the strongly basic anions $\text{Mn}(\text{CO})_5^-$,¹⁻³ $\text{CpM}(\text{CO})_3^-$ ($\text{M}=\text{Cr}$,¹ Mo ,^{1,4} W), $\text{Co}(\text{CO})_8^-$, PPh_3^- ,^{1,7} and $\text{CpFe}(\text{CO})_2^-$ ($\text{Cp} = \pi\text{-C}_5\text{H}_5$) all produce the corresponding thallium(III) derivatives as the stable products. We have observed formation† of thallium(I) derivatives of the relatively weakly basic anions $\text{Fe}(\text{CO})_4\text{R}^-$ (pK_a 's of 3-4) with $\text{R} = \text{CH}_2\text{CN}$, COPh , and SnPh_3 and of the weak base $\text{Fe}(\text{CO})_3\text{NO}^-$ by the metathetical reactions of thallium(I) nitrate and the sodium salts of these anions in a tetrahydrofuran-water mixture. These compounds can be recovered from CH_2Cl_2 unchanged. The reaction of elemental thallium with $\text{V}(\text{CO})_6$ gives the thallium(I) derivative of the weakly basic $\text{V}(\text{CO})_6^-$ anion.

It appears that the behaviour of thallium transition metal carbonyl derivatives is consistent with the behaviour of other thallium systems. Weakly basic metal carbonyl anions characterized by hydrido-derivatives with a pK_a of 5 or less give stable thallium(I) derivatives which are predominantly ionic with only weak covalency in the metal-thallium bond. These thallium(I) derivatives, like other ionic thallium(I) salts, are stable. More strongly basic anions, which form more covalent bonds, give thallium(I)

† All compounds prepared have been isolated and analysed satisfactorily.

derivatives which disproportionate rapidly to thallium(III) grants from the National Science Foundation and the derivatives and thallium metal as is observed during attempts to form thallium(I) alkyls.¹⁰ Purdue Research Foundation.

We gratefully acknowledge support of this work through

(Received, 24th June 1974; Com. 740.)

¹ J. M. Burlitch and T. W. Theyson, *J.C.S. Dalton*, 1974, 828.

² A. T. T. Hsieh and M. J. Mays, *J. Organometallic Chem.*, 1972, **38**, 243.

³ H. J. Haupt and F. Neumann, *J. Organometallic Chem.*, 1971, **33**, C56.

⁴ R. B. King, *Inorg. Chem.*, 1970, **9**, 1936.

⁵ W. Hieber and U. Teller, *Z. anorg. Chem.*, 1942, **249**, 48.

⁶ D. P. Schussler, W. R. Robinson, and W. F. Edgell, *Inorg. Chem.*, 1974, **13**, 153.

⁷ R. L. Cooper, E. O. Fisher, and W. Semmlinger, *J. Organometallic Chem.*, 1967, **9**, 333.

⁸ W. Hieber and E. Lindner, *Chem. Ber.*, 1961, **94**, 1417.

⁹ W. Hieber and W. Hubel, *Z. Elektrochem.*, 1953, **57**, 235.

¹⁰ A. McKillop, L. F. Elsom, and E. C. Taylor, *Tetrahedron*, 1970, **26**, 4041.