

tween the two bond lengths is 0.037 Å, which is crystallographically significant ($>25\sigma$), and may be ascribed to a stronger trans influence acting on the more nearly opposed atoms P(1) and P(1)'. By assigning the difference to trans influence, we imply that for a series of similar complexes we should expect to see a positive correlation between the Ru-P bond length and the P-Ru-P angle. Table VII lists a series of Ru complexes containing two or more tertiary P atoms bonded to the metal. While a variety of effects is presumed to be contributing to the observed Ru-P distances (coordination geometry, oxidation state, nature of the trans ligand, etc.), it is nonetheless interesting to note the trend of increasing Ru-P bond length with increasing P-Ru-P angle. Included in this table are the bond lengths for Ru-P(1) and Ru-P(2) which both fit into this series according to the appropriate P-Ru-P angle.

The Ru-Cl distance of 2.549 (1) Å is considerably longer than Ru-Cl bonds in which the chloro ligand is trans to Cl (2.398 (10) Å)²¹ or P (2.421 (5) Å).⁵ Although not many structures of hydride complexes are available for systematic comparison, it is usually felt that the hydride ligand does exert a strong trans influence. Thus this factor is used to explain the ca. 0.12 Å difference in Pt-Cl distances when the trans ligand is H as opposed to Cl.²³ However, it is of interest to note that the Rh-Cl distance in RhHCl(SiCl₃)(PPh₃)₂²⁴ is only slightly longer than that observed in RhCl₃(PPhEt₂)₃²⁵ (2.387 (4) and 2.362 (3) Å, respectively). Since there is no apparent structural element in the present complex which would prevent a shorter Ru-Cl bond, the closest nonbonded contact being 2.66 Å to HC(26), we conclude that the long Ru-Cl bond is the result of the trans influence of the hydride ligand. The

implication of this long bond, that the Ru-Cl bond may be weaker than normal, derives support from the behavior of the complex as an electrolyte in nitromethane, which initially suggested the complex was five-coordinate with a chloride counterion.⁴

The Ru-H distance of 1.68 Å, as deduced from a difference Fourier synthesis, is in good agreement with the values of 1.68 Å in RuH(acetate)(PPh₃)₃,⁶ 1.7 Å in RuHCl(PPh₃)₃,⁵ and 1.67 Å in RuH(naphthyl)(dmpe)₂,²⁶ all located in a similar manner.

The internal geometry of the (+)-diop ligand is normal, with mean distances of 1.851 (9), 1.520 (7), and 1.475 (5) Å for the P-C, C-C, and C-O bonds, respectively. The geometry of the phenyl rings is as expected with mean C-C distances of 1.39 (1) Å and mean C-C-C angles of 120 (1)°. The absolute configuration at both C(2) and C(3) is *S*, which is consistent with a positive specific rotation for the ligand²⁷ and a crystal structure of an iridium complex containing (+)-diop.²⁸

A stereoview of the unit cell packing is shown in Figure 3. There are no close intermolecular contacts, with the closest distance of approach being 2.19 Å between H1C(1) at (*x*, *y*, *z*) and H1C(22) at (\bar{x} , 1 - *y*, *z*).

Acknowledgment. We thank B. R. James for supplying the crystals, the National Research Council of Canada for financial support of this work, and the University of British Columbia Computing Centre for assistance.

Registry No. RuHC(diop)₂·2CH₃C₆H₅, 75171-73-2.

Supplementary Material Available: Table III, a listing of structure factor amplitudes (85 pages). Ordering information is given on any current masthead page.

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 (24) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970).
 (25) A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 1789 (1973).

- (26) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971).
 (27) B. R. James, private communication; ref 1 and 4.
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Notes

Contribution from Union Carbide Corporation,
 South Charleston, West Virginia 25303

Rhodium Carbonyl Cluster Chemistry under High Pressure of Carbon Monoxide and Hydrogen. 2. Synthesis of [Rh₁₄(CO)₂₅]⁴⁻

José L. Vidal* and R. C. Schoening¹

Received November 5, 1979

The study of rhodium carbonyl clusters has been in process for some time in our laboratory.²⁻⁴ As a result of that work, we have observed that high-yield, readily implemented synthetic procedures for rhodium carbonyl species could be developed by using high-pressure techniques as reported for

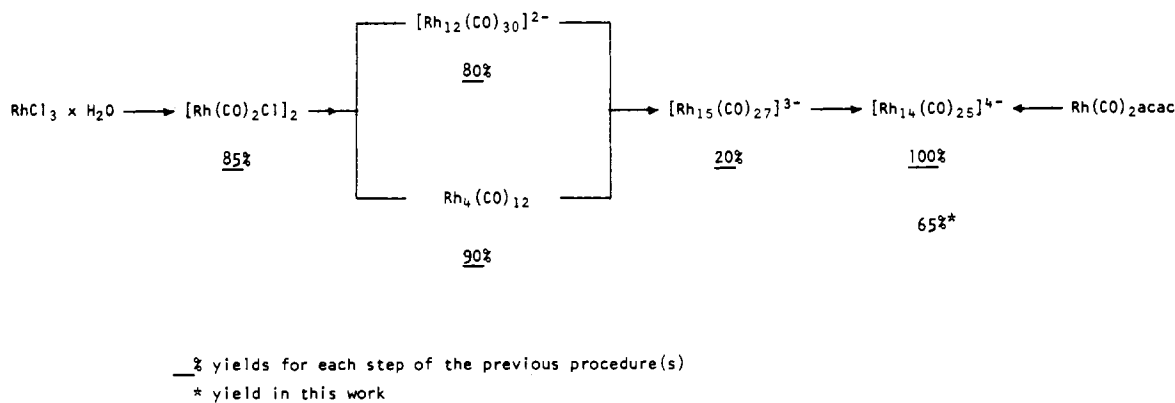
[Rh₁₇S₂(CO)₃₂]³⁻, [Rh₉E(CO)₂₁]²⁻, [Rh₁₀E(CO)₂₂]³⁻ (E = P, As), and an antimony-containing species under characterization.⁵⁻¹⁰

Transition-metal carbonyl clusters containing an unusually high number of rhodium atoms have been postulated as suitable models for the behavior of surfaces.¹¹ Specifically, the structural changes noted for [Rh₁₃(CO)₂₄H₃]²⁻, [Rh₁₅(CO)₂₇]³⁻, and [Rh₁₄(CO)₂₅]⁴⁻ have been correlated with those expected in the reconstruction of some surfaces.¹² The syn-

- (1) The structural studies were conducted by Dr. Jan Troup of Molecular Structure Corp., College Station, Texas.
 (2) E. S. Brown, U. S. Patent 3929969 (1976); E. S. Brown, W. E. Walker, and R. L. Pruett, U. S. Patents 3968136 (1976), 3878292 (1975), and 3878214 (1975).
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 (12) S. Martinengo, G. Ciani, A. Sironi, and P. Chini, *J. Am. Chem. Soc.*, **100**, 7097 (1978).

Scheme I



thesis of the latter compound, described for the first time in that work, resulted in low overall yields of ca. 17%.

The needs for selective and simple synthetic procedures for high-nuclearity rhodium carbonyl species have already been mentioned.¹³ These reasons and the requirements for relatively large amounts of salts of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ for our studies induced us to search for better methods for the preparation of this cluster. The previous successes with the application of high-pressure techniques to the synthesis of rhodium carbonyl clusters containing main-group atoms⁵⁻¹⁰ suggested extending this method to other polynuclear rhodium species. We describe now a new convenient high-yield synthesis of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ which utilizes commercially available starting rhodium carbonyl complexes and high-pressure techniques.

Results and Discussion

The inconveniences of the previously reported preparation(s) of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ originate in the intermediates required in these methods, the yields of the successive steps,^{14a} and the need for fractional precipitation methods in the isolation of some of these species^{12,14b} (Scheme I). In contrast, our procedure allows for the preparation of large amounts of salts of this anion, in high yields, without the need for the preparation of any intermediates.

We describe now the synthetic procedure used in our case. $\text{Rh}(\text{CO})_2\text{acac}$ (14.00 g, 55.1 mmol) is dissolved in 840 mL of tetraethylene glycol dimethyl ether, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OC}-\text{H}_3$, and cesium benzoate (3.40 g, 11.40 mmol) dissolved in 40 mL of ethylene glycol is added to the solution, together with *N*-methylmorpholine (10.80 g, 106.9 mmol). The resulting solution is stirred for ca. 0.5 h, and it is charged into an evacuated high-pressure autoclave. The system is warmed to 150–160 °C under 200 psi of carbon monoxide and hydrogen ($\text{CO}:\text{H}_2$ ratio of 1:1), and it is allowed to react for 6 h. The resulting solution is quickly brought to atmospheric pressure, collected by Schlenk techniques under argon, and filtered. A tenfold excess of toluene is added to the filtrate, and a dark oil is formed overnight. This oil is collected after decanting the solvent mixture, washed with 2-propanol (10×30 mL), and redissolved in acetone (2×100 mL). A solution of cesium hydroxide in methanol (6.5 g in 25 mL) is gradually added to the acetone filtrate while the system is monitored by infrared spectroscopy for the disappearance of the absorption band at 1990 cm^{-1} . A total of 40–50 mL of the alkali solution is usually required. This mixture is filtered to remove a solid

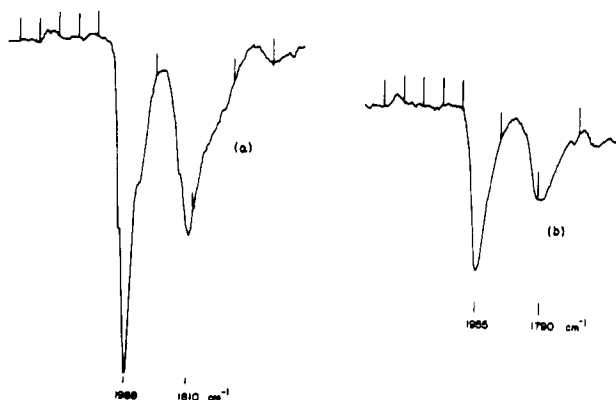


Figure 1. Infrared spectra: (a) $[\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3]^+$ and $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ salts of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ in acetone; (b) $[\text{Cs}(\text{C}_{12}\text{H}_{22}\text{O}_6)_{1.9}]^+$ salt of the isolated, yet uncharacterized, side product in dimethyl sulfoxide.²⁴

(6.33 g). This material is washed with 200 mL of acetone to remove a soluble material shown by infrared spectroscopy to be $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$, and the resulting extract is added to the filtrate above. The insoluble residue left in the filter (3.50 g) is soluble only in high-polarity solvents, e.g., dimethyl sulfoxide, giving infrared bands at 1955 and 1790 cm^{-1} (Figure 1). The resulting filtrate–extract mixture is treated with a sixfold excess of 2-propanol–hexane (3:1), and a solid (4.80 g) is immediately precipitated. This corresponds to a yield of ca. 60% of $\text{Cs}_4[\text{Rh}_{14}(\text{CO})_{25}] \cdot 4(\text{tetraglyme})$. Treatment of the same solution with alcoholic solutions of the chloride salts of $[(\text{CH}_3)_4\text{N}]^+$, $[(\text{C}_2\text{H}_5)_4\text{N}]^+$, and $[\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3]^+$ ¹⁵ results in the almost quantitative precipitation of the respective salts of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$. The infrared spectra of the cesium solvate salts (Figure 1) and of the benzyltriethylammonium salt (± 1 cm^{-1}) are very similar, except for small shifts of the bands probably caused by the differences in cations. The other product of the reaction is obviously a rhodium carbonyl cluster more reduced than $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$, as indicated by the respective infrared patterns. Work is actually under way to characterize this cluster and it will be reported elsewhere.

The structural characterization of the $[(\text{C}_2\text{H}_5)_4\text{N}]_4[\text{Rh}_{14}(\text{CO})_{25}]$ has been carried out in a complete X-ray single-crystal diffraction study. The structural parameters are in complete agreement¹⁶ with those reported previously¹² for this anion.

(13) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).

(14) (a) S. Martinengo, P. Chini, and G. Giordano, *J. Organomet. Chem.*, **27**, 389 (1971); *Inorg. Synth.*, personal communication; P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 299 (1969); *Inorg. Synth.*, in press; (b) P. Chini, personal communication.

(15) The conversion of the $[\text{Cs}(\text{tetraglyme})_2]^+$ salt of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ into $[(\text{C}_2\text{H}_5)_4\text{N}]^+$, $[\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3]^+$, and other tetraalkylammonium salts was achieved by a metathesis reaction of an acetone solution of the cesium salt (4.8 g in 100 mL) with an equal volume of a 2-propanol solution of the corresponding tetraalkylammonium chloride (1 g in 15 mL). The resulting ammonium salts were isolated by filtration, and the collected solids were washed with 2-propanol or methanol and vacuum dried. For the ¹³C NMR studies, the compound was dissolved in acetone and reprecipitated with 2-propanol.

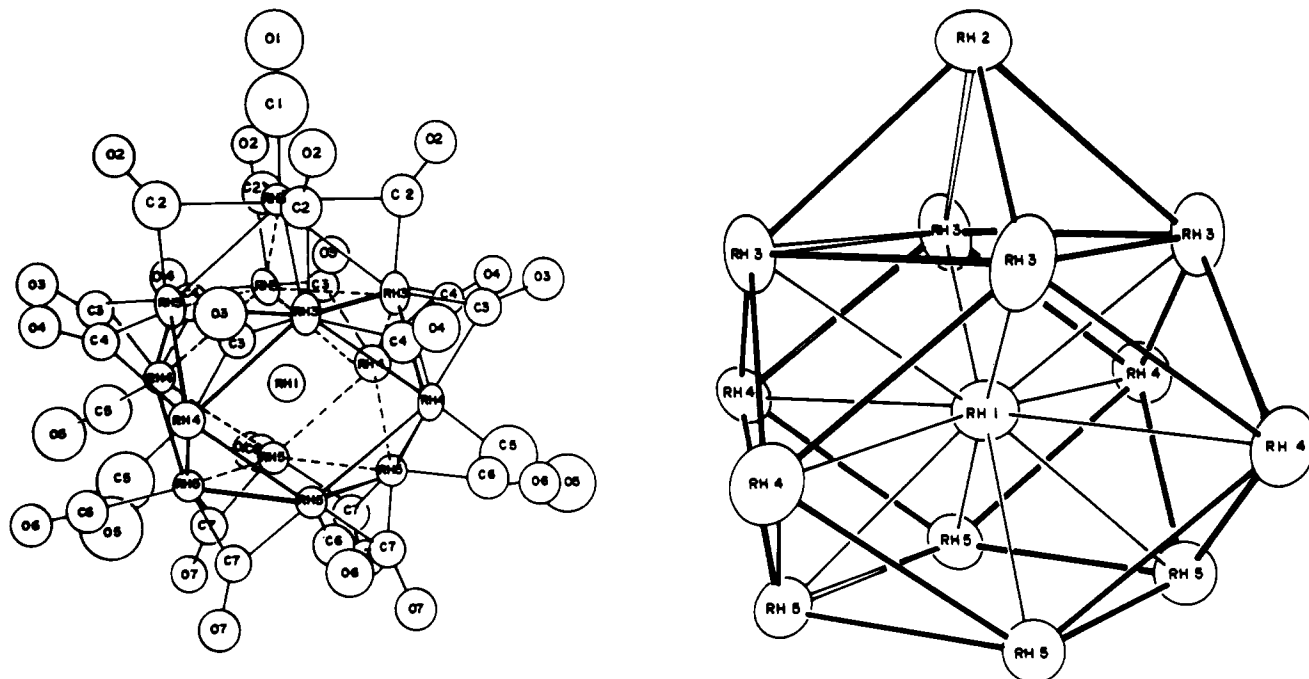


Figure 2. ORTEP diagram of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ with and without the carbonyl groups (ellipsoids at 50% probability).

Table I. Selected Interatomic Distances for $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$

(a) Rhodium-Rhodium Distances			
Rh(1)-Rh(2)	3.372 (5)	Rh(3)-Rh(4)	2.730 (2)
Rh(1)-Rh(3)	2.621 (3)	Rh(3)-Rh(5)	3.324 (2)
Rh(1)-Rh(4)	3.069 (2)	Rh(4)-Rh(4)	4.338 (2)
Rh(1)-Rh(5)	2.650 (3)	Rh(4)-Rh(5)	2.753 (2)
Rh(2)-Rh(3)	2.787 (3)		2.746 (2)
Rh(3)-Rh(3)	2.986 (2)	Rh(5)-Rh(5)	2.792 (2)
	4.223 (3)		3.948 (3)
Rh(3)-Rh(4)	2.714 (3)		
(b) Rhodium-Carbon Distances			
Terminal			
Rh(2)-C(1)	1.69 (9)	Rh(5)-C(6)	1.91 (3)
Rh(4)-C(5)	1.77 (4)		
Symmetrical Bridge			
Rh(3)-C(4)	2.01 (2)	Rh(4)-C(4)	2.02 (2)
Asymmetrical Bridge			
Rh(2)-C(2)	2.28 (3)	Rh(4)-C(3)	2.02 (2)
Rh(3)-C(2)	1.83 (3)	Rh(5)-C(7)	1.91 (2), 1.97 (2)
Rh(3)-C(3)	1.93 (2)		
(c) Carbon-Oxygen Distances			
C(1)-O(1)	1.14 (9)	C(4)-O(4)	1.14 (9)
C(5)-O(5)	1.12 (4)	C(3)-O(3)	1.20 (2)
C(6)-O(6)	1.07 (3)	C(7)-O(7)	1.24 (2)

Selected interatomic distances and angles are now reported by us (Tables I and II) while full structural results are included as supplementary material.

A comparison of the solid-state structure of the anion (Figure 2) with the present in solution has been made via variable-temperature ^{13}C NMR. This was of interest because of the presence of a square face in the cluster's cage and the suggestion that a "merry-go-round" carbonyl-scrambling process may be possible on this type of face.¹⁷ This may be

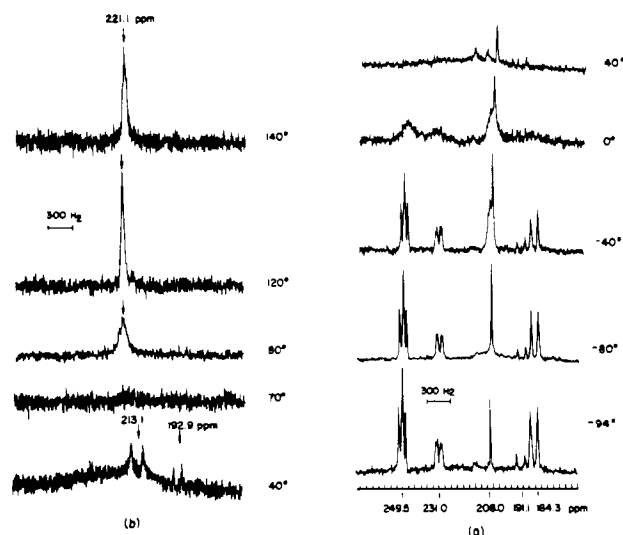


Figure 3. Variable-temperature ^{13}C NMR study of $[\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3][\text{Rh}_{14}(\text{CO})_{25}]$ in (a) acetone- d_6 solution between -94 and $+40$ $^\circ\text{C}$ and (b) sulfolane solution between $+40$ and $+140$ $^\circ\text{C}$.

relevant to the cluster-surface analogies¹¹ and to the fluxionality processes that could involve the carbonyl ligands located around octahedral holes usually found in the surfaces with body-center, hexagonal, and cubic packing of metal atoms.

Carbonyl fluxionality is detected above 0 $^\circ\text{C}$ (Figure 3) in agreement with previous results,¹⁸ but the carbonyl mobility is decreased at lower temperatures with a partially rigid structure already being observed at -40 $^\circ\text{C}$.¹⁹ A more drastic change of the spectra is noted at temperatures above 80 $^\circ\text{C}$.

(18) P. Chini, personal communication, Jan 1979.

(19) ^{13}C VT NMR studies have been carried out with ^{13}C -enriched samples of $[(\text{C}_2\text{H}_5)_3\text{N}]_4[\text{Rh}_{14}(\text{CO})_{25}]$; these samples were enriched by dissolving this compound in acetone and allowing the solution to stand stirred under 1 atm of 50% ^{13}C at 25 $^\circ\text{C}$ for 8 h. The enriched species was recovered by vacuum evaporation of the solvent. The solutions for the NMR studies were prepared by dissolving ca. 0.40 g of the salt in 2.5–3.0 mL of either acetone- d_6 or sulfolane. The former solutions were used between -94 and $+45$ $^\circ\text{C}$, and the latter ones at the higher temperatures.

(16) The single crystal of $[(\text{C}_2\text{H}_5)_3\text{N}]_4[\text{Rh}_{14}(\text{CO})_{25}]$ was obtained by the slow-diffusion method using acetone-2-propanol. The compound crystallized in the tetragonal space group $P4/ncc$ (No. 130) with $a = 17.027$ (3) \AA , $c = 27.258$ (6) \AA , $V = 7902.6$ \AA^3 , and $Z = 4$. The density is 2.24 g/cm^3 , $\mu = 28.2$ cm^{-1} , and $\alpha = \beta = \gamma = 90^\circ$. The structure was solved by direct methods using 928 independent reflections. The final R values are 5.3 and 6.6%.

(17) E. Band and E. L. Muetterties, *Chem. Rev.*, **78**, 639 (1978).

Table II. Selected Interatomic Angles for $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$

(a) Rhodium-Rhodium-Rhodium					
Rh(2)-Rh(1)-Rh(3)	53.67 (7)	Rh(3)-Rh(2)-Rh(3)	64.79 (8)		
Rh(2)-Rh(1)-Rh(4)	91.68 (7)	Rh(2)-Rh(3)-Rh(1)	77.1 (1)		
Rh(2)-Rh(1)-Rh(5)	131.86 (7)	Rh(2)-Rh(3)-Rh(3)	57.60 (4)		
Rh(3)-Rh(1)-Rh(3)	69.45 (7), 107.3 (1)	Rh(3)-Rh(3)-Rh(3)	90.00 (0)		
Rh(3)-Rh(1)-Rh(4)	56.30 (6), 56.69 (5), 126.13 (9), 125.73 (9)	Rh(3)-Rh(3)-Rh(4)	56.47 (7)		
Rh(3)-Rh(1)-Rh(5)	69.45 (7), 78.19 (5), 113.39 (6), 113.19 (6), 174.5 (1)	Rh(4)-Rh(3)-Rh(3)	105.7 (1)		
Rh(4)-Rh(1)-Rh(4)	89.95 (5), 176.6 (2)	Rh(3)-Rh(4)-Rh(3)	66.53 (8)		
Rh(5)-Rh(1)-Rh(5)	63.56 (8), 96.3 (1)	Rh(3)-Rh(4)-Rh(5)	75.02 (6)		
		Rh(5)-Rh(4)-Rh(5)	61.01 (7)		
		Rh(4)-Rh(5)-Rh(5)	59.62 (7)		
		Rh(5)-Rh(5)-Rh(5)	90.00 (0)		
(b) Central Rhodium-Rhodium-Carbon					
Rh(1)-Rh(2)-C(1)	180.0 (0)	Rh(1)-Rh(4)-C(3)	98.8 (6)		
Rh(1)-Rh(2)-C(2)	90.2 (7)	Rh(1)-Rh(4)-C(4)	99.9 (6)		
Rh(1)-Rh(3)-C(2)	131.5 (8)	Rh(1)-Rh(4)-C(5)	154 (1)		
Rh(1)-Rh(3)-C(3)	118.2 (6)	Rh(1)-Rh(5)-C(6)	148.3 (8)		
Rh(1)-Rh(3)-C(4)	116.9 (6)	Rh(1)-Rh(5)-C(7)	100.9 (6), 102.4 (7)		
(c) Rhodium-Carbon-Oxygen					
Rh(2)-C(1)-O(1)	180.0 (0)	Rh(3)-C(4)-O(4)	139 (2)	Rh(2)-C(2)-O(2)	127 (2)
Rh(4)-C(5)-O(5)	152 (4)	Rh(4)-C(4)-O(4)	135 (2)	Rh(3)-C(2)-O(2)	147 (2)
Rh(5)-C(6)-O(6)	178 (2)			Rh(3)-C(3)-O(3)	140 (2)
				Rh(4)-C(3)-O(3)	133 (2)
				Rh(5)-C(7)-O(7)	135 (2)

The broad band and the sharp doublet at 213.1 and 192.9 ppm, respectively, present at lower temperatures get transformed into a broad multiplet centered at 221.1 ppm. The reversibility of these changes, even after 3 h at 140 °C, suggests the absence of decomposition of the cluster and a high thermal stability of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$, as previously noted for $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$.¹⁹ The magnitude of the differences in shifts with respect to the expected average resonance for the carbonyl ligands of the former complex, 221.1 vs. 220.5 ppm, respectively, suggests that they may not be thermally induced shifts.²⁰ Instead, it appears to correspond to a rearrangement of the structure of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ to generate an isomeric form of the anion that is formed only at high temperatures. We are now working on this hypothesis, and the results will be published elsewhere.

The relative intensities and multiplicity of the ¹³C NMR bands present in the low-temperature limiting spectrum (Figure 4) are those expected on the basis of the solid structure of the anion, indicating the loss of mobility for the carbonyls A, B, C, and D. In contrast, the unresolved character of the band at 208.0 ppm indicates the scrambling of ligands E and F, at -40 °C, while it appears that this coalescence band is partially resolved at -94 °C (Figure 3). This behavior is indicative of a low activation energy scrambling process for the terminal and bridging ligands located on the basal square face. This is significant because carbonyl scrambling in clusters has previously been observed to be occurring by pathways involving triangular faces exclusively or a combination of triangular and square faces. The mechanism or causes of the facile carbonyl motion on this square face are not yet fully understood. The potential existence of a common conical surface shared by the fluxional carbonyls has previously been suggested as probably facilitating the merry-go-round scrambling process around the square face of a rhodium carbonyl cluster.¹⁷ This proposal has been advanced in the case of $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$, a cluster for which the fluxionality of the carbonyls could also be explained in another way.²¹ The presence of a merry-go-round process of this type has also been reported with $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_x]^{(5-x)-}$ ($x = 3, 2$).¹⁷ The recent report that an electrophile such as the hydrogen atom may be found over the center of some of the square faces of these

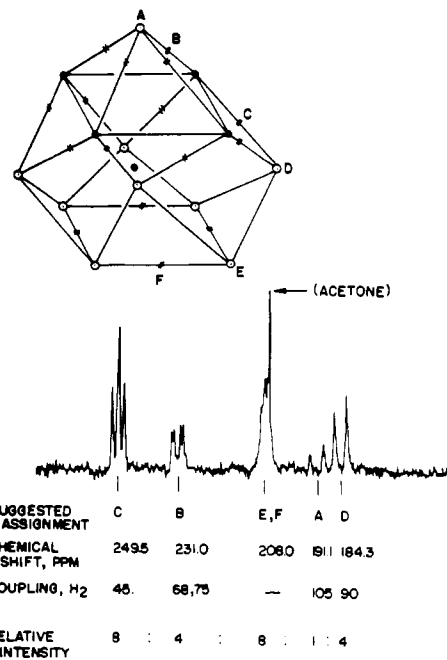


Figure 4. Low-temperature spectrum (-40 °C) of $[\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3]_4[\text{Rh}_{14}(\text{CO})_{25}]$ in acetone- d_6 and the suggested assignments of the resonances with respect to the solid-state structure: ⊙, rhodium atoms coordinated to terminal carbonyls; ⊕, cluster edges having bridging carbonyls.

clusters²² suggests that the concentration of electronic charge may be occurring in that region of the clusters. Perhaps the differences expected from having the square face involved in this scrambling process capped either by a main-group atom, e.g. sulfur, or by a transition-metal atom, e.g., rhodium, could be responsible for the ready merry-go-round process on the square face of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ (coalescence temperature lower than -90 °C) and for either the absence of such a process or the higher temperature required for its occurrence in the case of $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$ (coalescence temperature 80–100 °C).

Further results concerning the reactivity of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ and the structural changes this anion is undergoing in solution

(20) We have tested the influence of the solvent in the shift of this band, with the conclusion that this is not a solvent-dependent shift.

(21) J. L. Vidal, R. C. Schoening, R. L. Pruett, and R. A. Fiato, *Inorg. Chem.*, **18**, 1821 (1979).

(22) V. G. Albano, G. Ciani, S. Martinengo, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 978 (1979).

will be described in forthcoming reports.²³

Registry No. Cs₄[Rh₁₄(CO)₂₅], 75558-11-1; [(C₂H₅)₄N]₄[Rh₁₄(CO)₂₅], 68714-70-5; [PhCH₂N(C₂H₅)₃]₄[Rh₁₄(CO)₂₅], 75558-89-3; [(CH₃)₄N]₄[Rh₁₄(CO)₂₅], 75548-81-1; Rh(CO)₂acac, 14874-82-9.

Supplementary Material Available: Complete tables of structural factors, atomic distances and angles, and positional and thermal parameters (14 pages). Ordering information is given on any current masthead page.

- (23) The wide use of the method may be hindered by the requirements for high-pressure equipment, although pressure bombs with a safety limit of ca. 1000 psi are often found in most laboratories. The time required is less than ca. 2 days.
- (24) The compositions of the [Cs(CH₃OCH₂CH₂)₄OCH₃]₂⁺ and [Cs(C₁₂H₂₂O₆)_{1.9}]⁺ salts are proposed on the bases of their elemental analyses and ¹H NMR studies. It is proposed on the same bases that the side product soluble only in dimethyl sulfoxide could be the corresponding salt of [Rh₁₃(CO)₂₄H₂]^{(5-x)-} (x = 0, 1), a cluster previously observed by Chini et al. The glyme and 18-crown-6 solvates are obtained by conducting the synthesis of [Rh₁₄(CO)₂₅]⁴⁺ described here in these solvents.

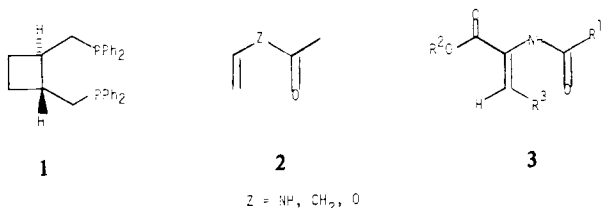
Contribution from the Chemical Research Department,
Hoffmann-La Roche Inc., Nutley, New Jersey 07110

Crystal Structure of
(η^6 -Hexadeuteriobenzene)[(1*R*,2*R*)-*trans*-1,2-bis((di-phenylphosphino)methyl)cyclobutane]rhodium(I)
Perchlorate: A Model for the Resting State of an
Asymmetric Hydrogenation Catalyst

John M. Townsend* and John F. Blount

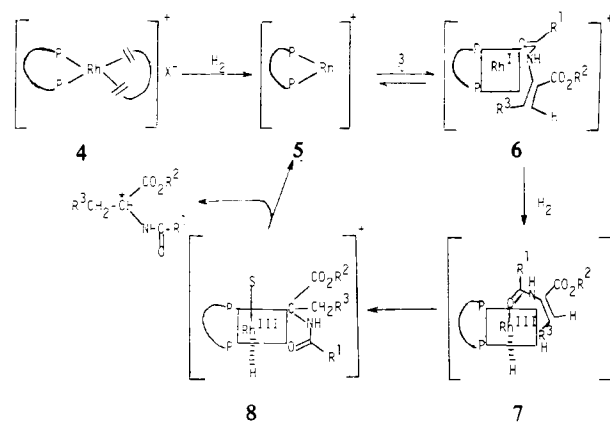
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Catalytic asymmetric hydrogenation has become a practical synthetic method to prepare enantiomers of many organic substances.¹ Hydrogenations which proceed with the highest enantioselectivities at the fastest rates typically involve rhodium complexes of chiral chelating bis(phosphines) such as **1**.²

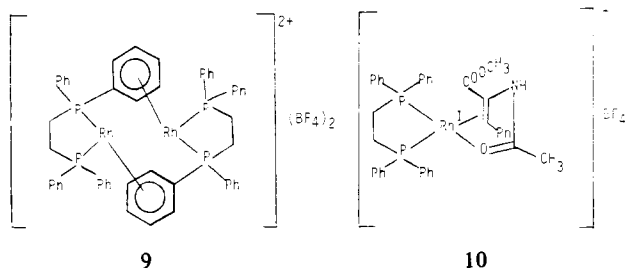


Substrates of general structure **2** which can also coordinate as bidentate ligands also give particularly good results. For the important case of hydrogenation of prochiral α -acyl aminoacrylic acid derivatives such as **3** catalyzed by cationic rhodium(I) complexes of chelating bis(phosphines), reaction Scheme I is supported by considerable experimental evidence.³⁻¹²

Scheme I



Several crystal structures of cationic diolefin catalyst precursors **4** have been reported.¹³⁻¹⁶ Under hydrogenation conditions, the diene is removed as saturated hydrocarbon to generate the highly coordinatively unsaturated "resting" state of the catalyst **5**. In methanol or acetone, these species have been characterized by ³¹P NMR and other spectroscopic methods and appear to exist as methanol (or acetone) solvated monomers, or dimers held together by solvent bridges.^{4-6,17-20} Another possibility is that of a dimer held together by π -arene bridges involving phenyl moieties of the phosphine. There is as yet no unambiguous evidence for this type of structure in solution, but it has been observed in the solid state for analogue **9**,⁴ where 1,2-bis(diphenylphosphino)ethane serves as a close model for chiral bis(phosphines) of the dipamp⁹ and chiraphos²¹ type.



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