Table I. Calculated Equilibrium Percent Decomposition (P_{tot} = 1 mmHg[a]) for $VCl_4(g) \rightarrow VCl_3(s) + {}^1/_2Cl_2(g)$

Temp, °C	This work	FRM[1]
120	23	
140	6	
160	2	0.1
180	0.5	0.07
200	0.1	

[a] If P_{tot} = 0.1 mmHg, the middle column entries become 3, 0.7, 0.2, 0.05, and 0.01%, respectively.

$+ C/T^2$. The results of these calculations are summarized in Table I.

It is seen that the correct thermodynamic data are much more conducive to a traditional interpretation of the reaction in terms of thermodynamics. The older data[2] are immediately suspect as they lead to a ΔH of −14 kcal for the reaction rather than our value of −25 or −26 kcal.[3]

Presumably the virtue of carrying out this or other reactions in an electrical discharge is that chemical bonds are broken, and hence activation energies are readily supplied, by a nonthermal process in an extremely complex system with a number of nonequilibrated degrees of freedom; yet with the great number of collisions occurring as the reactive species move toward the wall one expects rather rapid thermalization to take place at these pressures.

We have checked whether or not other possible reaction products, for which good thermodynamic data are available, might be present at equilibrium in more than trivial amounts by means of the computer programs of Gordon and McBride.[6-9] The other compounds considered were V(s), $VCl_2(s)$, $VCl_4(l)$, V(g), and Cl(g). At complete heterogeneous phase and chemical equilibria at these temperatures and pressures, the three condensed-phase substances had mole fractions identically zero while V(g) and Cl(g) had completely negligible mole fraction.

It would have been appealing to examine the equilibrium concentrations of VCl(s), VCl(g), $VCl_2(g)$, and $VCl_3(g)$ except that the appropriate thermodynamic data could not be located in the literature, in contrast to results for the corresponding chlorides of Ti[8,10] and Cr.[10]

We rationalize this omission as follows. Since these compounds are unstable enough to thus far avoid having their thermodynamic properties determined, they should have chemical potentials at least as high as those of other related compounds whose properties have been determined and which themselves turn out to be present at vanishingly small concentrations.

Acknowledgment. We are grateful to G. R. Eaton for bringing the work of FRM to our attention.

Registry No. VCl_4, 7632-51-1.

References and Notes

(1) B. Fisa, J. F. Revol, and R. H. Marchessault, *Inorg. Chem.*, **15**, 2931 (1976).
(2) J. H. Simons and M. G. Powell, *J. Am. Chem. Soc.*, **67**, 75 (1945).
(3) D. D. Wagman et al., *Natl. Bur. Stand.* (*U.S.*), **No. 270-5**, 3 (1971).
(4) K. K. Kelley, *U. S. Bur. Mines, Bull.*, **No. 584**, 56, 203–204 (1960).
(5) J. A. Creighton, J. H. S. Green, and W. Kynaston, *J. Chem. Soc. A*, 208 (1966).
(6) S. Gordon and B. J. McBride, Report NASA SP-273, National Technical Information Service, Springfield, Va., **1971**.
(7) A. L. Spinella, D. H. Yean, and J. R. Riter, Jr., *Metall. Trans.*, **4**, 2002 (1973).
(8) D. H. Yean and J. R. Riter, Jr., *Metall. Trans.*, **5**, 2473 (1974).
(9) A. R. Chughtai, H. M. Harris, and J. R. Riter, Jr., *Metall. Trans.*, **8B**, 507 (1977).
(10) A. R. Chughtai, H. M. Harris, and J. R. Riter, Jr., *Metall. Trans.*, **9B**, in press.

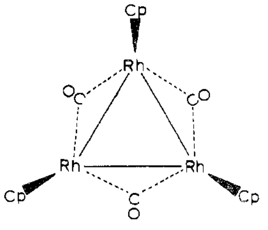
Contribution from the Department of Chemistry,
University of Illinois, Urbana, Illinois 61801

Carbonyl Ligand Mobility in the C_s Isomer of $Cp_3Rh_3(CO)_3$

R. Joe Lawson and John R. Shapley*

Received August 29, 1977

Two crystalline compounds, isolated after extended photolysis of $CpRh(CO)_2$ (Cp = η^5-C_5H_5), were characterized by x-ray diffraction as isomeric forms (**1** and **2**) of $Cp_3Rh_3(CO)_3$.[1-3] We[4] recently reported ^{13}C NMR spectra showing that the C_{3v} structure of **1** is maintained in solution and that the carbonyl ligands scramble over the Rh_3 triangle. We predicted that the carbonyls in C_s structure **2** also would scramble, without interconversion of **2** with **1**. At that time, a sample of isomer **2** was not available, but we have since developed a good procedure for preparing **2** and therefore have attempted to determine its solution structure and carbonyl ligand mobility.



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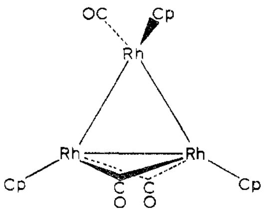

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Experimental Section

C_{3v}-$Cp_3Rh_3(CO)_3$ was prepared as previously described.[4] About 50% ^{13}CO-enriched $CpRh(CO)_2$ was used to prepare samples for ^{13}C NMR. Infrared spectra were recorded on a Perkin-Elmer 467 or Beckman IR-12 spectrophotometer and calibrated with polystyrene. ^1H NMR spectra were recorded on a Varian HA-100 instrument (100 MHz). ^{13}C NMR spectra were obtained on a Varian XL-100 (25.16 MHz) spectrometer with solutions containing ~0.015 M $Cr(acac)_3$. The solvents used were CD_2Cl_2/CH_2Cl_2, $CD_2Cl_2/CHFCl_2$, or $C_2H_3Cl/CHFCl_2$ (external ^{19}F lock), depending on the temperature range. Chemical shifts were measured relative to CH_2Cl_2 = 54.6 ppm downfield from Me_4Si. Field-desorption mass spectra were obtained on a Varian 731 mass spectrometer by Mr. J. C. Cook, Jr. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences. A medium-pressure 450-W mercury lamp (Hanovia) and a quartz apparatus (Ace Glass) were used for photolysis.

Preparation of C_s-$Cp_3Rh_3(CO)_3 \cdot {}^1/_2C_6H_{12}$. A solution of C_{3v}-$Cp_3Rh_3(CO)_3 \cdot {}^1/_2CH_2Cl_2$ (93 mg, 0.15 mmol) in 300 mL of benzene was deoxygenated by bubbling through a stream of N_2 for 15 min and then photolyzed for 4 h under a continuous N_2 flush. The solvent was removed on a rotary evaporator and the residue extracted with cyclohexane until the extracts were no longer green. The cyclohexane-insoluble residue was largely the C_{3v} isomer. The cyclohexane solution was taken to dryness, keeping the temperature below 40 °C. The residue was washed with pentane (3 × 5 mL) and vacuum dried. Yield: 70 mg, 0.11 mmol, 75%. Anal. Calcd for $C_{21}H_{21}O_3Rh_3$: C, 40.02; H, 3.36. Found: C, 40.19; H, 3.44. Mass spectrum (field desorption): *m/e* 588, M^+. ^1H NMR ($CDCl_3$; +25 and −50 °C): τ 4.48 (s, br), η^5-C_5H_5. IR(ν_{CO}) (cm^{-1}): 1973 (s), 1967 (s), 1851 (w), 1797 (m), 1748 (s) in KBr (lit.[2] 1973 (vs), 1827 (m), 1794 (m), 1744 (vs)); 1975 (m), 1827 (w), 1778 (m) in C_6H_{12}; 1961 (s), 1809 (w), 1761 (s) in CH_3CN; similar three-band spectra in CH_2Cl_2 and THF.

Results

Direct UV photolysis of a deoxygenated benzene solution of C_{3v}-$Cp_3Rh_3(CO)_3$ (**1**) provides C_s-$Cp_3Rh_3(CO)_3$ (**2**) in high yield. The usual chromatographic methods cannot be used to isolate **2**, since it decomposes on polar supports, largely into **1**. However, **2** is soluble in cyclohexane (whereas **1** is not)

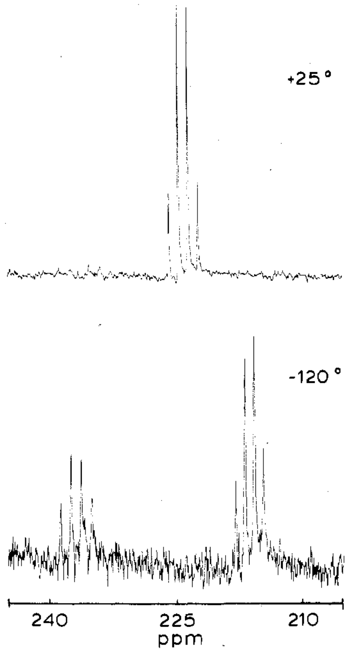


Figure 1. Carbonyl ^{13}C NMR spectra for C_s-$Cp_3Rh_3(CO)_3$ at +25 and -120 °C.

and can be isolated by selective extraction. Excessive heat must be avoided in handling solutions of **2**, since this also causes reversion to **1** (within ca. 30 min at 80 °C). Reexamination of the reaction of $CpRh(CO)_2$ with $Me_3NO{\cdot}2H_2O$,[4] from which **1** is obtained, has shown that 10–25% **2** can be isolated by extraction of the product mixture before chromatography.[5]

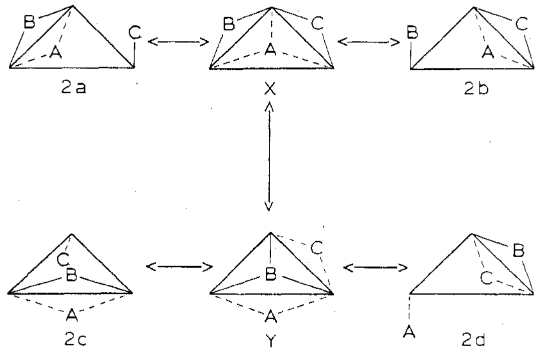
The ^{13}C NMR spectra recorded for ^{13}CO-enriched **2** at 25 °C and at -120 °C are shown in Figure 1. At 25 °C, the spectrum is a quartet at 219 ppm with J(Rh–C) = 29 Hz. As the sample temperature is lowered, the quartet collapses to a broad hump at ca. -55 °C and then separates and sharpens into the two quartets at 216 ppm (2 C, J(Rh–C) = 28 Hz) and 237 ppm (1 C, J(Rh–C) = 31 Hz) seen at -120 °C. Computer simulation of the spectrum at -55 °C provided $k \approx 5000\ s^{-1}$ and $\Delta G^{\ddagger}_{-55} \approx 8.9$ kcal/mol. Upon further cooling to -156 °C, each of these quartets collapses to a broad, featureless resonance. This obviously is not the limiting slow-exchange spectrum, but lower temperatures were not accessible.

Discussion

The infrared spectrum of **2** in solution displays the pattern of one terminal and two bridging CO stretching bands expected for the C_s solid-state structure. The same three-band pattern is observed in the various solvents examined, ranging in polarity from acetonitrile to cyclohexane, and no different bands appear. The additional bands observed for the KBr pellet are presumably due to site splitting in the solid.

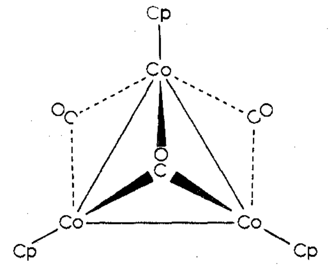
The limiting slow-exchange carbonyl ^{13}C NMR spectrum expected for C_s structure **2** would be a doublet due to the terminal carbonyl at about 192 ppm with J(Rh–C) ~83 Hz and two triplets for the bridging carbonyls at about 232 ppm with J(Rh–C) ≈ 47 Hz (cf. $CpRh(CO)_2$,[6] 193 ppm, 83 Hz; $Cp_2Rh_2(CO)_3$,[7] 192 ppm, 83 Hz; 232 ppm, 45 Hz; C_{3v}-$Cp_3Rh_3(CO)_3$,[4] 232 ppm, 49 Hz). Straightforward application of the pairwise bridge opening–closing type of mechanism proposed by Cotton[8] for carbonyl scrambling in $Fe_3(CO)_{12}$ led us to predict that the fast-exchange spectrum observed for **2** would be two quartets in a 2:1 ratio.[4] This prediction is consistent with the spectrum observed at -120 °C. The smaller quartet appears in the bridging region, but with an appropriately reduced average coupling constant ($J_{calcd} \approx 31$ Hz, J_{obsd} 31 Hz). The larger quartet appears about halfway between the expected bridging and terminal chemical shifts, also with a reasonable coupling constant ($J_{calcd} \approx 29$ Hz, J_{obsd} 28 Hz). The broadening observed at -156 °C indicates slowing of the scrambling process, which allows a rough estimate of $\Delta G^{\ddagger}_{-156} \approx 4.8$ kcal/mol (T_c = 117 K, $\Delta\nu$ = 1000 Hz). A comparable value of <5 kcal/mol was estimated[9] for the scrambling process in $Fe_3(CO)_{12}$, but data reported by Mays and co-workers[10] lead to an estimate of $\Delta G^{\ddagger}_{-25} \approx 10.6$ kcal/mol ($T_c \approx 248$ K, $\Delta\nu \approx 1080$ Hz) for $Cp_2Rh_2Fe(CO)_6$.

Scheme I



The fact that all three carbonyls become equilibrated, as evidenced by the single quartet at 25 °C, requires a mechanism allowing the carbonyls to visit both faces of the Rh_3 triangle. Localized rotation of the terminal CO and the Cp at the unique rhodium atom coupled with the bridge–terminal exchange discussed previously would accomplish the necessary result. However, if localized rotation is relatively facile (NMR time scale) and scrambling in both **1** and **2** is postulated to proceed via all-terminal intermediates, then it is difficult to see why **2** would not be converted rapidly at room temperature into **1**.

Recently published observations[11] on the congeneric compound $Cp_3Co_3(CO)_3$ form the basis for an alternative explanation. The crystal structure **3** determined for this species is different from either **1** or **2** and involves one face-bridging carbonyl and two edge-semibridging carbonyls. However, from solution IR data Cotton and Jamerson proposed that structure **3** equilibrates with an isomer of structure analogous to **2**. In polar solvents both structures apparently are present, but the spectrum observed in benzene (1959 (s), 1811 (s), 1753 (m) cm^{-1}) suggests the sole presence of the C_s-$Cp_3Co_3(CO)_3$ isomer. We have found no IR evidence for a Rh_3 isomer analogous to **3**, but such a structure may be only slightly (>2 kcal/mol) higher in energy than **2**. Scheme I depicts two rearrangement pathways, which involve intermediates analogous to **3** (X and Y) and serve to rationalize the dynamic behavior observed for **2**. A combination of edge–face and terminal–edge carbonyl motions interconverts **2** with X, which would allow the carbonyls to move over each face of the Rh_3 triangle (e.g., **2a** ↔ X ↔ **2b**) without traversing an intermediate with all carbonyls terminal. Furthermore, the interconversion X → Y provides



3

for face-to-face carbonyl scrambling. In this rearrangement carbonyl B undergoes an edge–face movement on the top face while carbonyl A undergoes the inverse face–edge movement below, and bridging carbonyl C flips from an upper edge position to a lower one. Intermediate Y then equilibrates with the lower energy forms (**2c**, **2d**) involving a terminal carbonyl. There does not appear to be any reported precedent for the bridge-flipping motion proposed, but the overall transformation X → Y is attractive in that the synchronous movement of the three carbonyls is sterically and electronically balanced.[12,13]

Registry No. **1**, 12148-54-8; **2**, 12305-50-9; ^{13}C, 14762-74-4.

References and Notes

(1) O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, **10**, 331 (1967).
(2) E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *J. Organomet. Chem.*, **10**, P3 (1967).
(3) E. F. Paulus, *Acta Crystallogr., Sect. B*, **25**, 2206 (1969).
(4) R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc.*, **98**, 7433 (1976).
(5) The IR (ν_{CO}) spectrum of **2** is masked by the presence of **1** and of $Cp_2Rh_2(CO)_3$ in the crude reaction mixture.
(6) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974).
(7) J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 79 (1973).
(8) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974).
(9) F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).
(10) J. A. S. Howell, T. W. Matheson, and M. J. Mays, *J. Organomet. Chem.*, **88**, 363 (1975).
(11) F. A. Cotton and J. D. Jamerson, *J. Am. Chem. Soc.*, **98**, 1273 (1976).
(12) The face-bridging carbonyls in $Cp_4Rh_4(CO)_2$ visit all four faces of the Rh_4 tetrahedron: R. J. Lawson and J. R. Shapley, unpublished results. Mechanisms involving face-to-face movement via an edge-bridged state can be envisioned.

(13) This work was supported by National Science Foundation Grant CHE 75-14460.

Contribution from Ames Laboratory-DOE and
the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Synthesis and Lanthanide Complex Formation Constants of *N′*-Benzylethylenediamine-*N*,*N*,*N′*-triacetic Acid

J. H. Miller* and J. E. Powell

Received May 5, 1977

One of the major practical uses of polyaminopolycarboxylic acids is in the ion-exchange separation of yttrium and the individual lanthanides. Although several such complexants have been found useful in this regard, each has one or more shortcomings which make the search for new complexing agents one of continued interest. The low water solubility of ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA) and its lanthanide complexes necessitates the use of a retaining ion other than hydrogen.[1] *N′*-Hydroxyethylethylenediamine-*N*,*N*,*N′*-triacetic acid (HEDTA) exhibits poor selectivity in the mid-lanthanon range (Sm–Ho), a fact which may be overcome only by working at elevated temperatures.[2] The use of certain other chelating agents is discouraged by the low lability of their metal complexes, a condition which leads to undesirably high plate heights in the ion-exchange process.[3-6]

Recently, *N′*-methylethylenediamine-*N*,*N*,*N′*-triacetic acid (MEDTA) has been synthesized and studied.[7,8] Like the unsymmetrical HEDTA species, it exhibits much better solubility characteristics than EDTA. Though producing no improvement with regard to plate heights (compared to HEDTA), it does show selectivity for the middle lanthanons at room temperature.

An article on the synthesis and cursory study of other unsymmetrical *N′*-benzyl- and *N′*-alkylethylenediamine-*N*,*N*,*N′*-triacetates (alkyl: *n*-butyl, *n*-octyl, *n*-dodecyl, cyclohexyl) reported some interesting results.[9] The *N′*-benzyl derivative (BEDTA) exhibited much higher stability constants for complexes formed with both Ca^{2+} and Cu^{2+} than did the alkyl-substituted acids. Steric arguments were invoked to explain the stability behavior with Cu^{2+}, but the explanation with Ca^{2+} was not so simple. The authors suggested that greater electron release by the benzyl moiety might explain the higher stability of its complexes (though this is in contradiction to the accepted order of aryl vs. alkyl inductive effects). Also of interest were the much lower constants obtained for the cyclohexyl-substituted analogue, since the cyclohexyl group would be expected to exhibit a steric effect similar to that of the benzyl group. Purity may have been a substantial factor, since all of the acids studied were only moderately pure. Nevertheless, the unique behavior of BEDTA suggests a favorable interaction attributable to the benzyl substituent and merits further study.

The purpose of the present work was to synthesize BEDTA in better purity and to study its complexing behavior with the tervalent lanthanide sequence (wherein cationic radius is the principal variable). Evaluation of its utility in possible rare-earth separation schemes was also of interest.

Experimental Section

Synthesis of *N′*-Benzylethylenediamine-*N*,*N*,*N′*-triacetic Acid. The previously reported[9] BEDTA synthesis involved carboxymethylation of *N*-benzylethylenediamine with formaldehyde and sodium cyanide. Product recovery was accomplished tediously and inefficiently by successive recrystallizations from an alcohol–water mixture containing a large amount of sodium sulfate, as well as substantial amounts of reaction by-products such as nitrilotriacetic acid (NTA). Since NH_3 forms in the carboxymethylation step, subsequent reaction to form NTA (or incompletely carboxymethylated intermediates) could be expected. The reported melting point was 130–131 °C. The potentiometrically determined molecular weight was 336 (theoretical 324).

The present procedure was a modification of the above, utilizing an ion-exchange purification scheme which previously proved useful in the preparation of MEDTA.[7] A solution of 2 mol of *N*-benzylethylenediamine dissolved in 500 mL of water and 500 mL of *tert*-butyl alcohol was heated to the boiling point. To this were added simultaneously (and slowly) 1 L of an aqueous solution containing 397 g of NaCN and 23.2 g of NaOH and a 1-L solution of 687 mL of 37% formaldehyde in water. During addition, the mixture was heated under reflux and swept with air. After 34 h the solution had turned deep red and the evolution of NH_3 had ceased. The *tert*-butyl alcohol was then eliminated and the pH adjusted to about 1 with H_2SO_4. (*Caution* noticeable HCN was evolved.) The acid solution was then refluxed for 7 h to complete the hydrolysis of the nitrile groups.

The cooled solution was next loaded onto the first of two 2-in. diameter × 4-ft length cation-exchange columns containing H^+-form Dowex 50W-X8. The loaded system was first rinsed with water to eliminate NTA and H_2SO_4 and then eluted with 0.1 N NaOH. During elution a light-colored band formed and progressed down the column system followed by a darker band and the increasing band of sorbed Na^+. The acid eluate was collected in fourteen 800-mL fractions. All fractions were evaporated to powders which were analyzed titrimetrically. Material from samples 7–11 (found to contain crude BEDTA) were combined. To achieve a high degree of purification, the combined material was reprocessed on the cation-exchange system. The new fractions were evaporated slowly, and the BEDTA which formed was removed periodically. The more soluble impurities remained in solution. After recrystallization from water, the yield was 70 g (11%) of a white powder that melted at 176–178 °C (much higher than previously reported). Anal. Calcd for $C_{15}H_{20}N_2O_6$: C, 55.55; H, 6.18; N, 8.64. Found: C, 55.95; H, 6.25; N, 8.65. Mol wt: calcd, 324.3; found, 325.5.

Measurements. All measurements were made in a sealed vessel thermostated at 25 ± 0.05 °C under a nitrogen atomosphere. The hydrogen ion concentration was measured using a Corning Model 101 digital electrometer, adjusted with standard HNO_3 or KOH. The ionic strength was adjusted with KNO_3.

The successive protonation constants, $K_n = [H_nL]/[H_{n-1}L][H]$, were determined from pH_c measurements on a series of independently

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