Communications to the Editor

^{103}Rh NMR Evidence for Charge Separation and Fluxionality among Rhodium Atoms in Metal Clusters

Sir:

Molecular metal clusters are a distinct class of compounds of interest not only for their intrinsic novelty and structural variety[1] but also because they may be reasonable models of metal surfaces of catalysts[2] and, in fact, are themselves evidently effective at promoting homogeneous and heterogeneous reactions.[3] X-ray crystal analysis is routinely performed for solid-state structural characterization, but determination of solute structure is less straightforward because the applicable infrared and ligand (^{1}H, ^{13}C) NMR techniques provide no direct information concerning the bonding or structure of the metal atoms in the cluster skeleton. This communication reports the first successful direct observation of ^{103}Rh NMR for rhodium clusters and demonstrates that such spectra provide evidence for both *charge separation* and *rhodium atom fluxionality* in this class of molecules, as well as being characteristic of molecular structure in solution. Herein we report results of a variable-temperature ^{103}Rh NMR study of $[(C_6H_5CH_2)N(C_2H_5)_3]_2[Rh_9P(CO)_{21}]$ and $[(C_6H_5CH_2)N(C_2H_5)_3]_3[Rh_{17}S_2(CO)_{32}]$ as well as comments regarding more preliminary data obtained for other rhodium clusters.

The ^{103}Rh nuclide has spin $I = \frac{1}{2}$ and a weak and negative nuclear moment, and, despite its 100% isotopic abundance, is only 0.003% as receptive for NMR as protons. This, combined with long relaxation times with $T_1 \gg T_2$ expected from the low gyromagnetic ratio,[4] hindered all except a few double resonance INDOR NMR studies of the nuclide until the first direct FT NMR detection in simple molecules at our Michigan State laboratories.[5] A recent report[6] of a ^{13}C[^{103}Rh] INDOR study of the $[(C_2H_5)_4N]_3[Rh_7(CO)_{16}]$ cluster provided rhodium chemical shift data which are in general agreement with those found here. Current FT NMR studies were performed with a Bruker WH-180 spectrometer operating at a nominal 5.7 MHz using 10-mL deuterioacetone solutions ~0.1 m in substrate with 0.02 M Cr(acac)$_3$ added as a T_1 relaxation agent.[7]

Spectra shown in the figures are characteristic of those observed for all clusters in that narrow lines with $\Delta\nu_{1/2} < 1$ Hz are obtained. We have chosen, as our chemical shift reference for cluster studies, the narrow-line, relatively intense signal of the symmetrical $[Rh_6C(CO)_{15}]^{2-}$ anion[8] in deuterioacetone solution. To facilitate comparison with earlier double resonance work, exact ^{103}Rh resonance frequencies reported in Table I are corrected to the field strength at which SiMe$_4$ protons in CDCl$_3$ resonate at precisely 200 MHz with a deuterium internal reference lock.

Table I. Chemical Shifts of Some Rhodium Cluster Anions in Acetone-d_6 Solution

compound	$\Xi(^{103}Rh)^a$	$\delta_{^{103}Rh}$	^1J(Rh–P), Hz
$[Rh_6C(CO)_{15}]^{2-}$	6 318 248	0	
$[Rh_{17}S_2(CO)_{32}]^{3-}$	6 325 556	+1156.8 (1^b)	
	6 315 963	−361.5 (8)	
	6 310 786	−1180.9 (8)	
$[Rh_9P(CO)_{21}]^{2-}$	6 311 006	−1146.2 (1)	46
	6 312 275	−945.3 (4)	32
	6 313 352	−774.8 (4)	46

[a] Resonant frequencies in a magnetic field where SiMe$_4$ protons in CDCl$_3$ resonate at exactly 200 MHz. [b] Relative intensities.

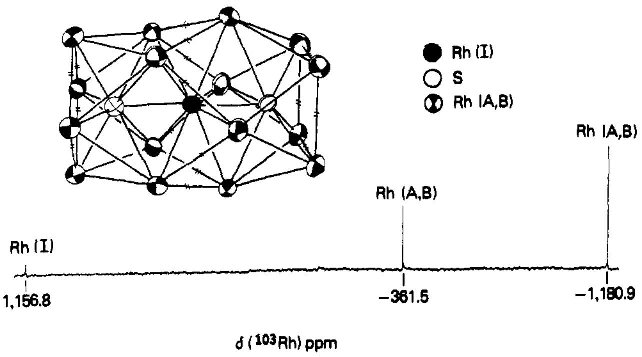


Figure 1. ^{103}Rh NMR spectrum and metal atom skeletal structure of the $[Rh_{17}S_2(CO)_{32}]^{3-}$ anion.

The solid-state structure for the $[Rh_{17}S(CO)_{32}]^{3-}$ anion whose rhodium skeleton is diagrammed in Figure 1 contains three chemically distinct rhodium species.[9] A central rhodium atom is unique, and is bonded to eight chemically identical rhodium atoms in the two inner square planes. The remaining eight equivalent skeletal rhodiums are disposed in the two outer square planes farthest from the central metal atom with the two sulfur atoms lying between the two sets of inner and outer rhodium planes. In the ^{103}Rh NMR spectrum of this cluster shown in Figure 1, we detect three resonances of relative intensity 1:8:8 in complete agreement with the crystal data. Of especial interest are the chemical shifts recorded for the three resonances at 115.68, −351.5, and −1180.9 ppm with the low-field resonance having the low relative intensity. Powdered rhodium metal on this chemical shift scale shows a broad band centered at −1093 ppm.[10] We note therefore that, in particular, the upfield planar atoms of rhodium appear to be quite metallic in character, with the lower field planar rhodium atoms bearing some positive charge. The remarkable deshielded position seen for the central rhodium atom marks it as an electropositive rhodium ion, its resonance being well downfield even of what we measured for a simple Rh(I) species such as $[Rh(CO)_2Cl_2]^-$ (349.8 ppm). Thereby, the cluster could preliminarily be viewed as a rhodium(I) disulfide centered in the midst of the 16-atom rhodium carbonyl skeleton. This interpretation receives some support from the short Rh–S bond distances measured for the central metal atom in the crystal structure.[9] Some ^{13}C NMR results[11] indicate that the metal skeleton might also show fluxionality at high temperatures, but current metal nuclide studies produced only the three-line pattern even at 90 °C.

However, temperature-dependent ^{103}Rh NMR spectra of $[(C_6H_5CH_2)N(C_2H_5)_3]_2[Rh_9P(CO)_{21}]$ exhibited in Figure 2 provide clear evidence that the rhodium skeleton of this cluster is stereochemically nonrigid. At temperatures below −80 °C, three doublets with relative intensities 1:4:4 are detected at −1146.2, −945.3, and −774.8 ppm, in agreement with the crystal structure diagrammed in the figure. When this sample is warmed to room temperature, ~23 °C, only a single doublet is measured at a chemical shift position near that of the weighted average of the three low-temperature values. The coupling constant determined at room temperature is likewise near that of the average of the −80 °C spectrum. These spectra can only be explained by invoking fluxionality of the rhodium atom skeleton of the cluster. It is not at this time possible to deduce a mechanism for this process, but instrumental im-

0002-7863/80/1502-2449$01.00/0

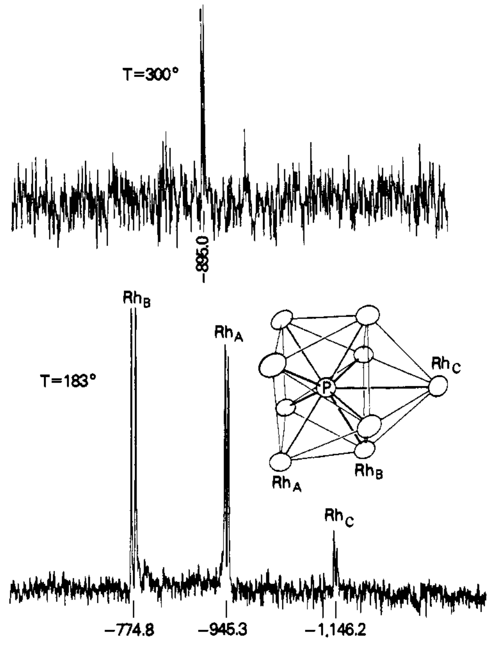


Figure 2. ^{103}Rh NMR spectra and metal atom skeletal structure of the $[Rh_9P(CO)_{21}]^{2-}$ anion.

provements now underway will hopefully make possible that research to complement earlier ^{31}P NMR work.[12]

Studies of the mechanism of exchange for the cluster anions $[Rh_7(CO)_{16}]^{3-}$, $[Rh_{12}(CO)_{30})^{2-}$, and $[Rh_{12}(CO)_{34}]^{2-}$ are also in progress. The seven-rhodium cluster, at low temperatures, is observed to give the expected three-line pattern of intensity ratio 3:1:3 at chemical shifts near those measured by Heaton et al. using $^{13}C[^{103}Rh]$ double resonance methods.[6] However, preliminary results for the two 12-atom clusters each show only two separate spectral resonances, even at very low temperatures. Those results are not consistent[13-15] with structures proposed in the literature; so we have made the 12-atom clusters and their derivatives the focus of our current efforts.

Acknowledgment. A research grant from the National Science Foundation to O.A.G. is gratefully acknowledged, Grant No. CHE 78-10241. The authors appreciate the permission of Union Carbide Corporation for the nonproprietary, collaborative ^{103}Rh NMR program.

References and Notes

(1) For reviews, see (a) P. Chini, *Inorg. Chem. Acta Rev.*, **2**, 31 (1968); (b) R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972); (c) J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.*, **44**, 43 (1975); (d) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976); (e) H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).
(2) E. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979), and references therein.
(3) A. K. Smith and J. M. Basset, *J. Mol. Catal.*, **2**, 229 (1977), and references therein.
(4) J. Kronenbitter and A. Schwenk, *J. Magn. Reson.*, **25**, 147 (1977).
(5) D. S. Gill, O. A. Gansow, F. J. Bennis, and K. C. Ott, *J. Magn. Reson.*, **35**, 459 (1979).
(6) C. Brown, B. T. Heaton, L. Longhetti, D. O. Smith, P. Chini, and S. Martinengo, *J. Organomet. Chem.*, **169**, 309 (1979).
(7) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).
(8) V. G. Albano, P. Chini, S. Martinengo, D. J. A. McCaffrey, D. Strumolo, and B. T. Heaton, *J. Am. Chem. Soc.*, **96**, 8106 (1974), and references therein.
(9) J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, **17**, 275 (1978).
(10) P. Sogo and C. D. Jeffries, *Phys. Rev.*, **98**, 1316 (1955).
(11) J. Vidal, R. C. Schoening, R. L. Pruett, and R. A. Fiato, *Inorg. Chem.*, **18**, 1821 (1979).
(12) J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Schoening, *Inorg. Chem.*, **18**, 129 (1979).
(13) V. Albano and P. L. Bellon, *J. Organomet. Chem.*, **19**, 405 (1969).
(14) P. Chini, S. Martinengo, and D. J. McCaffrey, *J. Chem. Soc., Chem. Commun.*, 310 (1974).
(15) S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, **102**, 344 (1972).
(16) Author to whom all correspondence should be addressed.

Otto A. Gansow,[16] Devinder S. Gill
Frank J. Bennis, James R. Hutchison
Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Jose L. Vidal, Richard C. Schoening
Chemicals and Plastics, Union Carbide Corporation
South Charleston, West Virginia 25303

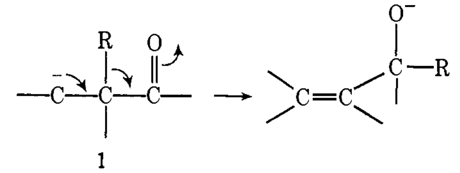
Received November 6, 1979

A Novel [1,2] Alkyl Shift in a Blocked Aromatic Anion

Sir:

Acid-catalyzed migrations of alkyl groups to electron-deficient centers are common reactions. In contrast, comparable base-catalyzed migrations are unknown, except for reactions such as benzilic acid rearrangements,[1] "acyloin rearrangements" of ketols,[2] "quasi-Favorskii" rearrangements of α-halo ketones,[3] and "semipinacolic" rearrangements of β-halo alcohols,[4] in which the migration origins are substituted with oxygen atoms.

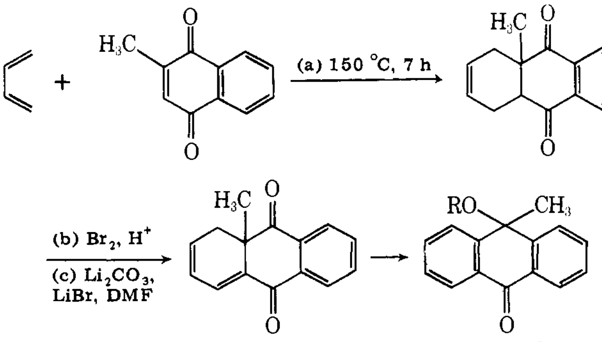
In principle, migration of an alkyl group from a non-hetero-substituted carbon atom to a carbonyl carbon might occur in an anion such as **1** (eq 1). In practice, rearrangements of such homoenolate anions, when they occur, have always been observed to proceed by cyclopropanol formation and reopening, rather than by [1,2] alkyl migrations.[5] We have now observed that reaction of diketone **2** with base results in the first observed instance of base-catalyzed migration of an alkyl group from a non-hetero-substituted carbon to an adjacent carbonyl carbon.



1

(1)

Diketone **2** was prepared in 23% overall yield as shown in eq 2.[6] In an attempt to convert **2** into its enol ether,[7] **2** was reacted with potassium *tert*-butoxide in hexamethylphosphoric triamide (HMPT) and then with methyl trifluoromethylsulfonate. However, none of the desired enol ether was formed. Instead, the major product was found to be 10-methoxy-10-methylanthrone (**3b**),[8] accompanied by smaller amounts of 10-hydroxy-10-methylanthrone (**3a**).[9] When **2** was reacted with potassium *tert*-butoxide in either HMPT or THF at −10 °C, the sole product obtained was **3a**, which could be converted into **3b** by reaction with methyl iodide in base.



(2)

2

3a, R = H
b, R = CH$_3$