atoms and the phenolate oxygen atom, which also bridges between the metal ions. The sixth coordination site is occupied by the oxygen atom of a THF molecule. The Mn–N(pyrazole) distances of 2.188 (5) and 2.208 (5) Å are significantly shorter than the Mn–N(3) distance of 2.319 (4) Å. The long Mn–N(3) bond is presumably the result of strain in the N(3)–Mn–O(1) moiety induced by the binding of the two metal centers in a binuclear fashion with a Mn–Mn separation of only 3.256 Å. It is also the result of the low basicity of the arylamino groups relative to the pyrazole nitrogen atom. It is noteworthy in this regard that the O(1)–Mn–N(3) angle of 76.1 (1)° is far more distorted than the other cis angles subtended by a single ligand, which lie in the range 85–97°. A larger Mn–Mn separation (of approximately 3.5 Å) would relieve the strain in this portion of the molecule but lead to an unacceptably short O(1)---O(1′) separation in the dimer. The actual O(1)---O(1′) separation of 2.736 (7) Å is approximately twice that of the van der Waals radius of oxygen (2.80 Å)[22,23] and probably represents a lower limit for the O---O separation in dimers of this type. Some of the steric strain in this portion of the molecule would be reduced by the insertion of a methylene unit between O(1) and N(3), since that would convert the present five-membered ring into a six-membered ring; in the Schiff base complex $[Mn(SALPS)]_2$,[10] where the analogous unit does form a six-membered ring, the O–Mn–N angle is widened to an average value of 81.4°, and in a related Mn(III) dimer with alkoxy bridges, the angle is opened to 93.66 (8)°.[24]

The Mn–O(1) bond lengths in the bridging unit are asymmetric, but the values of 2.096 (3) and 2.156 (4) Å are in the range expected for a binuclear manganese(II) complex.[28] As anticipated, these bond lengths are about 0.20 Å longer than those observed in aryloxy- and alkoxo-bridged binuclear manganese(III) complexes[9,24,25] and approximately 0.30 Å longer than those in mixed-valence Mn(III)/Mn(IV) systems.[3,4,6,8,26] The bridging Mn_2O_2 unit is rigorously planar, with a Mn–O(1)–Mn′ angle of 99.9 (1)°. This value is similar to that[9] of 99.8 (1)° in the phenoxo-bridged Mn(III) dimer $[Mn(sal)py]_2^{2-}$, larger than those in alkoxo-bridged Mn(III) dimers,[24,25] and slightly smaller than those of 100.5 (2) and 101.3 (1)° in the Mn(II) dimers $[Mn_2Cl_4(O\text{-}C_6H_4CH_3)_2]^{2-}$ and $[Mn(SALPS)]_2$, respectively.[10,11]

The THF ligand is tightly bound to the metal, and the Mn–O(1s) bond length is 2.300 (4) Å. This distance can be compared to those in a variety of recent reports, in which the M–O bond length ranges from 2.124 to 2.380 Å.[27-31]

The geometry of the perchlorate anion is close to that of a regular tetrahedron, although one angle appears to deviate from the ideal value by more than 6σ. The Cl–O bond lengths fall in the range 1.328 (7)–1.361 (5) Å, with an average length of 1.341 (14) Å, consistent with earlier observations.[32]

(B) Spectroscopic Properties. The room-temperature EPR spectrum of the solid complex **1** is the same as that obtained in a frozen CH_3CN solution at 77 K. Only a broad band is seen, which is centered at $g = 1.910$. The signal is evidently broadened as a result of the antiferromagnetic coupling (vide infra). At liquid-helium temperature, the spectrum remains very broad although some structure is observable.

The electronic spectrum shows only the ligand π–π^* transitions between 200 and 300 nm. One band at 215 nm ($\epsilon = 4.63 \times 10^4$ M^{-1} cm^{-1}) corresponds to the pyrazole π–π^* transition, and the other at 290 nm ($\epsilon = 8.73 \times 10^3$ M^{-1} cm^{-1}) is assigned to the benzene π–π^* absorption.

(C) Magnetic Properties. No maximum in the susceptibility data is observed in the temperature range 1.5–300 K. The plot of effective magnetic moment as a function of temperature, however, shows a gentle decrease from the room-temperature value of 5.83 μ_B (very close to the spin-only value of 5.92 μ_B for a high-spin d^5 ion) to 5.20 μ_B at 22 K. At lower temperatures, μ_{eff} declines rapidly to a value of 2.3 μ_B at 1.5 K. This behavior clearly indicates some antiferromagnetic interaction between two high-spin d^5 metal ions. The temperature at which the magnetic susceptibility for such a complex should maximize is given by the expression

$$-2J = 0.241(T_{max})$$

where $2J$ is defined by the simple Van Vleck Hamiltonian

$$\mathcal{H} = -2JS_1S_2$$

and the energies of the triplet, quintet, septet, nonet, and undecet are $-2J$, $-6J$, $-12J$, $-20J$, and $-30J$, respectively. As a result, the observation that T_{max} is less than 1.5 K leads to the conclusion that $-2J$ is smaller than 0.36 cm^{-1}.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (D.J.H.), and to the National Science Foundation (Grant No. CHE-8317080 to T.N.S.) for support of this research. We are very grateful to Dr. Erik Pedersen for his assistance with the magnetic measurements.

Registry No. **1**, 120206-24-8.

Supplementary Material Available: Tables SI and SII, listing hydrogen atom positions and thermal parameters (2 pages); a table of observed and calculated structure amplitudes (12 pages). Ordering information is given on any current masthead page.

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Kinetic Study of the Rhodium(I)-Catalyzed Decarbonylation of Phenylacetyl Chloride

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Received August 22, 1988

We have been engaged in investigations of the mechanisms of decarbonylations of acid chlorides catalyzed by Rh(I) complexes.[1] We have established that the product-forming step is the rate-determining step in these decarbonylation reactions and that the rate of the formation of decarbonylation products depends greatly on the structure of the acid chloride.[2,3] As part of our investigation

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[1] For a recent review of this decarbonylation chemistry, see: Doughty, D. H.; Pignolet, L. H. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 343–375.

[2] (a) Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478–1485. (b) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *Ibid.* **1981**, *103*, 1847–1849.

[3] (a) Kampmeier, J. A.; Mahalingam, S. *Organometallics* **1984**, *3*, 489–491. (b) Kampmeier, J. A.; Mahalingam, S.; Liu, T.-Z. *Ibid.* **1986**, *5*, 823–825.

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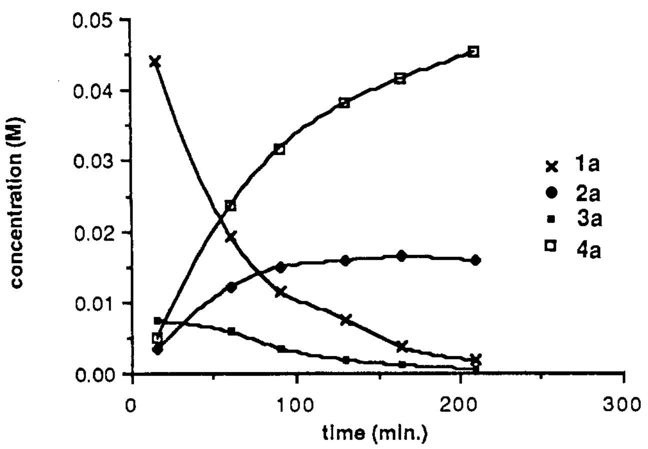


Figure 1. Concentration vs time plots for **1a**, **2a**, **3a**, and **4a** (10 °C).

of the mechanism of RCl formation[4–6] from this decarbonylation reaction, we did a kinetic study on the decarbonylation reactions of phenylacetyl chloride. We clarified the reaction sequence in which the intermediate complexes formed and equilibrated. We determined rate constant k_4, enthalpy of activation ΔH_4^{*}, and entropy of activation ΔS_4^{*} for the reductive elimination step in which decarbonylation product benzyl chloride is formed. This reaction sequence and its free energy profile give us a better understanding of this decarbonylation system.[7]

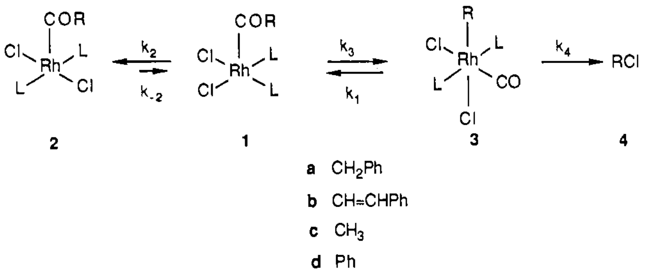
Experimental Section

Phenylacetyl chloride, $PhCH_2COCl$ (Aldrich), was freshly distilled before use. $CDCl_3$ (Aldrich) was distilled under nitrogen from P_2O_5. $RhCl(PPh_3)_3$ was prepared according to the literature procedure.[8]

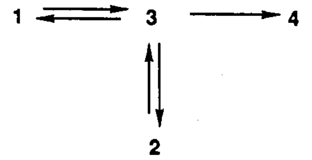
^1H NMR spectra were recorded on a General Electric QE-300 NMR spectrometer; chemical shifts are reported in ppm downfield from tetramethylsilane.

$PhCH_2COCl$ reacts with $RhCl(PPh_3)_3$ rapidly to form cis-acyl complex **1a** even at −40 °C. When the temperature is raised, **1a** isomerizes to trans-acyl complex **2a** and benzyl complex **3a**, and the decarbonylation product benzyl chloride **4a** is formed. **1a**, **2a**, and **3a** have been established previously as intermediates in decarbonylation reactions and characterized by IR and ^1H and ^{31}P NMR spectroscopy.[9,10] In the temperature range of −10 to +10 °C, changes in concentrations of **1a**, **2a**, **3a**, and **4a** can be conveniently followed by ^1H NMR spectroscopy. Chemical shifts of methylene protons (in ppm): **1a**, 5.34 (s); **2a**, 4.16 (s); **3a**, 3.83 (t of d, J = 5.1, 3.2, Hz); **4a**, 4.58 (s). In a typical experiment, $PhCH_2COCl$ (19.1 mg, 0.128 mmol) and $RhCl(PPh_3)_3$ (58.1 mg, 0.063 mmol) were weighed into a NMR tube; 1.0 mL of $CDCl_3$ was added at −40 °C. $PhCH_2COCl$ was used in excess to ensure its fast and complete reaction with $RhCl(PPh_3)_3$. The sample was kept at −40 °C for several hours until the formation of cis-acyl complex **1a** was complete, as judged by ^1H NMR spectroscopy. The sample was placed in the NMR spectrometer probe where temperature was set at 10.0 ± 0.1 °C, and ^1H NMR spectra were collected at regular time intervals. The concentration vs time plot is presented in Figure 1. Similar experiments were also carried out at 5.0, 0.0, −5.0, and −10.0 °C.[11]

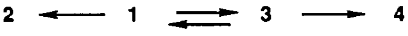
Scheme I



Scheme II



Scheme III



Scheme IV

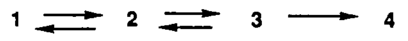


Table I. Reaction Rate Constants

T, °C	10^4k_4, s^{-1}	10^4k_2, s^{-1}	T, °C	10^4k_4, s^{-1}	10^4k_2, s^{-1}
10.0	9.8	0.99	−5.0	1.7	0.11
5.0	5.9	0.49	−10.0	0.95	0.060
0.0	3.0	0.21			

Rate constants were obtained by computer iteration on VAX-8600 computers using iteration subroutine ZXMIN from IMSL (International Mathematical and Statistical Library).[12] Computer programs were tested against a known system.[13]

Results and Discussion

$PhCH_2COCl$ reacts with $RhCl(PPh_3)_3$ to form cis-acyl complex **1a** even at −40 °C. **1a** subsequently isomerizes to trans-acyl complex **2a** and benzyl complex **3a**, and the decarbonylation product benzyl chloride **4a** is formed. From concentration–time data (Figure 1), we have the following observations:

(1) The concentration of cis-acyl complex **1a** decreases rapidly with concurrent buildup of trans-acyl complex **2a** and benzyl chloride **4a**. (2) The concentration of benzyl complex **3a** first builds up and then decreases, and it maintains a constant ratio with the concentration of **1a** after a short period of time. The ratio (**3a**/**1a**) is (1/3.3) at 10.0 °C. (3) The rate of formation of benzyl chloride is not proportional to the concentration of trans-acyl complex. From Figure 1 one can see that benzyl chloride is formed at a greater rate (the derivative of the concentration curve of **4a**) at earlier stages of reaction when there is less **2a** and that the formation of benzyl chloride becomes slower as **2a** builds up. Therefore, trans-acyl complex cannot be an intermediate leading to the formation of benzyl chloride. Instead, formation of **2a** slows the formation of benzyl chloride. (4) At longer reaction time, **1a** and **3a** cannot be observed; trans-acyl complex slowly disappears, and finally benzyl chloride is the only product. Thus, the formation of **2a** is reversible and the back reaction of **2a** is very slow.

The above observations can be summarized by either Scheme I or Scheme II. Earlier studies on the decarbonylation of cin-

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(4) Reductive eliminations of carbon–chlorine (and carbon–halogen in general) have not been carefully examined. See: Yamamoto, A. *Organotransition Metal* Chemistry; Wiley: New York, 1986; p 240.

(5) For studies on carbon–hydrogen reductive eliminations, see: (a) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221–226. (b) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834. (c) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838–840.

(6) For studies on carbon-carbon reductive eliminations, see: (a) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182–4186. (b) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892–1897.

(7) Part of this work was reported earlier: Kampmeier, J. A.; Liu, T.-Z. *Abstracts of Papers*, 17th Northeast Regional Meeting of the American Chemical Society, Rochester, NY; American Chemical Society: Washington, DC, Nov 1987; Abstract 226.

(8) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711–1732.

(9) (a) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508–1514. (b) Egglestone, D. L.; Baird, M. C.; Lock, C. J. L.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576–1582.

(10) (a) Harris, S. H. Ph.D. Thesis, University of Rochester, 1979. (b) Philip, J. B., Jr. Ph.D. Thesis, University of Rochester, 1980.

(11) The reaction system contains 1 equiv of free PPh_3 liberated from the catalyst. It has been shown[9a,10b] that PPh_3 does not affect the rate of decomposition of **1a** and the rate of the formation of **4a**. The independence of the rate of reductive elimination from free PPh_3 has also been observed in other systems.[5b]

(12) "IMSL User's Manual, Edition 9.2"; IMSL: Houston, TX, 1984.

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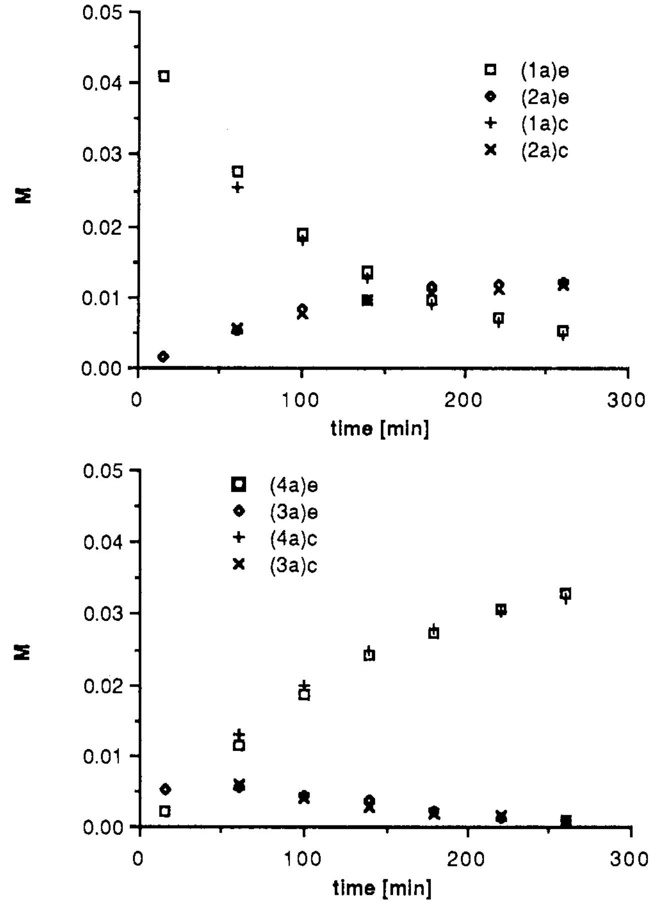

Figure 2. Calculated vs experimental concentration changes (5 °C).

namoyl chloride showed that the cinnamoyl complexes **1b** and **2b** are formed rapidly, whereas the formation of styryl complex **3b** at the expense of **1b** and **2b** is much slower.[10a] Scheme I can explain this sequence of events if $k_2 \gg k_3$ and **3b** is thermodynamically more stable. Scheme II cannot explain this sequence. Thus, Scheme II is ruled out.

We have obtained exact solutions (equations to calculate concentrations of **1a**, **2a**, **3a**, and **4a** at a given time) to the reaction system in Scheme I, using standard matrix techniques.[14,15] With these equations, one should be able to find rate constants by computer iteration. The system can be simplified into Scheme III because the reverse reaction of **2a** is so slow, especially in the early stages of reaction when concentration of **2a** is low. This general system has been thoroughly analyzed by others with both exact and approximate solutions.[13]

Thus, we are able to analyze our kinetic data and find rate constants by computer iteration. Approximate rate constants were estimated by using approximate solutions to Scheme III; these estimates were then used as starting points in the iteration. Using rate constants obtained from iteration, we can reproduce experimental concentration–time data. Figure 2 presents calculated vs experimental concentration changes at 5 °C. Rate constants of interest are presented in Table I Eyring plots yield the following activation parameters: $\Delta H_2{}^{*} = 20.4 \pm 0.9$ kcal/mol, $\Delta S_2{}^{*} = -4.8 \pm 3.3$ eu ($r = 0.997$); $\Delta H_4{}^{*} = 17.0 \pm 0.4$ kcal/mol, $\Delta S_4{}^{*} = -12.2 \pm 1.6$ eu ($r = 0.999$).

To discuss these results, we have the following comments:

(1) Decarbonylation reactions take place as described in Scheme I, contrary to a previous literature report (Scheme IV).[9b] This earlier report was based on observations on decarbonylation reactions of acetyl chloride. In ^{31}P NMR spectra, the first most concentrated complex was acetyl complex **1c**, followed by the corresponding acetyl complex **2c** and methyl complex **3c**. At longer reaction time, **1c** totally disappeared, and **2c** and **3c** had a ratio of about 3. Scheme I can easily accommodate these observations if the equilibrium constant between **2c** and **1c** is greater than that of **3c** and **1c** and both **2c** and **3c** are thermodynamically more stable than **1c** (which is indeed the case; vide infra). Scheme I also solves the puzzle that there are two phases in the formation of benzyl chloride from decomposition of **1a**:[10b] the first phase is a very rapid production of benzyl chloride in the early stages of the decomposition of **1a**, and the second phase is a much slower production of benzyl chloride when **1a** disappears and **2a** builds up. With Scheme I, we now understand these observations. In the first phase, when the concentration of **1a** is high, there is more **3a** (through fast equilibration from **1a**) so the formation of benzyl chloride is rapid. In the second phase, almost all rhodium(III) complex is in the form of **2a**, which slowly isomerizes back to **1a** and **3a**; consequently, the formation of benzyl chloride is much slower. More generally, the above analysis demonstrates the risk of basing conclusions on a few qualitative observations on a complex system. For example, **2a** is qualitatively the most concentrated intermediate complex in the reaction system following the decomposition of **1a**. This observation might conspire with the trans orientation of phosphines in **2a** and **3a** to make Scheme IV seem very attractive.[9b]

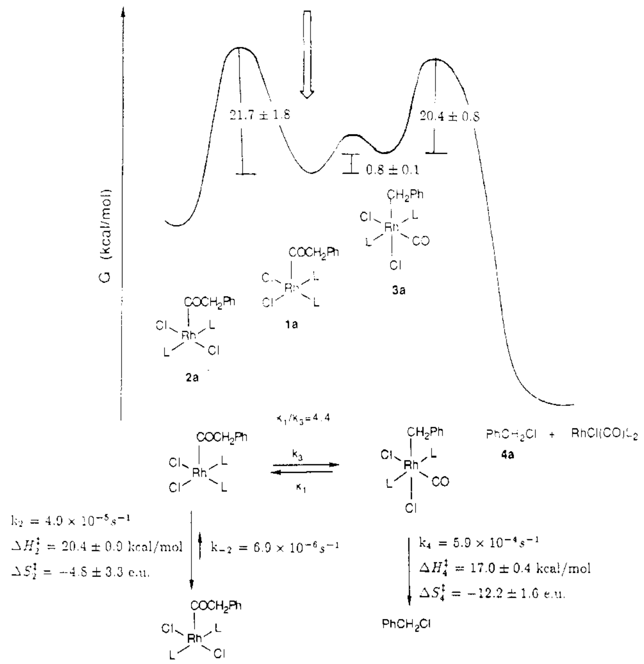

Figure 3. Free energy profile (5 °C).

(2) The equilibrium between **1a** and **3a** is much faster than that of **1a** and **2a**; i.e., benzyl migration is much faster than ligand rearrangement. However, the relative rates depend on acid chloride structure. For example, for the cinnamoyl complex **1b**, the migration is apparently slower than ligand rearrangement.[10a] The equilibrium **1a** $\rightleftharpoons$ **3a** implies that the configuration of phosphine ligands changes from mutually cis to trans in the benzyl migration step. This phenomenon has also been observed by others.[16] It neatly explains two literature reports that the acetyl and benzoyl complexes **1c** and **1d** isomerize rapidly at room temperature to the corresponding methyl and phenyl complexes **3c** and **3d**,[9] while their dppp counterparts (L_2 = dppp in **1c** and **1d**) are stable even at high temperatures.[17]

(3) A free energy profile for the decarbonylation of phenylacetyl chloride is presented in Figure 3. The trans-acyl complex **2a** is

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(14) Liu, T.-Z. Ph.D. Thesis, University of Rochester, 1989.

(15) Ritchie, C. D. *Physical Organic Chemistry, The Fundamental Concepts*; Marcel Dekker: New York, 1975; pp 7–30.

(16) (a) Bennett, M. A.; Jeffery, J. C. *Inorg. Chem.* **1980**, *19*, 3763–3767. (b) Empsall, H. D.; Hyde, E. M.; Jones, C. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1980–1985.

(17) (a) Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71–76. (b) McGuiggan, M. F.; Doughty, D. H.; Pignolet, L. H. *Ibid.* **1980**, *185*, 241–249.

thermodynamically most stable among all the equilibrating organorhodium(III) complexes. The formation of **2a**, therefore, slows the rate of the formation of benzyl chloride. In the general case, the acid chloride structure determines the relative stabilities of **1**–**3**. Thus, **2** is the most stable complex when R = benzyl or methyl (or alkyl in general),[17a] whereas **3** is the most stable complex when R = Ph, PhCH=CH, or CH_2Cl.[9,10a,17a] The effect of acid chloride structure on relative stabilities of these organorhodium(III) complexes and the barriers between them are small, however, compared to the effect of acid chloride structure on the barrier to the formation of decarbonylation products (alkyl or aryl chloride and olefin). For example, labeled acid chlorides $R^{13}COCl$ are formed from reactions of RCOCl (acetyl, butanoyl, cinnamoyl, benzoyl, and phenylacetyl chlorides, among others) with $RhCl(CO)(PPh_3)_2$ in the presence of ^{13}CO; decarbonylation products are not formed in significant amounts in competition with the labeling except for benzyl chloride.[3] The labeling of the acid chlorides RCOCl involves an excursion through the equilibrating organorhodium(III) complexes, but only benzyl substitution greatly reduces the barrier to the formation of decarbonylation product.

(4) Kinetic studies of reductive eliminations of *p*-chlorobenzyl chloride and methyl chloride from corresponding Rh(III) complexes have been reported.[9a,18] In general, these kinetic studies were carried out by monitoring the first-order disappearance of the corresponding Rh(III) complex without analyzing for the product *p*-chlorobenzyl chloride or methyl chloride. As we have just discussed, this decarbonylation reaction is a complex system of a set of equilibrating organorhodium(III) complexes. It needs more rigorous treatment than simple first-order approximations.

In summary, this kinetic study of the decarbonylation of phenylacetyl chloride gives us a clear picture of this decarbonylation system. We now have a better understanding of the various experimental observations on the general decarbonylation reaction. To establish mechanisms for this product formation step, we need more information from experiments other than kinetic measurements. We are continuing to investigate full details in the product formation step in decarbonylation reactions.

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(18) Weinberg, E. L.; Baird, M. C. *J. Organomet. Chem.* **1979**, *179*, C61–C64.

Contribution from the School of Chemical Sciences,
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(μ-4,4′-Dimethyl-2,2′-bipyridine)bis(pentacarbonylchromium): Isolation and Reactivity of a Novel Complex Relevant to Group 6 Metal Tetracarbonyl Chelate Formation

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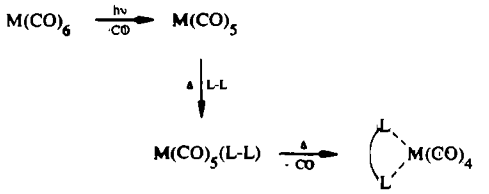
and Conor Long*

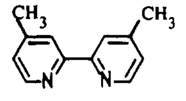
Received November 2, 1988

The photochemical formation of chelate $M(CO)_4(L\text{-}L)$ complexes from group 6 metal hexacarbonyls and bidentate ligands (L-L), such as 2,2′-bipyridine derivatives and other diimine type ligands, is a matter of current mechanistic investigations.[2-8] The formation of the chelate product is thought to occur subsequent to the photochemical generation of the $M(CO)_5(L\text{-}L)$ species, in which the ligand L-L is coordinated in a monodentate fashion (eq 1). Spectral characterization of $M(CO)_5(L\text{-}L)$ and kinetic data for its conversion into $M(CO)_4(L\text{-}L)$ have been obtained from FTIR[2] and UV–vis photodiode-array spectroscopy[3-7] and from laser flash-photolysis experiments.[8] However, it should be noted that in these experiments the $M(CO)_5(L\text{-}L)$ species were generated in situ in the presence of a large excess of L-L, which may influence the kinetics of the system. The IR spectroscopic identification of $M(CO)_5(L\text{-}L)$ was based on the similarity of the CO stretching vibrational pattern to that of the model compounds $M(CO)_5$(2-phenylpyridine).[2] Recently, several monodentate $M(CO)_5(L\text{-}L)$ complexes with L-L ligands such as 1,8-diazabiphenylene,[6] dipyridylalkane,[9] and ethylenediamine[10] have been isolated. However, these ligands do not have the same, if any, propensity to form chelate complexes as do 2,2′-bipyridines and other diimine type derivatives.



(1)

Therefore, we attempted the synthesis and isolation of a monodentately coordinated $Cr(CO)_5(L\text{-}L)$ complex, utilizing 4,4′-dimethyl-2,2′-bipyridine (dmbpy) as the L-L ligand and pentacarbonyl(η^2-(*Z*)-cyclooctene)chromium[11] as a source of the $Cr(CO)_5$ unit. The principal aim of this investigation was to monitor the kinetics of $Cr(CO)_4(L\text{-}L)$ formation in the absence of free bipyridine ligand. However, unexpectedly the product we isolated contained, not one, but two $Cr(CO)_5$ units per dmbpy ligand.



dmbpy

Experimental Section

Equipment and Materials. All solvents used in the syntheses and spectroscopic measurements were purified and deoxygenated by standard techniques.[12] Hexacarbonylchromium and 4,4′-dimethyl-2,2′-bipyridine were purchased from Strem Chemicals and Aldrich, respectively, and used as received. $Cr(CO)_5(\eta^2$-(*Z*)-cyclooctene)[11] and $Cr(CO)_4$(dmbpy)[5] were prepared according to the published procedures. Infrared spectra, with band positions accurate to ±3 cm^{-1}, were recorded on a Perkin-Elmer 983G instrument in nitrogen-purged solutions, using a cell with sodium chloride windows and $d = 0.1$ mm. UV–vis spectra, with ±2-nm wavelength accuracy, were obtained by means of a Hewlett-Packard 8452A diode-array spectrophotometer fitted with a ChemStation data station. Elemental analyses were conducted by the Microanalytical Laboratory, University College, Dublin.

Acquisition and Treatment of UV–Vis Spectroscopic Data. Solutions for recording UV–vis spectra were prepared by placing a sample of the solid complex **1** in a quartz cuvette ($d = 1$ cm) attached to a bulb containing the solvent. The solvent was degassed by three freeze–pump–thaw cycles and transferred in vacuo to the cuvette. The initial spectrum was obtained as soon as the solid had dissolved, usually within 1 min after adding the solvent. Each spectrum, which took 0.1 s to acquire, was measured five times. This allowed the absorbance to be determined to ±0.001 absorbance units. When the grow-in of the band of **2** at 518 nm was monitored, the actual monitoring wavelength was 510 nm, but the absorbance at 690 nm was subtracted from the absorbance at 510 nm in order to reduce the effect of light scattering and lamp intensity variations in the single-beam instrument. Kinetic parameters

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