

Pressure Tuning Spectroscopic Study of Electron-Tunnelling Processes in Solution

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Abstract: The first study of the effect of pressure on the intervalence transfer (IT) band of a very weakly coupled mixed valence binuclear, (μ -2,6-dithiaspiro[3.3]heptane)decaamminediruthenium(II,III) hexafluorophosphate in D₂O is reported. A red shift of more than 200 cm⁻¹ and a small increase in the oscillator strength of the IT band were observed over a pressure range of 1500 bars. These effects were interpreted as arising primarily from H-bonding between the ammine groups on the ruthenium atoms and the solvent D₂O molecules. A nonadiabatic, multiphonon electron-tunnelling theory was employed to calculate rates of thermal electron transfer at each pressure, and ΔV^* was estimated to be -7.5 ± 0.2 cm³/mol for the thermal electron exchange.

The study of intramolecular electron transfer using binuclear transition-metal mixed-valence complexes has seen much progress over the past two decades.^{1,2} Along with the design and preparation of new models, the application of new experimental techniques has played an important role in that advancement. One particular technique which has recently been applied to the study of mixed-valence compounds³⁻⁸ is pressure tuning spectroscopy (PTS). It is well known^{3,9} that pressure effects on the electronic spectrum of a material can provide very valuable information about its electronic structure and its interactions with the medium. This technique, therefore, may provide unique insight into the nature of the electronic transition that may occur in mixed-valence complexes.

The first application of pressure to the study of intervalence transfer (IT) bands was in 1986 when Drickamer and Hendrickson et al.⁴ reported that there was no substantial shift in the energy of the IT band for the ferrocenium binuclear or for the complex (bpy)₂ClRu(py₂)RuCl(bpy)₂³⁺ upon pressure-induced freezing of the solutions. Usually the energy of the IT band for a symmetrical mixed-valence molecule (E_{op} or λ) is treated as arising from two contributions—an inner-sphere reorganizational energy, λ_{in} , resulting from stretching and compressing of internuclear bonds prior to electron transfer, and λ_{out} , which results from reorientation of solvent molecules. Therefore, the following equation results.

$$\lambda = \lambda_{in} + \lambda_{out} \quad (1)$$

The dielectric continuum model is then usually employed to describe the solvent reorganization contribution, resulting in the equation:

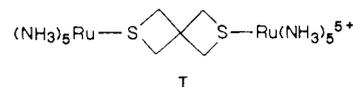
$$\lambda_{out} = (\Delta e)^2(1/2a_1 + 1/2a_2 - 1/R)(1/D_{op} - 1/D_s) \quad (2)$$

where Δe is the charge transferred, a_1 and a_2 are the radii of the two reactants, R is the distance between their centers, D_{op} is the optical dielectric constant, and D_s is the static dielectric constant of the medium. Normally, a solid has a much smaller D_s than the corresponding liquid, typically by a factor of 10 or more. Thus, eq 2 predicts that a large shift of E_{op} to lower energy should occur in a frozen medium. Drickamer and Hendrickson et al.^{4,8} employed pressure-induced freezing to test this idea and found that only small shifts occurred. They concluded that the dielectric continuum model is inadequate in determining the inner-sphere and outer-sphere reorganizational energies in intervalence electron transfer for localized systems.

Recently, Hendrickson and Drickamer et al.⁷ used PTS to examine the Creutz-Taube ion, (NH₃)₅Ru(py₂)Ru(NH₃)₅⁵⁺, which has been described variously as delocalized (valence averaged) or localized (valence trapped). In liquid D₂O, they ob-

served a shift of the IT band 35 cm⁻¹ to higher energy as the pressure was increased from 1 to 7000 bars. They concluded that the primary effect of pressure on the Creutz-Taube ion is to change the amount of electronic coupling between the metal centers and the vibronic coupling changes only slightly. These results are in agreement with an already high degree of coupling suggested by other evidence.^{1,10}

We report in this work the first effects of pressure on the IT band of a very weakly coupled binuclear, complex I, in which



electron transfer is significantly nonadiabatic. Our earlier investigations^{11,12} employing this complex showed that the position of the IT band was strongly dependent on the nature of the solvent,¹³ the counterions present, and even the redox potential of the oxidant¹⁴ used to generate the mixed-valence species. Since the metal atoms of metalloproteins often are separated by large distances of 25 Å or more,¹⁵ and therefore also often are very weakly coupled, this complex may be considered as an excellent model for biological redox processes.

Experimental Section

Chemicals and Reagents. The binuclear (complex I) (μ -2,6-dithiaspiro[3.3]heptane)decaamminediruthenium(II,III) hexafluorophosphate

- (1) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
- (2) Brown, D., Ed. *Mixed Valence Compounds*; Reidel: Dordrecht, 1980.
- (3) Drickamer, H. G. *Acc. Chem. Res.* **1986**, *19*, 355.
- (4) Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Chem. Phys. Lett.* **1986**, *132*, 231.
- (5) Sinha, U.; Lowery, M. D.; Hammack, W. S.; Hendrickson, D. N.; Drickamer, H. G. *J. Am. Chem. Soc.* **1987**, *109*, 7340.
- (6) Sinha, U.; Lowery, M. D.; Ley, W. W.; Drickamer, H. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 2471.
- (7) Hammack, W. S.; Lowery, M. D.; Hendrickson, D. N.; Drickamer, H. G. *J. Phys. Chem.* **1988**, *92*, 1771.
- (8) Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Inorg. Chem.* **1988**, *27*, 1307.
- (9) Drickamer, H. G.; Frank, C. W. *Annu. Rev. Phys. Chem.* **1972**, *23*, 39.
- (10) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
- (11) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693.
- (12) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596.
- (13) Lewis, N. A.; Obeng, Y. S. *J. Am. Chem. Soc.* **1988**, *110*, 2306.
- (14) Lewis, N. A.; Obeng, Y. S. *J. Chem. Soc., Chem. Commun.*, submitted for publication.
- (15) *Tunnelling in Biological Systems*; Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979; p 506.

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Table I. Experimental and Theoretical Parameters at Different Pressures

P , bars ^a	E_{op} ^{b,c}	ϵ ^d	$10^2 T_{abl} $ ^e	$10^{-8}k_{ab}$ ^f
1	10.47	43.0	1.65	1.8
300	10.43	43.5	1.66	1.9
600	10.38	44.2	1.67	2.1
900	10.34	44.5	1.67	2.3
1200	10.29	45.4	1.68	2.6
1500	10.26	45.9	1.69	2.8

^a ± 2 bars. ^b ± 0.01 kK. ^c The value of E_{op} at ambient pressure is different from that reported earlier.¹² We believe that the present value is more accurate because of the superior baseline subtraction capabilities of the instrument employed in this work. ^d Relative values with respect to the one previously reported¹² at ambient pressure over a 3-fold concentration range. In units of $M^{-1} cm^{-1}$. ^e In eV, calculated from eq 3. ^f In s^{-1} , calculated from eq 4.

was prepared¹¹ according to the literature and gave good elemental analyses. The oxidant employed was $(NH_4)_2Ce(NO_3)_6$ (Amend Drug and Chemical Co.); it was recrystallized from distilled acetone prior to use. Deuterated water, 99.8% (Aldrich), was stored under argon and handled with standard syringe techniques.

Spectral Measurements. The high-pressure vessel was constructed with sapphire windows and has been described elsewhere.¹⁶ The pressure generator, valves, and tubing were made of stainless steel (High Pressure Equipment Co., Erie, Pa.) and were used in a standard arrangement.¹⁶ Pressure was measured to within 2 bars by means of a calibrated Heise-Bourdon gauge (Dressler Industries). The pressurizing fluid was *n*-heptane. The observation cell was of the Le Noble-Schlott design,¹⁷ also known as the "pill-box" type. This cell is ideal for studying absorbance changes, since concentration corrections are not required, as they are compensated by proportional variation of the optical path length.¹⁶

The spectra were obtained at room temperature (24 ± 1 °C) in a Perkin-Elmer Lambda 9 UV-vis-NIR spectrophotometer interfaced to an IBM PC/XT, with the slit set in automatic servocontrol. The concentration of the binuclear was 3.54×10^{-3} M in all experiments, and the absorbance was measured every 0.5 nm from 1600 to 600 nm at intervals of 150 bars, beginning with the highest pressure in order to ensure expulsion of any dissolved gas. No significant changes were detected when going in the opposite direction. Duplicate measurements using the same concentration of complex yielded identical results. Electronic background correction was done at each pressure by subtracting spectra from parallel runs in which the cell contained only pure D_2O . The software for the Lambda 9 spectrophotometer was provided by Softways Inc.

Results

Table I lists the frequency values (E_{op}) for the IT bands of I at six different pressures. The accuracy of the instrument is better than $2 cm^{-1}$ in this region. At 1500 bars, the band had shifted more than $200 cm^{-1}$ toward lower energies. As a comparison, the band of the Creutz-Taube ion moved only $35 cm^{-1}$ in the opposite direction, over a pressure range almost five times as great.⁷ Figure 1 shows that the shift seems to be linear, with a slope of $0.148 cm^{-1}/bar$. If this line were extrapolated to 7000 bars to compare with the maximum pressure employed in the study of the Creutz-Taube ion, this would represent a shift of more than 1 kK for the spiro binuclear, I.

The width of the band at half-height did not change with pressure and was calculated to be 5.12 ± 0.01 kK. The absorbance, however, did rise with pressure, giving the relative¹⁸ extinction coefficients listed in Table I. In order to check further the significance of this result, we calculated the width for each half of the band. It was observed that, for the low-energy side of the band, the width decreased slightly, whereas for the high-energy side it increased at the same rate, thus balancing each other. There is the possibility that the band contains more than one element which may be affected differently by pressure.⁵

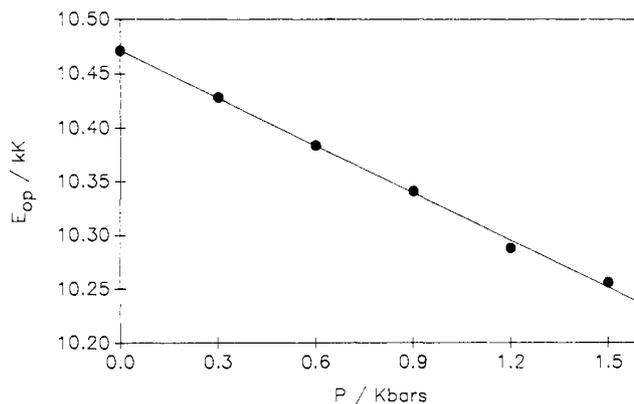


Figure 1. Plot of the intervalence transfer band maximum as a function of pressure for the ruthenium spiro binuclear, complex I.

Discussion

Hush¹⁹ has developed a theory that satisfactorily describes the properties of IT bands in mixed-valence compounds in which the valencies are localized and interactions between metal sites are weak. A remarkable number of intervalence systems have been rationalized by this theory. There is considerable controversy over whether the Creutz-Taube ion can be considered to be valence localized or valence trapped;¹ if the latter is true, the Hush theory can be applied to the IT band arising from this binuclear. If the electronic coupling is too strong (valence delocalized case), the overlap integral cannot be neglected and the Hush theory, which depends on this approximation, is no longer valid. On the other hand, when the coupling becomes too weak, as is the case with the spiro binuclear, complex I, again the Hush model cannot be used because, in calculating the rates of thermal electron transfer from optical properties, the assumption is made that the transfer is adiabatic. Intervalence bands of very weakly coupled metal centers are characterized by extremely small extinction coefficients and bands that are broader than those predicted by Hush's theory. For weakly coupled binuclears, solvent effects can be neglected and nuclear eigenfunctions can be obtained in the adiabatic approximation leading to simplified theoretical treatments. However, if the electron-exchange coupling is very weak, as in the spiro binuclear, I, then the theoretical treatment would have to include solvent effects, and the full vibronic problem has to be solved without the adiabatic approximation.

Hopfield²⁰ has developed a nonadiabatic, multiphonon electron tunnelling theory which has been used with considerable success in correlating and interpreting electron-transfer reactions between large biomolecules such as the cytochromes,²¹ Chromatium,²² and the bacteriochlorophylls,^{21,23} as well as in simple inorganic systems such as the ruthenium spiro binuclear (I) and related complexes and even in purely organic models.²⁴ Hopfield's theory correlates changes in the oscillator strength of the IT band with the tunnelling matrix element, $|T_{abl}|$, which is a measure of the separation between the potential energy surfaces of the two metal centers at the crossover point (see Figure 2). It is equivalent to H_{ab} as defined in Hush's theory¹⁹ and can be expressed as²⁰

$$|T_{abl}|^2 = \frac{(n^2 + 1)(3)(2300)E_{op}\hbar c\epsilon}{(2n)(2\pi^2)(N)a^2e^2(2\pi\sigma^2)^{1/2}} \exp[-(E_{op} + E_b - E_a - \Delta)^2/2\sigma^2] \quad (3)$$

where n is the refractive index of the connecting ligand (1.53 for the spiro ligand in I), E_{op} is the energy of the IT band, \hbar is Planck's constant/ 2π , c is the speed of light, N is Avogadro's number,

(16) Van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*, Elsevier: Amsterdam, 1986.

(17) Le Noble, W. J.; Schlott, R. *Rev. Sci. Instr.* **1976**, *47*, 770.

(18) These extinction coefficients were calculated from the ratios of the height of the band at each pressure with respect to the one at 1 bar, since the value at atmospheric pressure was determined before¹² over a 3-fold concentration range.

(19) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(20) Hopfield, J. J. *Biophys. J.* **1977**, *18*, 311.

(21) Hopfield, J. J. *Electrical Phenomena at the Biological Membrane Level*, Roux, E., Ed.; Elsevier: Amsterdam, 1977; p 471.

(22) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.

(23) Reference 15, p 730 ff.

(24) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.

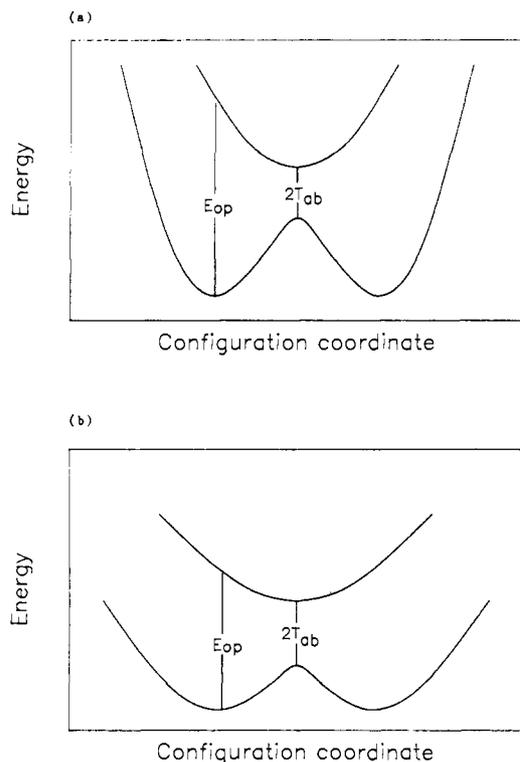


Figure 2. (a) Configuration coordinate diagram showing the shape of the potential wells at ambient pressure. (b) Configuration coordinate diagram showing the flattening of the wells which occurs at elevated pressures.

a is the distance between metal centers (11.3 Å), e is the charge of the electron, σ is the half-bandwidth at 0.61 height of the IT band (2.35 ± 0.01 kK), E_b and E_a are the redox energies, Δ is the vibronic coupling parameter, and ϵ is the extinction coefficient at the peak maximum. Since for a symmetrical binuclear $E_b = E_a$ and $\Delta = E_{op}$ at the peak maximum, $|T_{ab}|^2$ can be calculated and from that the rate of thermal electron transfer k_{ab} , namely²²

$$k_{ab} = (2\pi/\hbar)|T_{ab}|^2(2\pi\sigma^2)^{-1/2} \exp[-(E_a - E_b - \Delta)^2/2\sigma^2] \quad (4)$$

Our results with complex I indicate that while E_{op} is diminished (red shift), $|T_{ab}|$ is slowly augmented by pressure. The possible origin of these two effects is better illustrated by the schematic configuration coordinate diagram in Figure 2. A change in the shape of the potential energy surfaces that can accommodate the experimental observations would be a symmetrical flattening of the entire diagram, arising from a decrease in the spring constants defining the two vibronic wells. Because of the limited electronic coupling in our systems, it is expected that pressure effects on interactions with the medium will predominate over direct communication between the two metals. This would explain the observation that the ruthenium binuclear, I, is sensitive to our pressure range (1–1500 bars), whereas the Creutz-Taube ion was virtually unaffected because these pressures are too small to cause measurable changes in intramolecular distances in the binuclear. Small compressions of the Ru^{II} and Ru^{III} bond lengths of the Creutz-Taube ion leading the observed electronic coupling between the metal centers are possible at the higher pressures employed by Hendrickson and Drickamer et al.⁷ (up to 7000 bars in solution). At very high pressures, as high as 200 000 bars in the solid state, dramatic blue shifts of the IT band for the Creutz-Taube ion were observed owing to the large effect on the compression of bond lengths. Calculations based on the Piepho, Krausz, and Schatz (PKS) model⁷ of IT band contours for the Creutz-Taube ion indicated that the degree of vibronic coupling in the mixed-valence species changed an insignificant amount with pressure.

Our weakly coupled binuclear exhibits a large red shift over the pressure range 1–1500 bars. The origin of this effect almost certainly lies in H-bonding (D-bonding) interactions of the D₂O

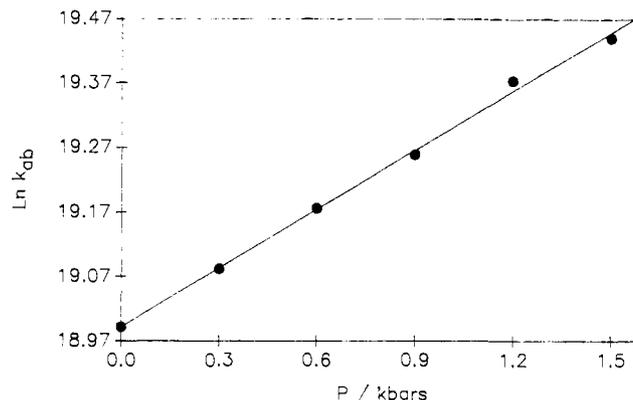


Figure 3. Plot of the ln of the calculated thermal rate constants against pressure.

with the amines of the ruthenium dinuclear, I. In the absence of intermolecular forces such as this, the opposite trend, i.e., a blue shift, would have been anticipated since compression of the molecules in the system by the application of pressure increases the forces of repulsion between neighboring molecules, and the bulk modulus always increases. This would steepen the curvatures of the potential wells that govern the vibrations. The most marked exception to this general pattern has been found in the stretching bands of H-bonded groups which often undergo large shifts to lower frequencies (red shift) with increasing pressure.^{23–25} This is a result of attractive forces between molecules participating in the H-bonding and tends to flatten the potential energy surfaces as we illustrate in Figure 2 by relaxing the spring constants defining these wells. However, at sufficiently high pressures not available to us at this time, the repulsive forces will dominate and a blue shift should be observed. As can be seen from Table I, the observed red shift leads to an increase in the rate of thermal electron transfer with pressure, as calculated from Hopfield's theory. The volume of activation, ΔV^\ddagger , may be estimated from these data and the equation:

$$\left(\frac{\delta \ln k_{ab}}{\delta P} \right)_T = \frac{-\Delta V^\ddagger}{RT} \quad (5)$$

A plot of $\ln k_{ab}$ vs. pressure is found in Figure 3. From the slope of the line, ΔV_{obs}^\ddagger may be calculated to be -7.5 ± 0.2 cm³/mol. This quantity may be accounted for by purely a consideration of outer-sphere (primarily solvent) rearrangements. Stranks has developed a quantitative treatment for the calculation of ΔV^\ddagger for outer-sphere electron transfer self-exchange processes where

$$\Delta V_{calc}^\ddagger = \Delta V_{coul}^\ddagger + \Delta V_{IR}^\ddagger + \Delta V_{DH}^\ddagger + \Delta V_{SR}^\ddagger$$

where the subscripts refer to calculated, coulombic, inner-sphere rearrangement, Debye-Hückel, and solvent rearrangement, respectively. For a binuclear, the Coulombic and Debye-Hückel terms are zero and the inner-sphere rearrangement will also be small for a ruthenium species. Thus, the ΔV^\ddagger can be approximated by a calculation of the solvent rearrangement term given below, as modified by Swaddle²⁸ for a molecule having the shape of an ellipsoid,

$$\Delta V_{SR}^\ddagger = \frac{N_A e^2 \sigma^2 S(\lambda_0)}{16\pi\epsilon_0 r^2 (2r + \sigma)} \left[\frac{\delta}{\delta P} \left(\frac{1}{n^2} - \frac{1}{D} \right) \right]_T$$

where N_A is Avogadro's number, e is the electronic charge, σ is the distance between the ruthenium centers (9.2 Å), $S(\lambda_0)$ is the shape factor,²⁹ ϵ_0 is the permittivity in a vacuum, r is the semiminor

(25) Fishman, E.; Drickamer, H. G. *J. Chem. Phys.* **1956**, *24*, 548.

(26) Moon, S. H.; Drickamer, H. G. *J. Chem. Phys.* **1974**, *61*, 48.

(27) Hamann, S. D.; Linton, M. *Aust. J. Chem.* **1975**, *28*, 2567.

(28) Reference 16, p 289.

axis of the ellipsoid (3.5 \AA), n^2 is the refractive index,³⁰ and D is the static dielectric constant of the medium.³¹ The value of $\Delta V_{\text{calc}}^{\ddagger}$ employing this expression was found to be $-8.4 \text{ cm}^3 \text{ mol}^{-1}$. Thus, the value of $\Delta V_{\text{obs}}^{\ddagger}$ can be accounted for almost exclusively by solvent electrostriction, and this dramatically illustrates the enormous role of the medium in this redox process.

We have previously shown¹³ that the dielectric continuum model is not appropriate for analyzing IT bands for the dinuclear, I, since the energies of the IT bands are dependent upon the ionic strength of the medium. Therefore, the values we quote in this work are valid, strictly speaking, only for an ionic strength of 0.081 M. An estimate of the value of $\Delta V_{\text{obs}}^{\ddagger}$ at zero ionic strength was made assuming that the effect of ionic strength was not markedly pressure dependent. This gave $\Delta V_{\text{obs}}^{\ddagger} = -7.1 \text{ cm}^3 \text{ mol}^{-1}$. Thus, the value of ΔV^{\ddagger} is not very sensitive to this parameter, and the

quoted value can be considered to be a reasonable estimate of this quantity.

This work confirms the hypothesis that for very weakly coupled binuclears such as I, in which electron tunnelling is the major mechanism for electron transfer between the metal centers, moderate increases in pressure may cause large changes in the rate of electron exchange, especially when significant van der Waals interactions are possible. Whether this will always result in an enhancement of electron transfer remains to be seen. We are presently examining pressure effects of other weakly coupled binuclears in a variety of media to determine the generality of these results.

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- (29) Cannon, R. D. *Chem. Phys. Lett.* **1977**, *49*, 299.
 (30) Narayanaswamy, C. K.; Narayanan, P. S.; Krishnan, R. S. *Nature (London)* **1957**, *180*, 497.
 (31) Srinivasan, K. R.; Kay, R. L. *J. Chem. Phys.* **1974**, *60*, 3645.

Lanthanide-Promoted and Nickel Cyanide Catalyzed Carbonylation Reactions under Phase-Transfer Conditions

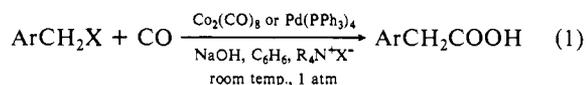
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Contribution from the Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4. Received April 11, 1988

Abstract: The nickel cyanide and phase transfer [NaOH , PhCH_3 , $\text{R}_4\text{N}^+\text{X}^-$] catalyzed carbonylation of benzyl chlorides is promoted by lanthanide salts [CeCl_3 , LaCl_3]. This simple reaction is sensitive to the concentration of the lanthanide compound, sodium hydroxide, quaternary ammonium salt, and nickel catalyst. The nature of the organic phase and phase transfer agent also influences the reaction rate. The acceleration of the reaction may be a consequence of coordination of a nickel cyanide nitrogen lone pair to the lanthanide salt.

The transition metal complex catalyzed carbonylation of halides is a useful method for the synthesis of carboxylic acids. Elevated temperatures and/or pressures are often required for the homogeneous hydroxycarbonylation reaction catalyzed by nickel, palladium, or platinum complexes.²

Phase-transfer catalysis has been utilized recently for metal complex catalyzed oxidation, reduction, and carbonylation reactions.³ These processes occur under mild conditions, and workup of the organic products is usually simple. For instance, cobalt carbonyl^{4,5} or palladium(0) complexes,⁶ are capable of catalyzing the carbonylation of benzylic halides to carboxylic acids under phase-transfer conditions.



Lanthanides have attracted considerable interest in recent years as reagents and catalysts in organic synthesis.⁷⁻⁹ It was envisaged

Table I. Carbonylation of Benzylic Chlorides Catalyzed by $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, and $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$ ^a

substrate	reaction time, h	% conversion	% isolated yield ^b
PhCH_2Cl	4.5	97	89
<i>p</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$	6.5	88	82
<i>o</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$	6.5	80	76
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	7.0	48	42
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	7.25	67	55
1-chloromethylnaphthalene	7.0	71	60
2-chloromethylnaphthalene	6.0	90	70

^a Conditions: $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ [1.0 mmol], $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$ [0.177 mmol], $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ [0.8 mmol], PhCH_3 (25 mL), 5 N NaOH [25 mL], ArCH_2Cl [10.0 mmol], CO (1 atm, $90 \pm 5 \text{ }^\circ\text{C}$). ^b Yields are of pure materials. Products were identified by comparison of physical data [mp, IR, NMR, MS] with those for authentic materials. Carboxylic acids are the only products formed in these reactions.

that lanthanide compounds could assist the carbonylation of benzylic halides possibly by interaction with the catalytic species. We now report that certain lanthanides successfully promote the carbonylation reaction, this being the first example of the use of lanthanide complexes as catalysts in a phase-transfer process.

- (1) Killam Research Fellow, 1986-88.
 (2) Heck, R. F. *Adv. Catal.* **1977**, *26*, 323. Mullen, A. *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980; pp 243-308.
 (3) Alper, H. *Adv. Chem. Ser.* **1987**, *326*, 8.
 (4) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* **1977**, *134*, C11.
 (5) Cassar, L.; Foa, M. *J. Organomet. Chem.* **1977**, *134*, C15.
 (6) Alper, H.; Hashem, K.; Heveling, J. *Organometallics* **1982**, *1*, 775.
 (7) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573.

- (8) Vougioukas, A. E.; Kagan, H. B. *Tetrahedron Lett.* **1987**, *28*, 5513, 6065.
 (9) Molander, G. A.; LaBelle, B. E.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 5259 and references cited therein.