in response to systemic modifications (i.e., isotopic composition, temperature, solvent, pressure, etc.) may be the result of perturbations in one or more of the individual rate constants of key excited-state processes. It is evident that a detailed understanding of the photochemical properties of transition-metal complexes requires detailed information regarding excited-state dynamics under photochemically relevant conditions.

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References and Notes

(1) (a) Reported in part at the 1978 Pacific Conference on Chemistry and Spectroscopy, San Francisco, Sept 1978. (b) A preliminary communication: M. A. Bergkamp, R. J. Watts, P. C. Ford, J. Brannon, and D. Magde, *Chem. Phys. Lett.*, **59**, 125 (1978).
(2) (a) University of California, Santa Barbara; (b) University of California, San Diego.
(3) For recent reviews see (a) A. W. Adamson and P. D. Fleischauer, "Concepts in Inorganic Photochemistry", Wiley, New York, 1975; (b) V Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, 1970; (c) P. C. Ford, J. D. Petersen, and R. E. Hintze, *Coord. Chem. Rev.*, **14**, 67 (1974).
(4) P. C. Ford, *Adv. Chem. Ser.*, **168**, 73 (1978).
(5) M. S. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(6) M. Incorvia and J. I. Zink, *Inorg. Chem.*, **13**, 2489 (1974).
(7) J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem.*, **80**, 949 (1976).
(8) L. G. Vanquickenborne and A. Ceulmans, *J. Am. Chem. Soc.*, **99**, 2208 (1977).
(9) P. C. Ford, *Inorg. Chem.*, **14**, 1440 (1975).
(10) J. D. Petersen, R. J. Watts, and P. C. Ford, *J. Am. Chem. Soc.*, **98**, 3188 (1976).
(11) M. K. DeArmond and J. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).
(12) T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971).
(13) T. R. Thomas, R. J. Watts, and G. A. Crosby, *J. Chem. Phys.*, **59**, 2123 (1973).
(14) P. E. Hoggard and H. H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, **77**, 1052 (1973).
(15) R. J. Watts and D. Missimer, *J. Am. Chem. Soc.*, **100**, 5350 (1978).
(16) R. B. Wilson and E. I. Solomon, *Inorg. Chem.*, **17**, 1729 (1978).
(17) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971).
(18) N. Sutin and C. Creutz, *Adv. Chem. Ser.*, **168**, 1 (1978).
(19) J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, **97**, 3843 (1975).
(20) J. N. Demas, E. W. Horris, C. M. Flynn, Jr., and D. Diemente, *J. Am. Chem. Soc.*, **97**, 3838 (1975).
(21) V. M. Miskowski, G. L. Nobinger, D. S. Kliger, G. S. Hammond, N. S. Lewis, K. R. Mann, and H. B. Gray, *J. Am. Chem. Soc.*, **100**, 485 (1978).
(22) M. S. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, **96**, 998 (1974).
(23) P. J. Giordano, S. M. Fredricks, M. S. Wrighton, and D. L. Morse, *J. Am. Chem. Soc.*, **100**, 2257 (1978).
(24) M. S. Henry and M. Z. Hoffman, *Adv. Chem. Ser.*, **168**, 91 (1978).
(25) D. Sandrini, M. T. Ganolfi, A. Juris, and V. Balzani, *J. Am. Chem. Soc.*, **99**, 4523 (1977).
(26) S. C. Pyke and M. W. Windsor, *J. Am. Chem. Soc.*, **100**, 6518 (1978).
(27) (a) J. A. Osborn, K. Thomas, and G. Wilkinson, *Inorg. Synth.*, **13**, 213 (1972); (b) G. U. Bushnell, G. L. Lalor, and E. A. Moelewyn-Hughes, *J. Chem. Soc. A*, 719 (1966).
(28) J. D. Petersen and P. C. Ford, *J. Phys. Chem.*, **78**, 1144 (1974).
(29) (a) H. H. Schmidtke, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 305 (1965); (b) C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 500 (1956).
(30) C. B. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(31) A. K. Covington, M. Paabo, R. A. Robinson, and R. G. Bates, *Anal. Chem.*, **40**, 700 (1968).
(32) (a) L. H. Skibsted, D. Strauss, and P. C. Ford, submitted for publication; (b) D. Strauss and P. C. Ford, *J. Chem. Soc., Chem. Commun.*, 194 (1977).
(33) R. J. Watts, J. S. Harrington, and J. VanHouten, *J. Am. Chem. Soc.*, **99**, 2179 (1977).
(34) G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **54**, 640 (1958).
(35) C. A. Parker and W. T. Rees, *Analyst (London)*, **85**, 587 (1960).
(36) C. A. Parker, "Photoluminescence of Solutions", American Elsevier, New York, 1968.
(37) G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **53**, 646 (1957).
(38) W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, **72**, 3251 (1968).
(39) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967.
(40) L. Moggi, *Gazz. Chim. Ital.*, **97**, 1089 (1967).
(41) T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, **76**, 1937 (1972).
(42) This result is in modest contrast to the report by Kelly and Endicott[41] that Φ_{NH3} for $Rh(NH_3)_5Cl^{2+}$ is $\leq 10^{-3}$ mol/einstein. The differences can probably be attributed to the choice of pH 2 $HClO_4$ solutions by these authors for the reaction medium and an underestimate of the upper limits for detection of NH_3 aquation by pH changes under those conditions. For the results described here, initial solution pHs as high as 4 were employed giving sensitivity improved by as much as two orders of magnitude.
(43) V. J. Shriner and M. L. Smith, *Anal. Chem.*, **28**, 1043 (1956).
(44) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).
(45) G. M. Coleman, J. W. Gesler, F. A. Shirley, and J. R. Kuempel, *Inorg. Chem.*, **12**, 1036 (1973).
(46) J. Lilie, M. G. Sinric, and J. F. Endicott, *Inorg. Chem.*, **14**, 2129 (1975).
(47) P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).

Metal–Metal Charge Transfer in Thallous Tetracarbonylcobaltate Ion Pairs. Spectroscopy and Equilibrium Constants

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Abstract: Ion pairs formed between the thallous cation and the tetracarbonylcobaltate anion exhibit an unusual metal-metal charge transfer electronic absorption band. The energy of the charge-transfer band varies with the solvent. Ion pair association equilibrium constants, calculated using the charge-transfer band, range from 1.2×10^5 in toluene to less than 10 in DMF, Me_2SO, and water. The distance of closest approach of the ion pair, calculated from electrostatic theory, is 3.1 Å. The carbonyl IR spectra support a contact ion pair of C_{3v} symmetry with a direct thallium-cobalt interaction.

Introduction

Recent studies of the association between metal cations and metal carbonyl anions in solution have elucidated both the structure of the ion pairs formed and the reactivity of the solution species.[1-15] Conductivity measurements and infrared spectroscopy have been the primary means of investigation. During our studies of ion-pairing effects upon the NMR parameters of thallium salts,[16] we examined $TlCo(CO)_4$ by a variety of spectroscopic techniques. As expected, infrared measurements demonstrated varying degrees of ion pairing depending upon the solvent. More surprisingly, we observed an intense visible absorption band in certain solvents which results from a metal to metal charge transfer in the $TlCo(CO)_4$ ion pair. This unique CT system is similar to the silver ion–

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Table I. Carbonyl Stretching Frequencies[a] and UV-Visible Absorption[b] of $TlCo(CO)_4$

solvent	D,[d] Z[e]	ν_{CO}, cm^{-1}	λ_{max}, nm
H_2O	78.5, 94.6	1917 vs	285, 325
Me_2SO	46.9, 71.1	1893 vs	285, 320
DMF	36.7, 68.5	1894 vs	287, 325
CH_3CN	38.8, 71.3	2027 w, 1927 m, 1898 vs	285, 325, 400
PhCN	25.2, –	2026 m, 1943 m (sh), 1924 vs	405[c]
2-propanol	19.9, 76.3	2034 m, 1954 m (sh), 1933 vs	283, 305, 387
CH_2Cl_2	8.93, 64.2	2044 m, 1968 m, 1937 s	287, 305, 467
toluene	2.38, –	2033 m, 1957 m, 1923 s	283, 435
benzene	2.274, –	2035 m, 1958 m, 1924 s	283, 435

[a] Solutions were all approximately 5×10^{-3} M except H_2O, 1×10^{-3} M. [b] Solutions were all approximately 1×10^{-3} M for visible wavelength measurements and 5×10^{-5} for UV wavelength measurements. [c] UV wavelength bands obscured by solvent. [d] Solvent dielectric constant taken from J. A. Riddick and W. B. Bunger, "Organic Solvents", "Techniques in Organic Chemistry", Vol. II, Wiley-Interscience, New York, 1970. [e] Kosower Z parameter, taken from ref 24.

Table II. Carbonyl Stretching Frequencies[a] and UV-Visible Absorption[b] of $PPNCo(CO)_4$

solvent	ν_{CO}, cm^{-1}	λ_{max}, nm[c]
Me_2SO	1890 s	260, 267, 274, 282, 320
CH_3CN	1893 s	261, 267, 273, 283, 320
CH_2Cl_2	1892 s	261, 267, 274, 283, 320

[a] Solutions were all approximately 5×10^{-3} M. [b] Solutions were all approximately 1×10^{-5} M. [c] The bands at 283 and 320 nm could be resolved by subtracting the absorption due to the PPN cation measured from a solution of (PPN)Cl at the same concentration.

Table III. Carbonyl Stretching Frequencies and Visible Absorption of $TlCo(CO)_4$ with Added Crown Ether[a]

solvent	ν_{CO}, cm^{-1}	λ_{max}, nm
benzene	2035 m, 1958 m, 1924 s	435
benzene and dibenzo-18-crown-6[b]	1894 s	no bands obsd[c]

[a] All spectra are of solutions with a $TlCo(CO)_4$ concentration of approximately 1×10^{-3} M. [b] The crown ether was present in 2:1 excess. [c] The absence of this band was verified at concentrations as high as 5×10^{-2} M.

aromatic hydrocarbon complexes studied by Mulliken[17] and the hexafluorometallate–xenon complexes of Webb and Bernstein.[18] However, the *metal to metal* nature of the $TlCo(CO)_4$ ion pair charge transfer is unusual for systems which are not bound in a strong covalent fashion, such as in metal dimers[19] and bridged metal dimer complexes.[20] In this paper we report the use of the CT band in the determination of ion pairing association constants and the relation of these data to the infrared spectra.

Experimental Section

All procedures involving the air-sensitive cobalt carbonyl salts were accomplished using standard Schlenk apparatus and septum caps and syringes. All equipment was flushed with prepurified nitrogen. All solvents were dried by an appropriate technique and distilled in a stream of prepurified nitrogen immediately prior to use. Dibenzo-18-crown-6 was purified as previously described.[21]

Thallium Tetracarbonylcobaltate. $TlCo(CO)_4$ was prepared by the procedure described by Schussler et al.[7] Thallium metal and $Co_2(CO)_8$ were stirred in toluene or benzene to form the yellow product. The infrared spectral parameters were identical with those reported by Burlitch and Theyson.[15]

μ-Nitrido-bis(triphenylphosphorus) Tetracarbonylcobaltate, $(PPN)Co(CO)_4$ was prepared by the metathesis of PPNCl and $NaCo(CO)_4$ as described by Ruff and Schlientz.[22] The $NaCo(CO)_4$ in THF solution was prepared by a reaction of $Co_2(CO)_8$ and NaOH in THF.[7] The infrared spectrum of the product was identical with that given by Ruff and Schlientz.

Spectral Studies. Ultraviolet and visible absorption spectra were obtained using a Cary 14 spectrometer. The samples were prepared by dissolving a weighed portion of the compound in the deaerated solvent in a volumetric flask fitted with a septum cap and previously flushed with nitrogen. The solutions were then transferred to matched 1-cm quartz cells also fitted with a septum cap and thoroughly flushed with N_2. The air-sensitive solutions turned purple when exposed to air producing a band at 550 nm which could be used to check all solutions for exposure and decomposition due to oxygen.

Infrared spectra were obtained using a Beckman IR-4 spectrometer. Solutions were prepared as above and transferred using syringes to CsBr or NaCl cells which had been flushed with N_2 and the deaerated solvent prior to use.

Ion pair association constants were determined by the method of Drago and Rose.[23] The absorbance at the band maximum in the visible region was measured at several concentrations using the procedure described above for ultraviolet and visible measurements. Equation 1 was used to construct the curves of association constant vs. molar absorptivity:

$$K_{IP}^{-1} = A/\epsilon - C_{Tl^+} - C_{Co(CO)_4^-} + \frac{C_{Tl^+} + C_{Co(CO)_4^-}}{A}\epsilon \quad (1)$$

where A is the absorbance measured for a given concentration C of Tl^+ and $Co(CO)_4^-$, ϵ is the molar absorptivity, and K_{IP} is the ion pair association constant. The error was calculated according to the procedure of Drago and Rose and their criteria for rejection of an experimental value was used. The absorbance of $Co(CO)_4^-$ at 283 and 320 nm was accounted for by subtracting the absorbance of $(PPN)Co(CO)_4$ from the measured absorbances to obtain the absorbance of the ion pair.

Results

The infrared spectra of $TlCo(CO)_4$ and $PPNCo(CO)_4$ in the carbonyl region were examined in a variety of solvents. The frequencies and qualitative intensities are given in Tables I and II. These results compare favorably with previously published spectra.[7,15] The spectrum of $TlCo(CO)_4$ varies considerably with solvent and consists of either a single band or three bands. The spectra of $PPNCo(CO)_4$, on the other hand, are remarkably independent of solvent and show only a single band at 1890 cm^{-1}.

The infrared spectrum of $TlCo(CO)_4$ changes upon addition of dibenzo-18-crown-6 as summarized in Table III. The three bands observed in pure benzene collapse to a single band at a lower frequency when a 2:1 excess of the crown ether is added.

The ultraviolet and visible absorption spectra for these systems in the region 200–800 nm were investigated. The results for $TlCo(CO)_4$ are shown in Table I. Bands in the ultraviolet region at about 283 and 320 nm were observed in all solvents except benzonitrile, which itself absorbs strongly in this region. In addition to these bands, a strongly solvent-dependent band was observed in the visible region in a number of solvents. The variation of this band with solvent is shown in Figure 1. All spectra are for solutions at approximately the same concentration (ca. 10^{-3} M).

$PPNCo(CO)_4$ also has a number of bands in the UV region. The bands at 260, 267, and 274 nm are all due to internal transitions of the PPN^+ cation. (PPNCl exhibits these same bands.) The bands observed at 283 and 320 nm for the thallium salt are also observed for the PPN salt. No absorption bands

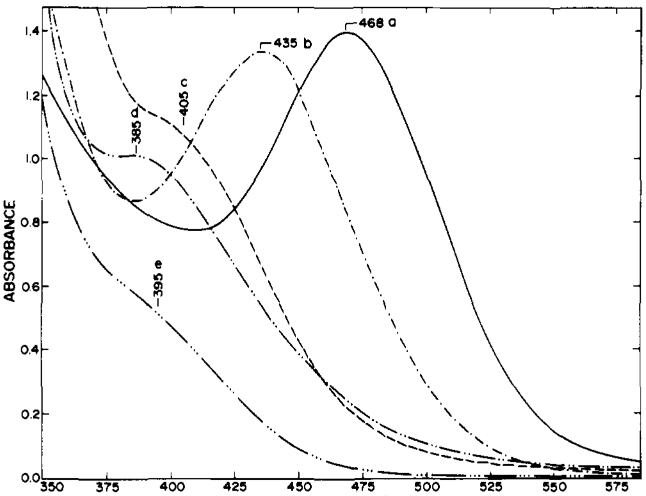

Figure 1. The charge transfer absorption spectra of 10^{-3} M $TlCo(CO)_4$ in (a) dichloromethane; (b) toluene; (c) benzonitrile; (d) 2-propanol; (e) acetonitrile.

above 350 nm are observed. These data are summarized in Table II.

Addition of the crown ether dibenzo-18-crown-6 also affects the UV-visible absorption spectrum of $TlCo(CO)_4$. The visible band disappears upon addition of dibenzo-18-crown-6 (Table III).

The wavelengths of the electronic absorption bands, and in particular those of the visible absorption bands, were invariant over a concentration range of nearly two orders of magnitude. For the visible band, no variation in wavelength was observed for concentrations ranging from 5×10^{-5} to 3×10^{-3} M.

In order to more quantitatively study the interaction of the Tl^+ and $Co(CO)_4^-$ ions in solution, association constants were calculated for the $TlCo(CO)_4$ ion pair assuming that the band in the visible region was a direct measure of the concentration of the ion pair (vide infra).[23] The measured association constants reported in Table IV are the average of two separate determinations. In no case did the measured values for the two determinations differ by more than the combined errors in their values.

Discussion

UV-Visible Absorption Spectra. The ultraviolet and visible absorption spectra of $TlCo(CO)_4$ and $PPNCo(CO)_4$ are dominated by intense bands at 283 and 320 nm. The presence of these bands is independent of the solvent and cation, although the highest energy band is not always resolved because of the solvent cutoff. These bands are assigned to internal charge transfer transitions on the $Co(CO)_4^-$ anion. Of more interest to this study is the presence or absence of a band at wavelengths greater than 350 nm. As the ensuing discussion will show, this band is present only in those solvents for which the carbonyl region infrared spectra show evidence of ion pair formation between the Tl^+ and $Co(CO)_4^-$ ions. More specifically, in those solvents in which $Co(CO)_4^-$ gives only a T_2 vibrational band in the carbonyl region, electronic absorption bands in the visible region are conspicuously absent. In contrast, in those solvents in which $TlCo(CO)_4$ gives a three-band carbonyl infrared spectrum indicative of ion pairing (vide infra), an electronic absorption band in the visible region is present. This band must therefore be due to an electronic transition involving the components of the ion pair. That an interaction of Tl^+ and $Co(CO)_4^-$ is necessary for this band to be observed is confirmed by addition of dibenzo-18-crown-6 to a solution of $TlCo(CO)_4$ in benzene. The crown ether is a strong chelating agent for metal ions and should effectively eliminate any direct interaction between the Tl^+ and $Co(CO)_4^-$ ions by complexing the Tl^+. The infrared spectrum shows that no contact ion pairs are formed in the presence of the crown ether. As the data in Table III show, no visible band occurs in the presence of the crown ether.

Table IV. Ion Pair Association Constants for $TlCo(CO)_4$

solvent	D^a	DN^b	$K_A{}^d$	ϵ^e
toluene	2.57	0.1	1.12×10^5	1520
CH_2Cl_2	8.93		1.11×10^5	1140
2-propanol	19.92		2.4×10^3	950
PhCN	25.2	11.9	1.6×10^3	1460
CH_3CN	37.5	14.1	1.2×10^2	520
DMF	36.1	26.6	$<10^c$	
Me_2SO	45.0	29.8	$<10^c$	
H_2O	78.0	33	$<10^c$	

[a] Solvent dielectric constant. [b] Gutman donor number taken from ref 25. [c] Estimated value based on minimum detectable absorbance at the concentrations used in this study. [d] Maximum error in the measured assocation constants is approximately 30% based on the standard deviation. In most cases the error did not exceed 10-15%. [e] Calculated molar absorptivity from Drago-Rose plot.

The interaction of Tl^+ and $Co(CO)_4^-$ in an ion pair is of a donor-acceptor nature with the acidic Tl^+ accepting electron density from the basic $Co(CO)_4^-$. As discussed below, the infrared data support this Lewis acid-base interpretation. The assignment of the charge-transfer band as a cobalt to thallium charge transfer is therefore suggested.

The energy of the charge transfer correlates with the Kosower Z parameter for the limited number of solvents for which the Z number is known, as is expected for a charge-transfer complex with a change in the net dipole moment between the ground and excited states.[24] Because of this correlation, the expected wavelength of the charge-transfer band can be calculated in solvents such as Me_2SO and DMF where no band is observed. The calculated wavelength in both solvents is in the vicinity of 400 nm. Neither of these solvents nor the $Co(CO)_4^-$ ion absorb in this region. Thus the absence of the charge-transfer band is not a result of obscuration from a more intense absorption but instead is a result of the small amount of ion pairing in these solvents.

Infrared Spectra. The infrared data can be interpreted using simple symmetry arguments. The line of reasoning is identical with that of Edgell and Lyford for the $NaCo(CO)_4$ system.[5] Briefly, $Co(CO)_4^-$ is expected to exist in three forms: a free ion, a solvent-separated ion pair, or a tight ion pair. For $Co(CO)_4^-$ as a free ion, the carbonyl vibrations are subject to a T_d symmetry and a single T_2 band is IR active. Similarly, a solvent-separated ion pair probably produces such a small perturbation on the $Co(CO)_4^-$ ion that the overall T_d symmetry of the anion is approximately maintained and one T_2 carbonyl band is observed. However, for a tight ion pair, the symmetry is reduced to either C_{3v} or C_{2v} depending upon the geometry of cation-anion interaction. If the cation interacted either directly with the cobalt or with a single carbonyl, then the symmetry would be C_{3v}. Three bands are then expected because the T_2 band is split into E and A_1 bands and the A_1 band not IR active in T_d symmetry now becomes active. The intensity of the latter A_1 band arises solely from the differences between the force constants of the unique carbonyl group and the three other carbonyls. C_{2v} symmetry would give rise to four bands, two of A_1 symmetry and one each of B_1 and B_2 symmetry.

The observed solution IR spectra in the CO stretching region show either a single band or a three-band pattern. The spectra of $TlCo(CO)_4$ in H_2O, Me_2SO, and DMA all show a single band of strong intensity and moderate bandwidth. Thus, in these solvents no direct interaction between anion and cation occurs. On the other hand, the three-band pattern observed in the other solvents studied clearly points to an interaction between the Tl^+ and $Co(CO)_4^-$, producing a species of C_{3v} symmetry. It is expected that a direct Tl–Co interaction is more likely than a Tl–O–C–Co interaction (vide infra).

The PPN salt shows only a single band at about 1890 cm^{-1} in all of the solvents studied. Again, no direct interactions between the cation and anion are taking place.

The energies and intensities of the carbonyl bands can be used to interpret the degree and type of cation–anion interaction in these systems. On the basis of the above discussion, no interaction takes place between Tl^+ and $Co(CO)_4^-$ in H_2O, Me_2SO, and DMF, and no interaction between PPN^+ and $Co(CO)_4^-$ takes place in any of the solvents studied. In the lower dielectric constant solvents, a direct interaction is indicated by the three-band pattern observed. The highest frequency band in these solvents is assigned to the unique A_1 vibration. The next highest frequency band is the $A_1(T_2)$ vibration and the most intense and lowest frequency band is the $E(T_2)$ vibration. The frequencies of all bands in these solvents are higher than that of the single band in the high dielectric constant solvents. Thus, the degree of π bonding between the cobalt and the carbonyls is decreased by ion pairing to the thallium ion, indicating that a covalent interaction between the cobalt and thallium occurs with electron density being donated to the thallium by the cobalt.

The unique A_1 band also changes intensity from solvent to solvent. In CH_3CN, it appears only as a very weak band at 2027 cm^{-1}. In benzonitrile it is somewhat stronger, and in 2-propanol it is nearly as intense as the $A_1(T_2)$ band. In benzene, toluene, and CH_2Cl_2 the $A_1(T_2)$ and unique A_1 bands are of essentially identical intensity. The intensity changes in the first three solvents support the conclusion that CH_3CN, PhCN, and 2-propanol interact as bases with the Lewis acid Tl^+. The interaction decreases in the order CH_3CN > PhCN > 2-propanol. The interaction reduces the acidity of Tl^+ in its interaction with the $Co(CO)_4^-$. Benzene, toluene, and CH_2Cl_2 interact only weakly or not at all with the Tl^+ and therefore do not reduce its effective acidity. The stronger the acidity of the Tl^+, the more it can interact with the $Co(CO)_4^-$ and increase the bonding differences between the unique carbonyl and the other three carbonyls. The greater the difference, the greater the intensity of the unique A_1 vibration. Both the intensity increase and the shift of ν_{CO} to higher frequencies as the solvent interaction decreases are observed.

Association Constants. The carbonyl region infrared and the ultraviolet–visible absorption data indicate that a metal to metal charge transfer occurs in solvents where an ion pair occurs and is absent in the solvents where the ion pair does not occur. The quantitative value of the ion pairing equilibrium constant may be calculated using the intensity of the charge transfer absorption band. Two important conditions implicit in the calculation are fulfilled. First, only two absorbing species are present. Although some triple ion formation could occur,[7] especially at higher concentrations in the lowest dielectric constant solvents, the concentration is small based on the IR data and on the results of studies of the similar sodium system, $NaCo(CO)_4$.[1-8] Secondly, for a single species, the band maximum should not exhibit a concentration dependence. No such dependence is observed within the limits of resolution of the Cary 14 spectrometer (vide supra). The ion pair is therefore primarily a 1:1 complex.

The calculated association constants, given in Table IV, vary over five orders of magnitude. Their magnitudes are affected by both electrostatic and solvation effects. As Table IV shows, the association constants roughly correlate with the dielectric constants and with the donor numbers of the solvents (a measure of solvent basicity),[25] although reversals occur in both comparisons. For example, CH_3CN and DMF have nearly identical dielectric constants (37.5 and 36.1, respectively), but the association constant is 1.2×10^2 in CH_3CN and less than 10 in DMF. Donor numbers could be important when dielectric constants are similar. No clear degree of relative importance of the electrostatic and solvation effects is apparent.

The association constants can be treated in a purely electrostatic sense using an approach developed by Denison and Ramsey.[26] The thermodynamic evaluation of ion pairing leads to the equation

$$\ln K_A = \ln K_A^* + e^2/\mathring{a}DkT \qquad (2)$$

where $\mathring{a}$ is the distance of closest approach of the anion and cation and K_A^* is the non-Coulombic contribution to association. Thus a plot of log K_A vs. $1/D$ should be linear for a pure electrostatic ion pair. The value for $\mathring{a}$ can be calculated from the slope. The plot of the data except toluene fits a straight line with $R = 0.97$. The best fit line through the data points gives a value for $\mathring{a}$ of 3.1 Å. The upper limit of the Tl^+ covalent radius is 1.9 A. Using this value, the covalent radius calculated for $Co(CO)_4^-$ is 1.2 Å, in good agreement with the reported covalent radius of 1.3 Å for $RCo(CO)_4$.[27] The Tl–Co distance of 3.1 Å is in surprisingly good agreement with the Tl–Co single bond distance of 3.2 Å calculated in ref 7. The Tl–Co distance is reasonable for a contact ion pair rather than a solvent-separated ion pair in which the point of contact is the cobalt itself rather than one or more of the carbonyls. The other possibilities would result in values for $\mathring{a}$ greater than 3.1 Å. The deviations from linearity in plots of this type have been explained as a result of specific solvent–solute interactions.[26] Because of the limited number of data points and the assumptions inherent in eq 2, the value of $\mathring{a}$ is best regarded as a semiquantitative estimate.

Conclusions

The existence of a charge-transfer complex involving a metal carbonyl anion provides a new method of determining anion–cation association constants for these species. The charge-transfer band observed in the visible region of the spectrum is assigned as a direct cobalt to thallium charge transfer. Both the dielectric constant and basicity of the solvent influence the formation constant of the complex. The energy of the charge-transfer band correlates with the Z number of the solvent. The IR spectra and the calculated interionic separation suggest that Tl^+ $Co(CO)_4^-$ forms a tight ion pair of C_{3v} symmetry.

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References and Notes

(1) W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965).

(2) W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 1815 (1966).

(3) W. F. Edgell, J. Lyford, IV, R. Wright, W. R. Risen, and A. Watts, *J. Am. Chem. Soc.*, **92**, 2240 (1970).

(4) W. F. Edgell, J. Lyford, IV, A. Barbetta, and C. I. Jose, *J. Am. Chem. Soc.*, **93**, 6403 (1971).

(5) W. F. Edgell and J. Lyford, IV, *J. Am. Chem. Soc.*, **93**, 6407 (1971).

(6) W. F. Edgell and A. Barbetta, *J. Am. Chem. Soc.*, **96**, 415 (1974).

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

(8) W. F. Edgell, S. Hegde, and A. Barbetta, *J. Am. Chem. Soc.*, **100**, 1406 (1978).

(9) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976).

(10) M. Y. Darensbourg and C. Borman, *Inorg. Chem.* **15**, 3121 (1976).

(11) M. Y. Darensbourg, D. J. Darensbourg, and H. C. L. Barros, *Inorg. Chem.*, **17**, 297 (1978).

(12) R. D. Ernst, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2090 (1977).

(13) R. D. Ernst, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2098 (1977).

(14) R. D. Ernst and T. J. Marks, *Inorg. Chem.*, **17**, 1477 (1978).
(15) J. M. Burlitch and T. W. Theyson, *J. Chem. Soc., Dalton Trans.*, 828 (1974).
(16) C. M. Schramm and J. I. Zink, manuscript in preparation.
(17) R. S. Mulliken and W. B. Person, "Molecular Complexes, a Lecture and Reprint Volume", Wiley, New York, 1969.
(18) J. D. Webb and E. R. Bernstein, *J. Am. Chem. Soc.*, **100**, 483 (1978).
(19) M. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
(20) T. J. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978).
(21) C. Srivanivit, J. I. Zink, and J. J. Dechter, *J. Am. Chem. Soc.*, **99**, 5876 (1977).
(22) J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, **15**, 84 (1974).
(23) R. S. Drago and N. J. Rose, *J. Am. Chem. Soc.*, **81**, 6178 (1959).
(24) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).
(25) V. Gutman, "Coordination Chemistry in Nonaqueous Solution", Springer-Verlag, New York, 1968.
(26) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).
(27) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 19 (1970).

Preparation and Characterization of Tantalum(III) Olefin Complexes and Tantalum(V) Metallacyclopentane Complexes Made from Acyclic α Olefins

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Abstract: TaCp(CHCMe$_3$)Cl$_2$ (Cp = η^5-C$_5$H$_5$) reacts rapidly with ethylene and propylene to give the ethylene and propylene metallacyclopentane complexes, $\mathrm{CpCl_2\overline{TaCH_2CH_2CH_2CH_2}}$ and $\mathrm{CpCl_2\overline{TaCH_2CHMeCHMeCH_2}}$, respectively. Analogous Cp″ metallacyclopentane complexes (Cp″ = η^5-C$_5$Me$_5$) can be formed from (and are in equilibrium with) TaCp″(olefin)Cl$_2$ complexes and olefin (olefin = ethylene, propylene, 1-pentene, and neopentylethylene). The analogous styrene, *cis*-2-pentene, and cyclooctene complexes do not form observable metallacycles. A mixed ethylene/RCH=CH$_2$ metallacycle (R = e.g., methyl) can be observed on adding RCH=CH$_2$ to TaCp″(ethylene)Cl$_2$ at low temperatures. The configuration of $\mathrm{Cp''Cl_2\overline{TaCH_2CHRCHRCH_2}}$ is trans by ^{13}C NMR while a mixed metallacycle has two β-substituted isomers. Cp″ metallacycles decompose irreversibly by β-hydride elimination followed by reductive elimination to give primarily the 2,3-disubstituted 1-butene dimer. The dimer is displaced by the free olefin which is always present to give back the olefin complex quantitatively. The greater stability of the ethylene metallacycle compared to the propylene metallacycle toward β-elimination suggests that a β hydrogen bound to a tertiary carbon atom is abstracted more rapidly than one bound to a secondary carbon atom. A deuterium-labeling experiment has shown that D$_\alpha$ atoms do not scramble singly or pairwise in a hex-1-ene-*1,1-d$_2$*/ethylene metallacycle before or during decomposition. This result has been used as evidence against degenerate olefin-metathesis-like methylene exchange in Ta metallacyclopentane complexes.

Introduction

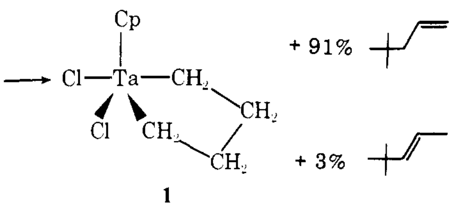
Metallacyclopentane[2] complexes can be prepared from high-energy olefins such as norbornadiene,[3] 3,3-dimethylcyclopropene,[4] methylenecyclopropane,[4] butadiene,[5] or allene,[6] but simple α olefins or ethylene fail to give observable analogous metallacyclopentane complexes. A simple tetramethylene complex (for example) therefore must be prepared from a metal dihalide and the 1,4-di-Grignard or dilithiobutane[7] (or, more recently, $\mathrm{\overline{MgCH_2CH_2CH_2CH_2}}$[8]). Therefore we were surprised to find that Ta(V) metallacyclopentane complexes are the ultimate organometallic products when the neopentylidene ligand is cleaved from TaCp(CHCMe$_3$)Cl$_2$ by ordinary olefins such as ethylene or propylene,[9] or dienes such as 1,7-octadiene.[10] We now find that we can prepare a large class of similar metallacyclopentane complexes more simply from new α-olefin complexes of the type Ta(η^5-C$_5$Me$_5$)(α-olefin)Cl$_2$. Since other workers have now shown that Zr(IV),[11] Ti(IV),[12] or Ni(II)[2c,12] metallacyclopentane complexes can also be prepared from simple olefins, this type of reaction may be more widespread than had heretofore been believed. The reason why such metallacycles have not been observed more commonly is due in part to the fact that they are normally not very stable. This is important since they can therefore be useful intermediates in catalytic processes.[10,12b,13]

In this paper we disclose full details of the preparation and characterization of monocyclopentadienyl dichlorotantalum(V) metallacyclopentane complexes made from olefins of the type RCH=CH$_2$ along with a study of how several decompose. How others decompose and how this type of complex can be used to selectively dimerize α olefins will be the subject of a subsequent paper.[14]

Results

η^5-C$_5$H$_5$ Metallacyclopentane Complexes (η^5-C$_5$H$_5$ = Cp). Orange TaCp(CHCMe$_3$)Cl$_2$[9] reacts rapidly with ethylene in pentane at 25 °C. The color first deepens to red, then lightens to yellow-orange as orange crystals of $\mathrm{CpCl_2\overline{TaCH_2CH_2CH_2CH_2}}$ (**1**) fall from solution in high yield (eq 1). The organic products of this reaction are Me$_3$C-

TaCp(CHCMe$_3$)Cl$_2$ + 3C$_2$H$_4$



(1)

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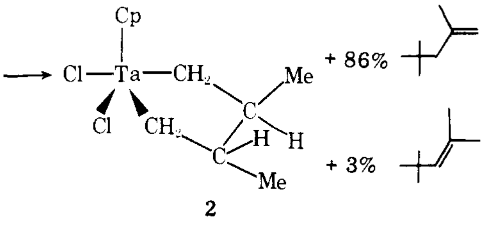
TaCp(CHCMe$_3$)Cl$_2$ + 3CH$_3$CH=CH$_2$



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