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Synthesis and Fluxional Properties of Monothio-β-diketonatorhodium(I) Diolefin Complexes

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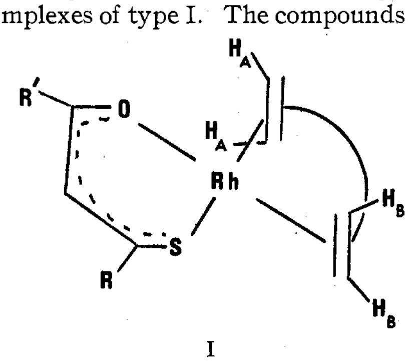
Asymmetric complexes of rhodium(I) with a monothio-β-diketonate ligand and one of the chelating diolefins norbornadiene, cycloocta-1,5-diene, cyclooctatetraene, duroquinone, or 2,5-di-*tert*-butyl-*p*-benzoquinone have been synthesized and studied by pmr spectroscopy. The compounds show thermally induced intramolecular proton exchange between nonequivalent sites at different rates depending upon the diolefin. In the presence of dimethyl sulfoxide or triphenylarsine the exchange is accelerated. The rate is first order in added nucleophile and a mechanism involving a fluxional five-coordinate intermediate is proposed for this case. In the absence of nucleophiles the rate equation has both first- and second-order terms in complex concentration. Indirect evidence is presented for a five-coordinate intermediate in the absence of added ligand. Kinetic parameters obtained by comparison of observed and computer-simulated pmr spectra are reported.

Introduction

A number of diolefin complexes of rhodium(I)[2,3a] and iridium(I)[3b] have temperature-dependent proton nuclear magnetic resonance (pmr) spectra indicating exchange of olefinic protons between nonequivalent sites. One extensively studied system[2] was the group of compounds formed by reaction of tertiary phosphines and arsines (L) with the halide-bridged dimers [(diene)MCl]$_2$ (M = Rh(I), Ir(I)) to form complexes of the type (diene)MLCl. Depending on the choice of L and the L:M ratio these complexes showed a variety of intermolecular reactions not all of which caused olefinic proton site exchange. In the fluxional five-coordinate compounds of the type (CH$_3$)Rh(diene)L$_2$,[3] intermolecular exchange of phosphine is apparently also independent of proton site exchange. To eliminate intermolecular exchange in a four-coordinate system, the labile monodentate ligands were replaced by an asymmetric chelating monothio-β-diketonate ligand to form several complexes of type I. The compounds previously described in a preliminary account of this work[4] were the first olefin complexes containing this ligand. A number of additional olefin complexes have since been prepared, and the system was extensively studied by pmr spectroscopy in order to determine the mechanism of the exchange reaction. The results are presented and discussed in this report.



I

Experimental Section

General Information.—All chemicals and solvents employed for synthesis were of reagent grade quality and used without further purification. The *o*-dichlorobenzene used in the kinetic studies was vacuum distilled from calcium hydride, and nitrobenzene was distilled from barium oxide. Solutions were prepared in a nitrogen-filled drybox. The nitrobenzene sample was sealed under vacuum. Decalin was passed through a silver nitrate impregnated column to remove olefins and distilled from sodium under nitrogen. Triphenylarsine was recrystallized from ethanol. Dimethyl sulfoxide (DMSO), DMSO-d_6, and Diaprep bromobenzene-d_5 were used without further purification. Olefins were obtained commercially, and their abbreviated labels are shown in Figure 1.

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Molecular weights were determined at 37° in chloroform using a Mechrolab 301A vapor pressure osmometer calibrated with benzil; the estimated error was ±7.5%. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Ligands and Their Salts.—3-Mercapto-1,3-diphenylprop-2-en-1-one, monothiodibenzoylmethane (SDBM-H), was synthesized by Claisen condensation[5] and recrystallized from petroleum ether (bp 30–60°). 1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one, thiothenoyltrifluoroacetone (STTA-H), was synthesized by the method of Livingstone.[6] The crude product was found by pmr spectroscopy to contain a substantial amount of the starting material. The lead salt Pb(STTA)$_2$ was synthesized by adding an alcohol solution of the crude ligand to an aqueous solution of lead acetate and acetic acid.

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[1] National Science Foundation Predoctoral Fellow, 1968–1971.

[2] K. Vrieze, P. W. N. M. van Leeuwen, and H. C. Volger, *Inorg. Chim. Acta Rev.*, **3**, 109 (1969), and references contained therein.

[3] (a) D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, **30**, C84 (1971); (b) J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, **92**, 6976 (1970).

[4] H. I. Heitner and S. J. Lippard, *ibid.*, **92**, 3486 (1970).

[5] E. Uhlemann and Ph. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966).

[6] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

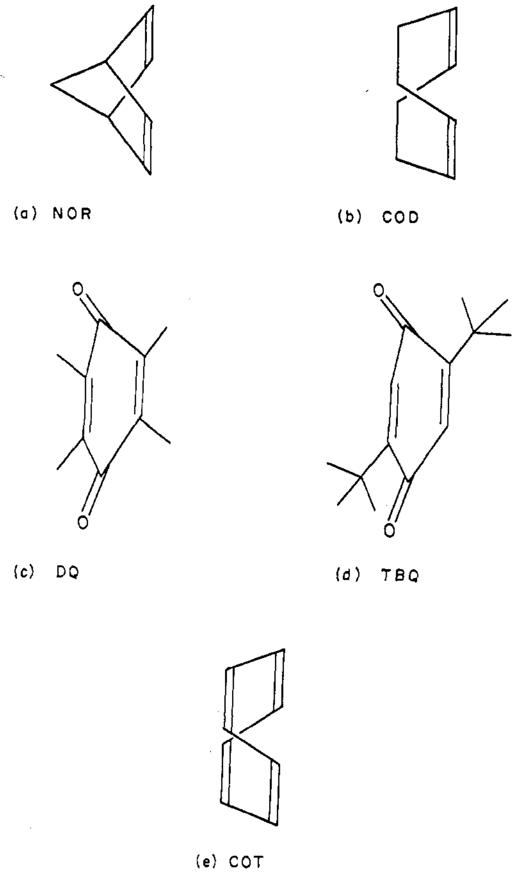

Figure 1.—Olefins used in this work: (a) bicyclo[2.2.1]hepta-2,5-diene (norbornadiene); (b) cycloocta-1,5-diene; (c) 2,3,5,6-tetramethyl-*p*-benzoquinone (duroquinone); (d) 2,5-di-*tert*-butyl-*p*-benzoquinone; (e) cyclooctatetraene.

The thallium salt Tl(SDBM) was made either by adding a basic solution of the ligand to a hot, aqueous thallium(I) sulfate solution[7] or by adding a solution of the ligand in petroleum ether to a petroleum ether solution of thallium(I) ethoxide. Dibenzoylmethane and trifluoroacetylacetone (Peninsular) were used without further purification.

3-Thiolo-1,3-diphenylprop-2-en-1-onebicyclo[2.2.1]hepta-2,5-dienerhodium(I), (NOR)Rh(SDBM).—Tl(SDBM) (1.18 g, 2.66 mmol) was added to a solution of 0.625 g (1.36 mmol) of di-μ-chloro-bis(norbornadiene)dirhodium(I)[8] in 30 ml of methylene chloride and stirred for 5 min. The solution was filtered and concentrated at reduced pressure. The residue was recrystallized by dissolving it in a minimum volume of chloroform and carefully adding a layer of ethanol on top. Diffusion of the two layers overnight at 0° yielded 0.478 g (41%) of product as dark red crystals (mp 170–173° dec). *Anal.* Calcd for $C_{22}H_{19}OSRh$: C, 60.8; H, 4.33; S, 7.31; mol wt 434. Found: C, 60.8; H, 4.40; S, 7.38; mol wt 428.

1,3-Diphenyl-1,3-propanedionatobicyclo[2.2.1]hepta-2,5-dienerhodium(I), (NOR)Rh(DBM).—This compound was synthesized in 71% yield by the same method and recrystallized twice from chloroform–ethanol (mp 199–201° dec). *Anal.* Calcd for $C_{22}H_{19}O_2Rh$: C, 63.2; H, 4.58. Found: C, 62.5; H, 4.59.

3-Thiolo-1,3-diphenylprop-2-en-1-onecycloocta-1,5-dienerhodium(I), (COD)Rh(SDBM).—This compound was prepared from di-μ-chloro-bis(cycloocta-1,5-diene)dirhodium(I)[9] by the same method in 32% yield (mp 148–150° dec). *Anal.* Calcd for $C_{23}H_{23}OSRh$: C, 61.3; H, 5.15; S, 7.12; mol wt 450. Found: C, 61.7; H, 5.21; S, 8.43; mol wt 436.

The compounds (NOR)Rh(SDBM) and (COD)Rh(SDBM) could also be synthesized by allowing monothiodibenzoylmethane to react with the appropriate chloride-bridged dimer in petroleum ether in the presence of potassium carbonate. The products were identical by pmr and melting point.

Bis(3-thiolo-1,3-diphenylprop-2-en-1-one)-μ-cyclooctatetraene-dirhodium(I), (COT)Rh$_2$(SDBM)$_2$.—Di-μ-chloro-bis(cyclooctatetraene)dirhodium(I)[10] (0.272 g, 0.56 mmol) and 0.3 g of potassium carbonate were suspended with stirring in a solution of monothiodibenzoylmethane (0.272 g, 1.13 mmol) dissolved in 70 ml of petroleum ether. After 24 hr the solid material was filtered off and extracted with 20 ml of benzene. Ethanol (150 ml) was added to the extract and the solution was partially evaporated at 40° under reduced pressure. When the product began to precipitate, the mixture was cooled to yield 0.212 g (48%) of orange crystals (mp 236–237° dec). *Anal.* Calcd for $C_{38}H_{30}O_2S_2Rh_2$: C, 57.9; H, 3.83; S, 8.13; mol wt 789. Found: C, 58.1; H, 3.95; S, 8.05; mol wt 760.

3-Thiolo-1,3-diphenylprop-2-en-1-one-2,5-di-*tert*-butyl-*p*-benzoquinonerhodium(I)–Benzene, (TBQ)Rh(SDBM)·C_6H_6.—Di-μ-chloro-tetrakis(cyclooctene)dirhodium(I)[11] (0.615 g, 0.84 mmol) was suspended with stirring in a solution of 0.405 g (1.84 mmol) of recrystallized 2,5-di-*tert*-butyl-*p*-benzoquinone in 30 ml of petroleum ether for 12 hr. The red solid product (0.530 g, 86% yield assuming the formula [(TBQ)RhCl]$_2$) was filtered off and washed with petroleum ether. A methylene chloride slurry of 0.499 g (0.606 mmol) of this red solid and 0.601 g (1.39 mmol) of Tl(SDBM) was stirred for 1 hr. The solution was filtered and chromatographed on alumina to yield a red solution which was evaporated to give a red oil. Crystallization from benzene–petroleum ether gave 0.201 g (23%) of red crystals (mp 195–197° dec) which were shown by the analytical data and pmr spectroscopy to have a benzene molecule of crystallization. *Anal.* Calcd for $C_{35}H_{39}O_3SRh$: C, 65.5; H, 5.82; S, 5.00. Found: C, 65.4; H, 5.75; S, 5.56.

3-Thiolo-1,3-diphenylprop-2-en-1-one-2,3,5,6-tetramethyl-*p*-benzoquinonerhodium(I), (DQ)Rh(SDBM).—This compound (mp 217–219° dec) was synthesized in 29% yield by the procedure described above for (TBQ)Rh(SDBM). *Anal.* Calcd for $C_{25}H_{23}O_3SRh$: C, 59.3; H, 4.58; S, 6.33. Found: C, 59.1; H, 4.48; S, 6.35.

1,1,1-Trifluoro-4-(2-thienyl)-4-thiolobut-3-en-2-onebicyclo[2.2.1]hepta-2,5-dienerhodium(I), (NOR)Rh(STTA).—Pb(STTA)$_2$ (0.630 g, 0.92 mmol) was added to a solution of di-μ-chloro-bis(norbornadiene)dirhodium(I) (0.434 g, 0.94 mmol) in 30 ml of methylene chloride and stirred for 1 hr. The solution was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in petroleum ether and chromatographed on a silica gel column to yield a red solution which was evaporated in air to give 0.482 g of crude product. The product was sublimed at 125–132° *in vacuo* to give 0.394 g (50%) of dark red solid (mp 118–122°). *Anal.* Calcd for $C_{15}H_{12}F_3OS_2Rh$: C, 41.7; H, 2.80; S, 14.8; mol wt 432. Found: C, 40.8; H, 2.93; S, 14.7; mol wt 411.

1,1,1-Trifluoro-4-methyl-2,4-butanedionatobicyclo[2.2.1]-hepta-2,5-dienerhodium(I), (NOR)Rh(TFA).—Di-μ-chloro-bis-(norbornadiene)dirhodium(I) (0.530 g, 1.15 mmol) was stirred in a petroleum ether solution of 0.6 g (3.9 mmol) of trifluoroacetylacetone with 0.3 g of potassium carbonate. The solution was filtered and evaporated and the residue was sublimed at 75–80° *in vacuo* to yield 0.608 g (76%) of yellow product (mp 110–111°). *Anal.* Calcd for $C_{12}H_{12}O_2F_3Rh$: C, 41.4; H, 3.47. Found: C, 41.8; H, 3.60.

Kinetic Studies and Pmr Measurements.—All kinetic studies (except for the rate measurements with added DMSO at −36°) were carried out on a Varian HA-100 nmr spectrometer equipped with a V-4343 temperature controller. Other experiments were performed on a Varian A-60A spectrometer, also with temperature control. The temperature was calibrated with standard Varian ethylene glycol and methanol samples; the temperatures measured by this method agreed with those determined using an iron–constantan thermococuple immersed in an oil-filled nmr tube inserted in the probe. Care was taken to avoid saturation and to ensure slow-passage conditions. For line shape calculations the absorption was measured by hand directly from the chart paper at different frequencies. Most spectra were measured at 30–60 points, and the frequencies were spot-checked with an external frequency counter. Tetramethylsilane was used as an internal standard and lock signal.

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(7) S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, in press.

(8) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(9) J. Chatt and L. M. Venanzi, *ibid.*, 4735 (1957).

(10) M. A. Bennett and J. D. Saxby, *Inorg. Chem.*, **7**, 321 (1968).

(11) L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, 336 (1965).

To conserve complex and solvent, samples were mixed by weighing the sample into the nmr tube and filling to a calibrated mark or by adding a known volume of solvent and correcting the concentration for the partial molar volume of solute. In the rate studies with added DMSO the relative concentration of DMSO was determined from the measurement of integrated intensities of the DMSO methyl and complex methylene proton resonances. The change in concentration of (NOR)Rh(SDBM) upon addition of DMSO was negligible.

Calculations.—A computer program HEPLOT[12] was used to determine the exchange lifetime, τ. The program varies τ to give the best least-squares normalized fit of calculated to observed spectra. The program uses the complete formula of Gutowsky and Holm[13] for the uncoupled two-site exchange case and was found to give results consistent with another program, EXCNMR,[14] which generates spectra by the Kubo–Sack method.[15] Using the definition of τ given by Gutowsky and Holm[13] the pseudo-first-order rate constant is $1/2\tau$.

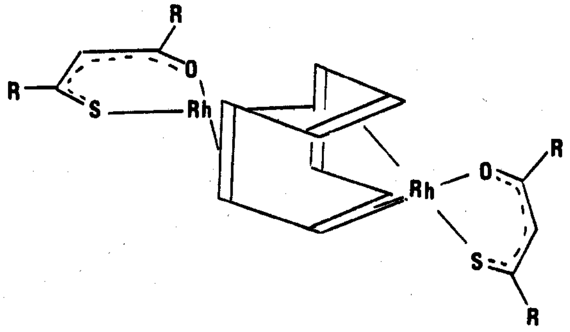
The chief sources of error in the analysis are (1) possible temperature-dependent changes in the chemical shift differences between pmr peaks not caused by exchange and (2) neglect of spin–spin coupling for the norbornadiene and cycloocta-1,5-diene complexes. The first source of error probably has a negligible contribution since no large temperature-dependent chemical shift changes were observed for the olefin resonances of nonfluxional complexes. The second source of error is difficult to correct exactly by complete line shape analysis because of the complexity of the spectra. Systematic errors arising from neglect of spin–spin coupling could be responsible for the negative intercepts observed in certain plots of rate *vs.* ligand concentration which are discussed later.

Activation parameters were calculated from the Arrhenius equation using the routine in EXCNMR.[14] Rate constants were computed by simple linear least-squares methods. Calculations were performed on an IBM 360-91 computer.

Results and Discussion

Syntheses and Structural Assignments.—The complexes were prepared by simple replacement of chloride in $[(\text{diolefin})\text{RhCl}]_2$ by the monothio-β-diketonate or β-diketonate anions. The synthesis of (NOR)Rh(STTA) demonstrates that lead salts may be used instead of the usual thallium compounds. An alternative method in which a β-diketone is allowed to react directly with the chloride-bridged dimer in the presence of potassium carbonate, previously used to prepare acetylacetonatocyclooctatetraenerhodium(I),[10] worked for the monothio-β-diketonate complexes using norbornadiene and cycloocta-1,5-diene but not the quinone ligands.

Analytical data as well as the relative integrated intensities in the pmr spectra of the norbornadiene, cycloocta-1,5-diene, duroquinone, and 2,5-di-*tert*-butyl-*p*-benzoquinone complexes are consistent with structure I for these molecules. The planar configuration has been established by X-ray diffraction studies of the related acetylacetonato(duroquinone)rhodium(I)[16] and acetylacetonatobis(ethylene)rhodium(I)[17] complexes and the chelating nature of the monothio-β-diketonate ligand by solid-state structural work on two π-allylpalladium derivatives.[7,18] The monomeric nature of these complexes in solution is confirmed by osmometry. The cyclooctatetraene compound is shown by its molecular weight and the relative integration of phenyl protons to olefin protons (5:2) to have the dimeric structure II. The initial red product in the synthesis exhibits three olefinic proton resonances in the ratio 2:1:1. The disproportionation of this product to give free cyclooctatetraene and dimer II may be observed by pmr spectroscopy. The initial product is presumably a monomer of type I analogous to the known compound acetylacetonatocyclooctatetraenerhodium(I).[10]



II

Chemical shift data for all the complexes are summarized in Table I. The assignments are straightforward since the relative chemical shift values for the different types of ligand protons do not change in going from free to coordinated olefin. The feature of interest in the SDBM complexes is the nonequivalence of the H_a and H_b protons (I) in the NOR, COD, COT, and TBQ complexes. The DQ and TBQ compounds show an analogous nonequivalence of methyl group resonances. The olefin resonances are shifted upfield upon coordination (Table I). The protons trans to the sulfur atom are presumably farther away from the rhodium atom because of the greater trans-labilizing effect of sulfur compared to oxygen. The downfield resonance (H_a) can therefore be assigned to these trans protons, which experience less metal orbital shielding. Since exchange is observed between two equally populated sites, the mechanistic conclusions derived from pmr experiments do not depend on this assignment.

TABLE I

PROTON CHEMICAL SHIFT DATA AT AMBIENT PROBE TEMPERATURE[a]

	Chem shift (τ), ppm				
Compd	H_a	H_b	Bridgehead	Other	Solvent
(NOR)Rh(SDBM)	5.25	5.85	6.20	8.55[b]	$CDCl_3$
	5.50	6.10	6.50	8.80[b]	$o\text{-}C_6H_4Cl_2$
	5.50	6.10	6.50	8.80[b]	C_6H_5Cl
(NOR)Rh(STTA)	5.25	5.85	6.20	8.95[b]	$CDCl_3$
(NOR)Rh(DBM)	6.10	6.10	6.50	8.95[b]	$o\text{-}C_6H_4Cl_2$
(NOR)Rh(TFA)	6.10	6.10	6.50	8.95[b]	$o\text{-}C_6H_4Cl_2$
(COD)Rh(SDBM)	5.05	5.85	....	7.4–8.2[b]	$CDCl_3$
	5.25	5.85	...	7.8–8.5[b]	$o\text{-}C_6H_4Cl_2$
(DQ)Rh(SDBM)	...	...	...	8.05[c,d]	$o\text{-}C_6H_4Cl_2$
(TBQ)Rh(SDBM)	4.15	4.80	...	8.55, 8.60[c]	$CDCl_3$
$(COT)Rh_2(SDBM)_2$	5.25	5.95	...	...	$CDCl_3$
NOR	4.45	4.45	6.65	8.10[b]	$o\text{-}C_6H_4Cl_2$

[a] *Ca.* 40°. Coupling constants, where relevant, are discussed in the text and shown in the figures. Protons H_a and H_b are defined in structure I. [b] Methylene. [c] Methyl. [d] Singlet, since this compound is in the fast-exchange limit at 40°.

Proton Site Exchange (Fluxional Behavior).—The temperature dependence of the pmr spectra of all the complexes was studied to detect any thermally induced exchange processes. The nonequivalent ($\Delta\tau = 0.06$ ppm) methyl peaks of (DQ)Rh(SDBM) coalesced at

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[12] Modified for a Stromberg-Carlson 4060 plotter from a program furnished by Professor T. L. Brown, University of Illinois.

[13] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[14] Provided by Professor G. M. Whitesides, Massachusetts Institute of Technology.

[15] For a review containing details of this method, see C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

[16] G. G. Alexandrov, Yu. T. Struchkov, V. S. Khandkarova, and S. P. Gubin, *J. Organometal. Chem.*, **25**, 243 (1970).

[17] J. A. Evans and D. R. Russell, *J. Chem. Soc. D*, 197 (1971).

[18] S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, **91**, 2504 (1969).

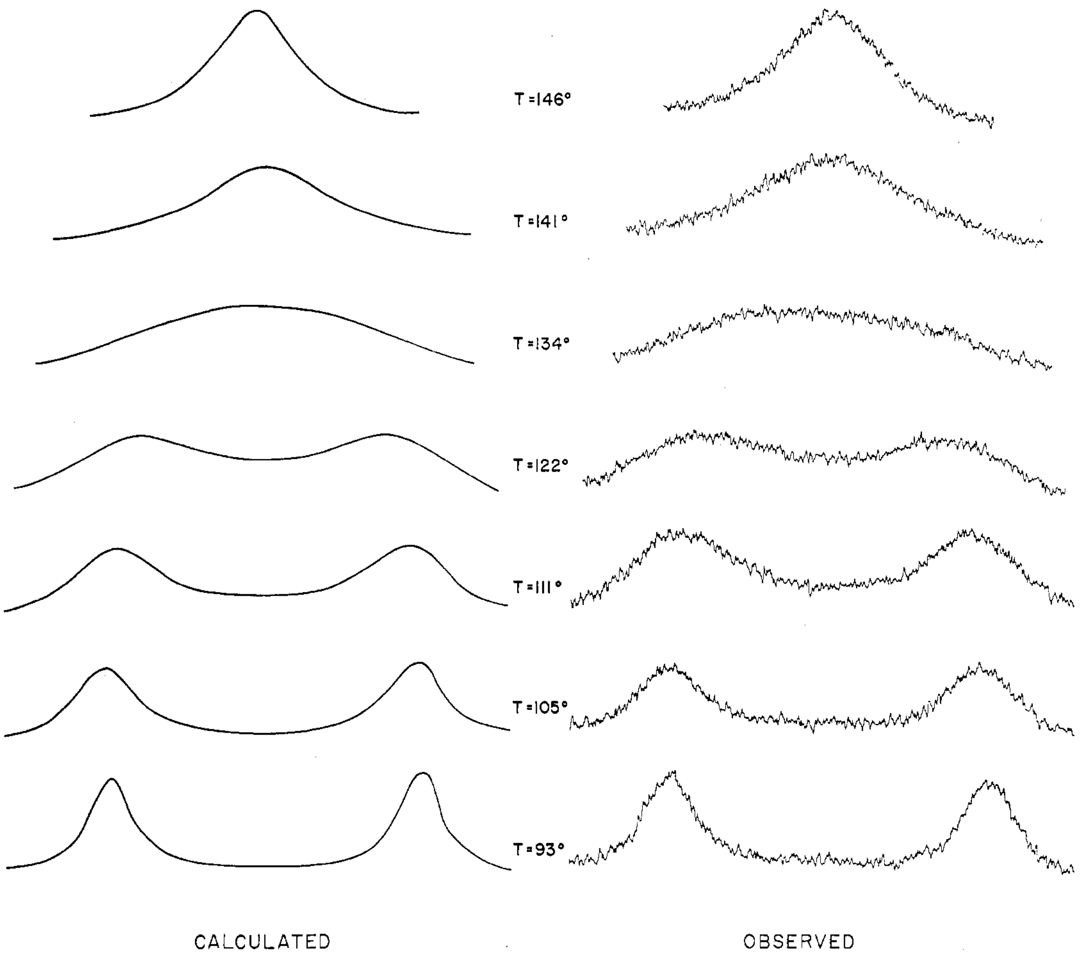

Figure 2.—Observed and calculated temperature dependence of the H_a and H_b resonances of a solution of (NOR)Rh(SDBM) in nitrobenzene. The inverse-means lifetime ($1/2\tau$) values used to calculate the spectra are as follows (in sec^{-1}): 10.2 (93°); 18.8 (105°); 38.6 (111°); 72.5 (122°); 142 (134°); 254 (141°); 415 (146°).

ca. 14° and were in the fast-exchange limit at 40°. Similarly, the H_a and H_b resonances of (NOR)Rh(SDBM) began to broaden at 40° and coalesced above 120° in *o*-dichlorobenzene and nitrobenzene (Figure 2). A coalescence temperature of 89° was observed for the nonequivalent *tert*-butyl groups of (TBQ)Rh(SDBM) in *o*-dichlorobenzene. The H_a and H_b resonances of this compound began to broaden at ~140° in C_6D_5Br. The compounds (COD)Rh(SDBM) and (COT)Rh_2(SDBM)$_2$ were heated to decomposition (155°) in *o*-dichlorobenzene and showed no broadening of the H_a and H_b resonances. The observed spectral changes were reversible with temperature. The samples were darkened somewhat after heating, indicating partial decomposition. Heating above 150° produced irreversible changes in the pmr spectra and the formation of a black precipitate, indicating extensive decomposition. The decomposition process was not investigated.

From the above data, the rates of exchange may be ordered as follows: DQ > NOR > TBQ > COD $\simeq$ COT. The (DQ)Rh(SDBM) complex has the greatest rate since it is in the fast-exchange limit before the others show exchange. Since the chemical shift difference between coalescing olefinic peaks in (NOR)Rh(SDBM) is an order of magnitude greater than the nonequivalent methyl peaks of (TBQ)Rh(SDBM) (Table I), exchange is slower in the latter compound even though it has a slightly lower coalescence temperature. The COD and COT complexes are obviously the slowest since they exhibit no detectable exchange on the pmr time scale. Computer line shape analyses of the temperature-dependent spectra (see Figure 2, for example) confirmed this ordering of rates and furnished information from which the activation parameters tabulated in Table II were computed.

TABLE II

KINETIC ACTIVATION PARAMETERS

Compd	Solvent	E_a, kcal/mol	Log *A*
(NOR)Rh(SDBM)	$C_6H_5NO_2$	21.0 ± 0.9	13.5
	o-$C_6H_4Cl_2$	17.7 ± 0.6	12.2
(TBQ)Rh(SDBM)	*o*-$C_6H_4Cl_2$	16.3 ± 0.9	10.4
(COD)Rh(SDBM)[a]	*o*-$C_6H_4Cl_2$	11.1 ± 0.5	9.1

[a] In the presence of triphenylarsine, As:Rh = 1.25.

Several possible mechanisms for exchange were ruled out by the following experiments. An *o*-dichlorobenzene solution 0.11 *M* in norbornadiene and 0.11 *M* in (NOR)Rh(SDBM) was heated to 139°. The chemical shift difference between the H_a and H_b peaks is greater than the chemical shift difference between the bridgehead protons of free norbornadiene and the complex (Table I). The H_a and H_b resonances coalesced at this temperature while the bridgehead resonances had not. Therefore, the H_a–H_b exchange rate is much faster than exchange with free norbornadiene, and the mechanism

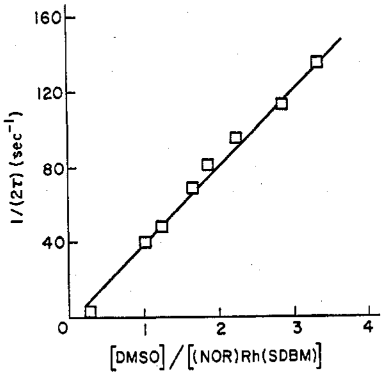

Figure 3.—Dependence of the exchange rate of a deuteriochloroform solution of (NOR)Rh(SDBM) on the concentration of added DMSO at −36°.

cannot involve complete dissociation of the olefin. In a related experiment, a solution containing equimolar amounts of (NOR)Rh(SDBM) and (NOR)Rh(DBM) was heated to 98°. The (NOR)Rh(DBM) resonance at τ 6.10 did not broaden and retained its fine structure, indicating no exchange. Assuming that DBM is at least as labile as SDBM (in fact, monothio-β-diketonates have been shown to be generally less labile than β-diketonates for complexes of "soft" metal[19]), complete dissociation of the monothiodibenzoylmethane anion is eliminated as a possible exchange mechanism. Finally, a solution of (DQ)Rh(SDBM) and (NOR)Rh(TFA) in *o*-dichlorobenzene was heated to 105°. No new resonances were observed in the pmr spectrum. From this experiment it is clear that intramolecular ligand exchange to form (NOR)Rh(SDBM) and (DQ)Rh(TFA) is not occurring even on a time scale of several minutes.

The rate of proton site exchange was increased substantially by the addition of nucleophilic ligands such as triphenylarsine, alkylamines, and DMSO. Even (COD)Rh(SDBM) was fluxional in the presence of triphenylarsine and was found to have an activation energy lower than the norbornadiene analog in the absence of added base (Table II). A plot of $1/2\tau$ for (NOR)Rh(SDBM) against DMSO concentration at −36° in $CDCl_3$ gave a straight line (Figure 3).[20] Similar plots for the addition of triphenylarsine to (NOR)Rh(SDBM), (TBQ)Rh(SDBM), and (COD)-Rh(SDBM) at 37° in $CDCl_3$ gave straight lines from which the second-order rate constants reported in Table III were obtained.[22]

The exchange process in the presence of nucleophiles was shown to be intramolecular in the following experiment. The spectrum of (NOR)Rh(SDBM) in DMSO-d_6 at ambient temperature consisted of a single line at τ 5.60 which showed the "quartet" structure (Figure 4b) identical with the fine structure shown by the individual H_a and H_b resonances of this compound in the low-temperature limiting spectrum in $CDCl_3$ (Figure 4a). Clearly the H_a and H_b protons are in the fast-exchange limit. Decoupling of the bridgehead protons (Figure 4c) causes collapse of the "quartet" into a sharp doublet ($J \approx 2$ Hz; N.B. this coupling constant was incorrectly reported as 1 Hz in ref 4), whereas irradiation of the methylene resonance produced no effect. The observed "quartet" is therefore assigned to the splitting of the apparent[23] triplet of the olefin resonance by coupling to the ^{103}Rh nucleus. The retention of this coupling in the fast-exchange limit rules out any intermolecular exchange of norbornadiene in the presence of added DMSO and probably all nucleophiles.

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE ADDITION OF TRIPHENYLARSINE TO (diolefin)Rh(SDBM) IN $CDCl_3$ AT 37°

Compd	$10^{-3}k_2$,[a] M^{-1} sec^{-1}
(NOR)Rh(SDBM)	9.6 (1.1)
(TBQ)Rh(SDBM)	1.1 (2)
(COD)Rh(SDBM)	0.14 (3)

[a] The numbers in parentheses represent two standard deviations in the least significant figures tabulated.

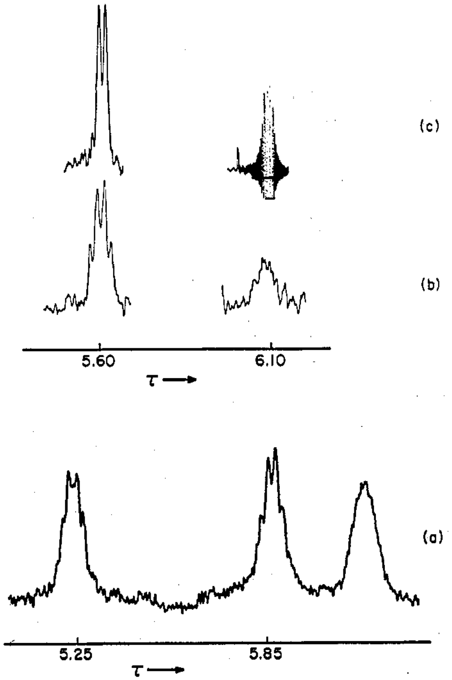

Figure 4.—Proton nmr spectra of (NOR)Rh(SDBM) (a) in $CDCl_3$ at −14°, (b) in DMSO-d_6 at 37°, and (c) in DMSO-d_6 at 37° with spin decoupling of bridgehead protons.

The dependence of the rate on the concentration of complex was measured in C_6D_5Br. The rates of H_a–H_b exchange of two samples of (NOR)Rh(SDBM), the concentrations of which differed by a factor of 5.80, were found by careful line shape calculations to differ by a factor of 2.14. This result is not wholly consistent with either a first- or a second-order process. A series

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(19) E. Uhlemann, Ph. Thomas, G. Klose, and K. Arnold, *Z. Anorg. Allg. Chem.*, **364**, 153 (1969).

(20) The rates for this plot were calculated using approximate equations.[21] Intuitively, computer line shape analysis is considered to be the best method of determining τ. However in this case the use of computer-calculated rates gave a plot with an appreciable negative intercept (*cf.* footnote 22). Hence the approximate calculation fortuitously gives the physically more reasonable result. The two slopes differed by a factor of 1.5.

(21) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

(22) The fact that the plot for the addition of triphenylarsine to (TBQ)-Rh(SDBM) had a zero intercept and that for (COD)Rh(SDBM) had a negative intercept (using computer-calculated rates) suggests that neglect of spin–spin coupling may cause a systematic error in calculating $1/2\tau$. The analogous plot for NOR(Rh)SDBM has a positive intercept corresponding to the rate of exchange in the absence of added ligand at this temperature (*vide infra*).

(23) For a derivation of the pmr spectrum of norbornadiene, see F. S. Mortimer, *J. Mol. Spectrosc.*, **3**, 528 (1959).

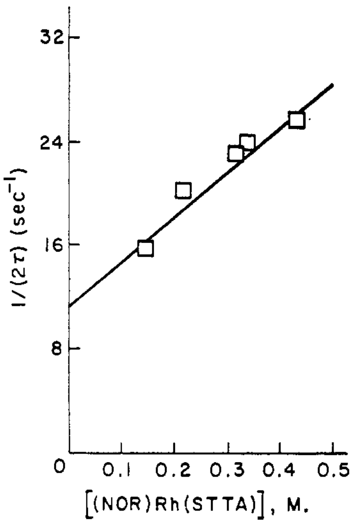

Figure 5.—Dependence of $1/2\tau$ for the olefinic protons of (NOR)Rh(STTA) on the concentration of complex at 74° in bromobenzene-d_5.

of measurements was then carried out at 74° and 105° using the more soluble complex (NOR)Rh(STTA) to increase the concentration range. Plots of the exchange rate *versus* concentration (Figure 5) indicated a dependence of the form written in eq 1. This result

$$1/2\tau = k_1 + k_2[\text{complex}] \qquad (1)$$

requires the previous conclusion[4] of concentration independence, derived from a comparison of spectra at low absolute concentrations in C_6F_5Br (a poorer solvent than C_6D_5Br), to be modified since at higher absolute concentrations a second-order contribution to the rate is readily apparent (Figure 5). The widely made assumption that the rate of exchange of a fluxional molecule is either entirely first- or entirely second-order and that a large relative change in concentration will produce either a large effect on the line shape or no effect at all can lead to erroneous conclusions.

Despite careful temperature calibration and the use of highly purified samples, repeated measurements using different batches of complex showed a qualitatively similar concentration dependence and gave rates of the same order of magnitude, but it was not possible to achieve quantitative agreement between any two sets of data. This irreproducibility might be accounted for by the presence of small quantities of impurity in the solid material, a possibility discussed in more detail below.

Mechanistic Considerations. (a) **Behavior in the Presence of Added Ligands.**—The first-order dependence of the line broadening on added ligand concentration [L] gives the rate law of the exchange reaction denoted by eq 2. This rate law is the same as

$$\text{rate} = k_2[\text{complex}][\text{L}] \qquad (2)$$

that for ligand substitution reactions of planar d^8 complexes for which a five-coordinate intermediate is proposed.[24] Such an intermediate is also proposed to explain the fluxional behavior of molecules of the type (diene)RhLCl in the presence of free L[25] and for ligand substitution reactions in the same class of compounds.[26] A general mechanism consistent with the observed rate law is shown in eq 3, where step a involves reversible

$$\text{(diolefin)Rh(SDBM)} + \text{L} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{(diolefin)Rh(SDBM)L} \qquad (3a)$$

$$\text{(diolefin)Rh(SDBM)L} \xrightarrow{k_b} \text{(diolefin*)Rh(SDBM)L} \qquad (3b)$$

complex formation and step b involves intramolecular rearrangement. A simple way to rationalize the need for step b is to realize that, by the principle of microscopic reversibility, it is not possible to achieve cis–trans exchange simply by forming a five-coordinate transition state in the usual manner,[24] followed by loss of the entering ligand. The kinetic analysis does not provide sufficient information to distinguish between the two possibilities in which (1) rearrangement b is the rate-determining step so that $k_b \ll k_a \simeq k_{-a}$ and $k_2 = k_b(k_a/k_{-a})$ and (2) the formation of the five-coordinate intermediate is the rate-determining step so that $k_a \ll k_b \simeq k_{-a}$ and $k_2 = k_a$. If five-coordinate complexes containing NOR and COD of the type $(CH_3)Rh(diene)L_2$[3a] may be considered as models for the five-coordinate intermediate in eq 3, the observed differences (Table III) in rate constants, especially the greater rate for norbornadiene compared to cycloocta-1,5-diene complexes, strongly suggests that the rearrangement is the rate-determining step. As for the topology of this rearrangement, the different available pathways[27] cannot be distinguished experimentally in the cases studied here.

(b) **Behavior in the Absence of Added Ligands.**—Since the observed rate law (eq 1) has two terms, each must be explored separately. The first-order (concentration independent) term might result from a solvent-assisted process involving a five-coordinate intermediate, a planar–tetrahedral–planar twist, or dissociation of one end of either chelating ligand to form a trigonal intermediate which might then reassociate in the opposite sense.[4] The last mechanism is unlikely from energetic considerations and the fact that the partial dissociation of the monothio-β-diketonate anion to form a polar transition state is not in agreement with the lower activation energy observed for (NOR)Rh(SDBM) in the less polar solvent (Table II). Although the planar–tetrahedral–planar twist is thermally forbidden[28] from the standpoint of conservation of state symmetry, planar–tetrahedral equilibria are observed for a variety of first-row transition metal bis-chelate complexes in noninteracting solvent media.[29] However the loss of crystal field stabilization energy would make a tetrahedral intermediate less favorable for a second-row metal. In support of the solvent-assisted mechanism, there is some evidence that planar d^8 complexes can form weak five-coordinate adducts with chlorinated hydrocarbons.[30] Although, as stated before,[4] it is not possible on the basis of present information to make an absolute assignment of the mechanism,[31] we favor the

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(24) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 19.

(25) K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometal. Chem.*, **15**, 195 (1968).

(26) L. Cattalini, A. Orio, and R. Ugo, *J. Amer. Chem. Soc.*, **90**, 4800 (1968).

(27) E. L. Muetterties, *ibid.*, **91**, 4115 (1969).

(28) T. H. Whitesides, *ibid.*, **91**, 2395 (1969).

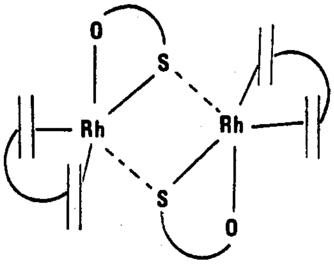
(29) D. H. Gerlach and R. H. Holm, *ibid.*, **91**, 3457 (1969).

(30) P. Haake and R. M. Pfeiffer, *ibid.*, **92**, 5243 (1970).

(31) The planar–tetrahedral–planar twist could be proved by the existence of a first-order term in a noninteracting solvent. A sample of (NOR)Rh(STTA) in a sealed tube with purified decalin as solvent showed fluxional behavior. However the solubility was too low to permit quantitative concentration dependence measurements.

solvent-assisted pentacoordinate intermediate for the reasons mentioned above and because of the similarity to the process shown in eq 3, where L might be a solvent molecule.

There are two possible explanations for the second-order term. The mechanism might involve a bimolecular interaction to form a five-coordinate rhodium dimer such as III which might either undergo an intramolecular rearrangement or exchange monothio-β-diketonate ligands. Such a mechanism has been proposed for the second-order rate law observed for compounds of the type (diene)RhLCl in the absence of added ligand.[25] The second possibility is that, despite efforts to purify the complex, an impurity or decomposition product is present in the solid which acts as an added ligand in solution. The low value of the second-order rate constant, compared to the values obtained in the presence of a strong nucleophile (Table III),[32] and the nonreproducibility (mentioned previously) in measuring this constant support this explanation.



III

In the absence of additional evidence, some insight into the principal type of mechanism involved in the exchange can be derived from the observed differences in rate for different olefins. The observed ordering of rates NOR ≫ TBQ ≫ COD in the absence of added ligand is the same as the second-order rate constants in the presence of added triphenylarsine (Table III).[33] From this result it is likely that a fluxional five-coordinate species is the major intermediate for the site exchange where the fifth ligand might be provided by the solvent, an impurity, or another molecule of complex.

In conclusion it may be noted that the fluxional behavior of the (diolefin)Rh(SDBM) compounds studied here is similar to previously studied systems[2,3] in several respects. First, involvement of a five-coordinate intermediate, or transition state, is indicated. Second, faster exchange rates for norbornadiene compared to cycloocta-1,5-diene complexes have been demonstrated. Finally, the independence of intramolecular rearrangements and intermolecular exchange is confirmed, the latter process being greatly suppressed if not eliminated by the use of chelating ligands in compounds of types I and II.

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(32) Assuming an activation energy of 17 kcal/mol, an impurity with a basicity comparable to that of triphenylarsine would have to be present only to the extent of ~0.02% of the (NOR)Rh(SDBM) concentration to account for the observed k_2 of 37 M^{-1} sec^{-1} at 74°.

(33) The second-order rate constants can be compared despite systematic errors[22] in calculating the exchange rates of (NOR)Rh(SDBM) and (COD)-Rh(SDBM). The application of a 50% maximum error (calculated in a related system in which H_a–H_b coupling is neglected[21]) does not affect the relative ordering of the rate constants.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA,
AND MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

Metal Carbonyl Complexes of Cyclic Azines. I. Reactions of $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, and $[Rh(CO)_2Cl]_2$ with 3,5,7-Triphenyl-4*H*-1,2-diazepine and 3,5,7-Triphenyl-4,5,6-trihydro-1,2-diazepine

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3,5,7-Triphenyl-4*H*-1,2-diazepine reacts with $Fe_2(CO)_9$ to yield a nitrogen-bridged complex $(C_{23}H_{18}N_2)Fe_2(CO)_6$ lacking an N–N bond and with two nonequivalent iron atoms. The nuclear magnetic resonance, mass and Mössbauer spectra of this compound are discussed in the light of the X-ray molecular structure. An analogous complex, $(C_{23}H_{20}N_2)Fe_2(CO)_6$, is the product obtained from 3,5,7-triphenyl-4,5,6-trihydro-1,2-diazepine and $Fe_2(CO)_9$. By contrast $[Rh(CO)_2X]_2$ (X = Cl, Br) yield square-planar complexes of the types $(C_{23}H_{18}N_2)Rh(CO)_2X$ (X = Cl, Br) and $(C_{23}H_{20}N_2)[Rh(CO)_2X]_2$ (X = Cl, Br) with these azines. In the former compounds the heterocyclic azine is bonded to rhodium *via* a nitrogen atom, the N–N bond being retained. In the latter the diazepine behaves as a bridging ligand using both nitrogen atoms as donors. The nuclear magnetic resonance spectrum of $(C_{23}H_{18}N_2)Rh(CO)_2Cl$ indicates that the conformation of the seven-membered ring is identical in the complex and the free ligand. Reactions of these azines with $Ru_3(CO)_{12}$ are also described.

Introduction

The reactions of metal carbonyl derivatives with olefinic ligands have provided a diverse variety of organometallic π complexes.[2] By contrast few studies have been reported on the coordination properties of ligands containing the azine chromophore >C=N—N=C<. From the reaction of benzalazine with diiron enneacarbonyl, Otsuka and coworkers[3a] isolated a derivative of composition $(C_6H_5CH{=}NN{=}CHC_6H_5)Fe_2(CO)_6$ to which the structure I was assigned. The N-N bond of

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(1) (a) University of Waterloo. (b) McMaster University.

(2) H. W. Quinn and J. H. Tsai, *Advan. Inorg. Chem. Radiochem.*, **12**, 217 (1969).

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