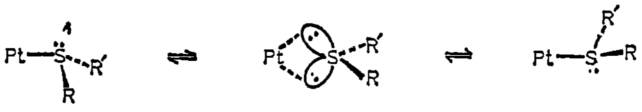
a benzyl sulfoxide appears to invert by a dissociative mechanism and most sulfoxides appear to invert *via* a planar state.

Inversion through a Partially Dissociated State. The multiple bonding possibilities available in platinum(II) complexes lead us to suggest an inversion mechanism in which sulfur retains its distorted tetrahedral configuration and some bonding to platinum persists through the inversion process. This process is depicted below.


9

The configuration **9**, midway in the inversion process, could be an intermediate or a transition state, but a reasonable hypothesis is that there is bonding to both sulfur unshared pairs so that the platinum atom has a distorted pentacoordinate configuration in **9**.[21] The inversion process then is really an internal displacement of one sulfide pair by another sulfide pair in a rearrangement mechanism similar to that suggested for displacement on platinum(II).[22] This proposal is consistent with the retention of Pt–S–C–H coupling above the coalescence temperature, since bond weakening and bond strengthening are involved but there is never opportunity for dissociation of the sulfide ligand.

In **9**, R, R′, Pt, and S are coplanar, but the important difference between this proposal and the suggested mechanism of inversion at nitrogen and at sulfoxide sulfur is that the configuration of sulfur is tetrahedral, not trigonal, in **9**.[23] Also, this proposal would mean there is an internal displacement at platinum rather than true inversion at sulfur in these complexes.

Platinum–Proton Coupling Constants. The average ratio of J_{trans}/J_{cis} is 0.83 (Table II). Three explanations are possible based on coupling through σ bonds, π bonds, and space. Coupling through space is rare.[24] The amount of s character in the π bonds must be small. Therefore, the most reasonable explanation for this ratio is the increased strength of the σ Pt–S bonds in the *cis* isomers due to increased Pt→S π bonding which makes the *cis* sulfurs better ligands than the *trans* sulfurs.[8,25]

Acknowledgment. We are particularly indebted to the late Dr. A. J. R. Bourn and to Professor F. A. L. Anet for valuable discussions and help with the instrumentation.

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(21) (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966); (b) L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, 3, 453 (1964).

(22) (a) P. Haake, *Proc. Chem. Soc.*, 278 (1962); (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(23) A similar proposal has been advanced for sulfide–borane complexes where the state corresponding to **9** should be a transition state: T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).

(24) F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *ibid.*, 87, 5249 (1965).

(25) P. S. Braterman, *Inorg. Chem.*, **5**, 1085 (1966).

Olefin Coordination Compounds of Rhodium. V. The Relative Stabilities and Rates of Exchange of Olefin Complexes of Rhodium(I)

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Abstract: The stabilities of a number of olefin complexes of rhodium(I) have been compared. Alkyl substituents on olefin carbons destabilize rhodium(I) complexes much more than the corresponding silver compounds. Conversely, coordination is enhanced by electronegative substituents, and this is attributed to a stronger π or back-bond. Since C_2F_4 (which coordinates very strongly) displaces ethylene from rhodium(I) much more slowly than do propene or butenes (which coordinate weakly), it is inferred that formation of a π bond plays a minor role in the development of the transition state for nucleophilic olefin exchange.

The bond uniting olefins and transition metals is currently described[1] as comprising (1) a σ bond formed by overlap of the filled π orbital of the olefin with an empty σ-type orbital of the metal atom and (2) a π-type "back-bond" from overlap of a filled, metal d_{xy} or other dπ–pπ hybrid orbital with the antibonding π orbital of the olefin. It is expected that the strength of both the σ bond and π "back-bond" are affected by olefin structure. For example, an electronegative olefin substituent, by reducing the electron density of the olefin, would weaken the σ bond and strengthen the π bond. Depending upon the relative contributions of each, the

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(1) M. J. S. Dewar, *Bull. Soc. Chim. France*, 18, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

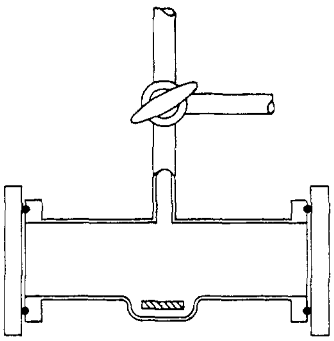

Figure 1. Reaction cell for spectrophotometric analysis.

complex of a substituted ethylene might be more or less stable than that of ethylene itself.

Considerable attention has been given to the effect of structure on the stability of hydrocarbon complexes, particularly of silver;[2] much less information is available on silver compounds of functionally substituted olefins.[3a] Some quantitative results are also reported for copper(I) compounds of alkyl- and functionally substituted olefins[3] and for platinum(II) complexes of olefins of the type $RRC{=}CR(CH_2)_nL^+R_3$[4] (L = N, P, As; n = 1 or 2; R = H or alkyl, not necessarily identical).

The results may be summarized as follows. (1) Enthalpy increments (determined through the change with temperature of the vapor pressure of the unsaturated ligand over the appropriate solid complex) indicate that alkylated olefins form stronger bonds to silver(I)[2b] or copper(I)[3c] than does ethylene. Also, copper is more strongly bonded to acrylonitrile[3d] (ΔH_f = -14.9 kcal mole^{-1}) and acrolein[3e] (ΔH_f = -11.8 kcal mole^{-1}) than to propylene[3c] (ΔH_f = -11.0 kcal mole^{-1}) or ethylene[3c] (ΔH_f = -11.0 kcal mole^{-1}). (2) In spite of the enthalpy values, $CuCl \cdot C_3H_6$ dissociates more completely than $CuCl \cdot C_2H_4$ over a wide temperature range. The vapor pressures (in atmospheres) developed at 0° by copper(I) compounds increase in the following order: $CuCl \cdot CH_2{=}CHCN$ (0.014, extrapolated)[3d] < $CuCl \cdot CH_2{=}CHCHO$ (0.038)[3e] < $CuCl \cdot C_2H_4$ (1.95)[3b] < $CuCl \cdot C_3H_6$ (2.6, extrapolated).[3b] In solution, propylene–silver complex dissociates more completely than the ethylene compound.[2a] (3) Stabilities of platinum complexes[4a,d] increase with structure modifications which reduce electron density at the olefin bond.

In addition to these quantitative results, a special stabilization of olefin complexes by electronegative substituents[5] is indicated by the facile synthesis and relatively high stability of numerous compounds. These include complexes of manganese,[6a] iron,[6b] nickel,[6c,d] copper,[6e] rhodium,[6b,g] and platinum[6h] with olefins substituted by carboxyl,[6b,d,f,h] cyano,[6a–c,e,f,h] or halogen.[6g,h]

The properties of 2,4-pentanedionatobis(ethylene)-rhodium(I), $acacRh(C_2H_4)_2$, suggest it may be used conveniently to measure the effect of olefin substituents on the stability of complexes with rhodium(I). This compound is thermodynamically stable; thus, the extent of dissociation of ethylene in ethylene glycol solution is less than 0.1% at 80°. However the coordinated ethylene is kinetically labile; in the presence of free ethylene at $-50°$ the half-life of coordinated ethylene is less than 10^{-2} sec. When solutions of the complex are treated with an olefin, ethylene is displaced to some extent according to eq 1. In an open reactor an excess

$$acacRh(C_2H_4)_2 + \text{olefin} \rightleftharpoons acacRh(C_2H_4)(\text{olefin}) + C_2H_4 \quad (1)$$

of olefin will generally replace both ethylene ligands to give $acacRh(olefin)_2$, but measurements may be confined to concentrations appropriate to eq 1. Its equilibrium constant reflects the strength of the coordination bond between rhodium(I) and the added olefin as compared to the rhodium–ethylene bond.

The extent and rate of ethylene displacement from $acacRh(C_2H_4)_2$ was measured by infrared spectrophotometric analysis of the gas over the reaction solution using the cell shown in Figure 1. A dilation of the cell held a solution of $acacRh(C_2H_4)_2$, which was stirred by a polytetrafluoroethylene-covered magnet. Gaseous olefins were used in most experiments, and these were introduced through a three-way stopcock. The cell-holder was a polyethylene dish in which the cell dilation was immersed in water at a controlled temperature. The technique is very convenient and moderately precise.

Equilibrium was generally attained within a few minutes, but with some highly substituted olefins or in dilute solutions reaction was slow enough to obtain kinetic data.

Experimental Section

A Perkin-Elmer Model 237 spectrophotometer was used at slow scan speed. The general procedure was to charge the cell with a measured amount of olefin and $acacRh(C_2H_4)_2$ in toluene solution. The quantity of ethylene released was measured through the absorptivity of the gas phase at 10.5 μ, and this was supplemented in some experiments by a similar evaluation of noncoordinated added olefin based on a characteristic absorption. From these data and estimates of the solubilities of ethylene and the other olefin in the reaction medium, approximate equilibrium constants could be calculated.

The detailed procedures depended upon the nature of the olefin which was employed to displace ethylene. Typical examples follow.

Displacement by Vinyl Chloride. A solution of 0.0129 g (0.050 mmole) of $acacRh(C_2H_4)_2$ in 2.00 ml of toluene was pipetted into the cell and frozen by immersing the dilation in liquid nitrogen. The

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(2) (a) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962), and references cited there; (b) H. W. Quinn and D. N. Glew, *Can. J. Chem.*, 40, 1103 (1962).

(3) (a) J. Chatt in "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., W. Heffer and Sons, Ltd., Cambridge, England, 1953, pp 44–47; (b) E. R. Gilliland, J. E. Seebold, J. R. FitzHugh, and P. S. Morgan, *J. Am. Chem. Soc.*, 61, 1960 (1939); (c) E. R. Gilliland, H. L. Bliss, and C. E. Kip, *ibid.*, **63**, 2088 (1941); (d) G. N. Schrauzer, *Chem. Ber.*, **94**, 1891 (1961); (e) S. Kawaguchi and T. Ogura, *Inorg. Chem.*, 5, 844 (1966).

(4) (a) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc., Sect. A*, 324 (1967); (b) *ibid.*, 328 (1967); (c) F. R. Hartley and L. M. Venanzi, *ibid.*, 333 (1967); (d) R. G. Denning and L. M. Venanzi, *ibid.*, 336 (1967).

(5) *Cf.* G. N. Schrauzer, *Chem. Ber.*, 94, 642 (1961).

(6) (a) M. L. Zeigler and R. K. Sheline, *Inorg. Chem.*, 4, 1230 (1965); (b) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963); (c) G. N. Schrauzer, *J. Am. Chem. Soc.*, 81, 5310 (1959); (d) E. Weiss and K. Stark, *Z. Naturforsch.*, 20b, 490 (1965); (e) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962); (f) L. Porri and A. Lionetti, *J. Organometal. Chem.* (Amsterdam), **6**, 422 (1966); (g) R. Cramer and G. Parshall, *J. Am. Chem. Soc.*, **87** 1392 (1965); (h) W. J. Bland and R. D. Kemmitt, *Nature*, 211, 963 (1966).

cell windows were positioned; the cell was evacuated, placed in the holder containing water at 25 ± 0.2°, and pressured with nitrogen to 100 mm. Vinyl chloride was introduced in increments by hypodermic syringe through a septum attached to one of the arms of the cell stopcock. After each addition the solution was stirred and the spectrum recorded after equilibration (less than 10 min). The amount of ethylene liberated was estimated by comparison of the absorbance at 10.5 μ with an empirical curve relating optical density to ethylene charge in this cell under the conditions of the experiment. Assuming eq 1, the amounts of C_2H_4, C_2H_3Cl, acacRh$(C_2H_4)_2$, and acacRh$(C_2H_4)(C_2H_3Cl)$ in the cell could be calculated. The results are shown in Table I.

Table I. Equilibrium: C_2H_3Cl + acacRh$(C_2H_4)_2$ $\overset{25°}{\rightleftarrows}$ C_2H_4 + acacRh$(C_2H_4)(C_2H_3Cl)$

Added C_2H_3Cl, ml	Released C_2H_4, mmole	Noncoord C_2H_3Cl, mmole	acacRh-$(C_2H_4)_2$, mmole	K_E
0.25	0.0088	0.0012	0.0412	0.187
0.50	0.0156	0.0044	0.0344	0.197
1.00	0.0224	0.0176	0.0276	0.126
1.50	0.0300	0.0300	0.0200	0.182
2.00	0.0336	0.0464	0.0164	0.181
2.50	0.0344	0.0656	0.0156	0.142
			Average	0.170 ± 0.019[a]

[a] The probable error is calculated as 0.674 × sample standard deviation; see E. B. Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p 255.

Ethylene and vinyl chloride are distributed between the gas and liquid phases in proportions which depend upon their solubility in toluene. Thus at 25° and an ethylene pressure of 1 atm, 3.02 ml of ethylene dissolves in 1 ml of toluene.[7] Since the volume of the cell was 83.0 ml and it contained 2.00 ml of toluene, about 2 × 3.02/[2 × 3.02 + (83.0 − 2.0)] or 0.0694 of the ethylene in the cell was dissolved. The solubility of vinyl chloride is estimated (see following paragraph) to be 52.9ml/ml of toluene. A similar calculation indicates 0.567 of the vinyl chloride was dissolved. Equilibrium constants were calculated using the formula

$$K_E = \frac{[\text{acacRh}(C_2H_4)(C_2H_3Cl)][C_2H_4]f_{C_2H_4}}{[\text{acacRh}(C_2H_4)_2][C_2H_3Cl]f_{C_2H_3Cl}}$$

where concentrations are in millimoles and $f_{C_2H_4}$ = fraction of C_2H_4 in solution. It is assumed that mmole of acacRh(C_2H_4)-(C_2H_3Cl) = mmole of C_2H_4.

Since solubilities in toluene have not been reported for most of the olefins used here, it was generally assumed that these all give ideal solutions and that the solubilities of the gaseous olefins are inversely proportional to their saturation pressures. These saturation pressures were calculated by interpolation of data from various sources and are given along with the estimated gas solubilities in Table II.

Displacement by Tetrafluoroethylene. Unlike most olefins listed in Tables III and IV, tetrafluoroethylene displaces ethylene from acacRh$(C_2H_4)_2$ so slowly that the rate may be followed conveniently by observing the change in absorbance at 10.5 μ. The kinetics (reaction of 0.5 mmole each of acacRh$(C_2H_4)_2$ and C_2F_4 in 2.00 ml of toluene) correspond to a second-order reaction since a plot of $OD/(OD_\infty - OD)$ against time is linear[8] (Figure 2).

For tetrafluoroethylene, the equilibrium in eq 1 lies far to the right, so it is experimentally advantageous in determining the equilibrium constant to measure unreacted C_2F_4 (using the absorption at 8.4 μ) rather than liberated C_2H_4. Since it was expected that tetrafluoroethylene might deviate widely from ideal solubility, measured solubilities of ethylene[7] and tetrafluoroethylene were employed for calculations. The values used were: ethylene, 4.35 (0°), 3.02 (25°); tetrafluoroethylene, 2.00 (0°), 1.43 (25°) ml of gas/ml of solvent (1 atm gas pressure).

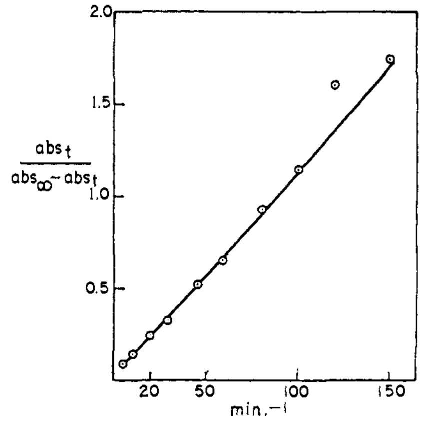

Figure 2. Rate of displacement of C_2H_4 from acacRh$(C_2H_4)_2$ by C_2F_4.

Displacement by Styrene. This experiment is typical for liquid olefins. The dilation of the cell was charged with 0.100 mmole of styrene in 2.0 ml of toluene. The solution was frozen with liquid nitrogen, and 0.050 mmole of solid acacRh$(C_2H_4)_2$ was added. The cell was closed, evacuated, warmed to 25.0 ± 0.2°, and pressured to 100 mm with nitrogen. The amount of released ethylene,

Table II. Saturation Pressures and Solubilities of Olefins

	0°		25°	
	Satn pressure, mm	Solubility, ml of gas/ml of toluene	Satn pressure, mm	Solubility, ml of gas/ml of toluene
Ethylene[b]	30,500	(4.35)	51,500[f]	(3.02)
Propylene[b]	4,400	30.2	8,700	17.9
1-Butene[a,b]	964	138	2,200	70.6
cis-2-Butene[a]	658	202	1,600	97.2
trans-2-Butene[a]	733	181	1,780	87.5
Isobutylene[a]	988	134	2,300	67.6
Vinyl fluoride[c]	11,000	12.1	21,000	7.40
Vinyl chloride[d]	1,290	103	2,940	52.9
cis-1,2-Difluoroethylene[e]	2,137	62.1	4,930	31.6
trans-1,2-Difluoroethylene[e]	6,210	21.4	12.900	12.1

[a] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp 115–123. [b] Footnote *a*, Vol. II, 1965, pp 61–66. [c] E. I. du Pont de Nemours and Co., Inc., Organic Chemicals Department, New Products Report -201-F, Sept 11, 1959. [d] R. A. McDonald, S. A. Shrader, and D. R. Stull, *J. Chem. Eng. Data*, **4**, 311 (1959). [e] 1,2-Difluoroethylene was prepared by dechlorination of CHFCl-CHFCl (W. S. Durrell, G. Westmoreland, and M. G. Moshonas, *J. Polymer Sci.*, **A3**, 2975 (1965)), and the isomers were separated by glc. The vapor pressure of *cis*-1,2-difluoroethylene was measured from −36 to +10° and over this range it corresponds to the equation $\log P = 7.635 - 1.175T^{-1} \times 10^3 \pm 0.003$. The tabulated pressure at 0° is the measured value while the pressure at 25° was obtained by extrapolation. The vapor pressure of *trans*-1,2-difluoroethylene was measured between −53 and −26° and over that range corresponds to $\log P = 7.564 - 1.029T^{-1} \times 10^3 \pm 0.006$. The tabulated pressures were obtained by extrapolation. [f] This value for the "saturation pressure" of ethylene at 25° was obtained by extrapolating the log vapor pressure *vs.* $1/T$ plot beyond the critical temperature of ethylene.

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(7) Calculated from data of D. B. Todd and J. C. Elgin, *A.I.Ch.E. J.*, 1, 20 (1955).

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, pp 28–30, 37–38.

Table III. Equilibrium Constants, Enthalpies, and Entropies

$\text{olefin} + \text{acacRh}(C_2H_4)_2 \rightleftharpoons \text{acacRh}(C_2H_4)(\text{olefin}) + C_2H_4$

Olefin	$K_E \times 10^3$ (25°)	$K_E \times 10^3$ (0°)	ΔH, kcal mole^{-1}	ΔS, eu
$CH_2{=}CHCH_3$	78 ± 7	63 ± 8	1.4 ± 0.9	−0.5 ± 0.5
$CH_2{=}CHC_2H_5$	92 ± 18	79 ± 12	1.0 ± 1.4	−1.7 ± 5.0
cis-C_4H_8	4.1 ± 0.3	3.1 ± 0.3	1.8 ± 0.8	−4.9 ± 3.0
trans-C_4H_8	2.0 ± 0.3	1.5 ± 0.1	1.9 ± 0.7	−6.1 ± 2.6
i-C_4H_8	0.35 ± 0.02	0.19 ± 0.02	3.9 ± 0.7	−2.6 ± 2.5
$CH_2{=}CHCl$	170 ± 19	150 ± 10	0.8 ± 0.8	−0.8 ± 2.9
$CH_2{=}CHF$	320 ± 22	410 ± 70	−1.6 ± 1.1	−7.5 ± 3.8
trans-$CHF{=}CHF$	1240 ± 360	1320 ± 410		
cis-$CHF{=}CHF$	1590 ± 330	2080 ± 460		
$CH_2{=}CF_2$[a]	100 ± 10			
$CH_2{=}CHOCH_3$[b]	18 ± 2			

[a] Based on a measured value for the solubility of $CH_2{=}CF_2$ of 2.46 ml of $CH_2{=}CF_2$/ml of toluene. [b] Based on a measured valued for the solubility of $CH_2{=}CHOCH_3$ of 167 ml of $CH_2{=}CHOCH_3$/ml of toluene.

measured as described earlier, was found to be 0.036 mmole. The vapor pressure of styrene at 25° is about 7 mm, and if it is assumed that the partial pressure is proportional to the mole fraction (about 0.005), virtually all the unreacted styrene is in solution. Since, as calculated earlier, 0.0694 of the ethylene is in solution, $K_E = (0.036)(0.036 \times 0.069)/(0.014 \times 0.064) = 0.100$.

Synthesis of acacRh($CH_2{=}CHCl)_2$. A flask was charged with 0.50 g of acacRh$(C_2H_4)_2$, evacuated, and chilled to −25°. Vinyl chloride (about 10 ml) was condensed in the flask which was then warmed slightly to distil unreacted vinyl chloride within 20 min. The residue was again treated in similar fashion with about 10 ml of vinyl chloride to get a yellow oil. This crystallized when washed with isobutane at −50°. The product (0.48 g, 76% yield) was recovered (by removing isobutane at −50° under nitrogen through a filter stick) and dried at 1 mm (20°) for 0.5 hr. It melted at 42–43°. *Anal.* Calcd for $C_9H_{13}O_2RhCl_2$: C, 33.06; H, 4.01; Cl, 21.69. Found: C, 32.38; H, 4.21; Cl, 21.11. A sample (KBr wafer) absorbed at 3000 (m), 2930 (w), 1620 (?, sh), 1570 (s), 1458 (sh), 1428 (w), 1378 (s), 1309 (m), 1274 (m), 1230 (w), 1197 (w), 1023 (m), 954 (w), 936 (w), 922 (sh), 782 (m), and 677 (s) cm^{-1}.

The nmr spectrum (in d_6-acetone) has sharp absorptions corresponding to a 2,4-pentanedionato group (−4.99 and −1.53 ppm) and two broad absorptions attributed to vinyl chloride. One is centered at −4.50 ppm and the other at −3.05 ppm (integrated ratio 1/2.4).

Synthesis of acacRh$(C_3H_6)_2$. A 0.5-g sample of acacRh$(C_2H_4)_2$ was treated three times with about 20 ml of liquid CH_3Cl and 10 ml of liquid C_3H_6 as described earlier for synthesis of the vinyl chloride complex. (Methyl chloride was used to raise the reflux temperature of the reaction mixture.) The product was a light brown solid melting at 40°. The yield was 0.4 g (73%). *Anal.* Calcd for $C_{11}H_{19}O_2Rh$: C, 46.16; H, 6.69. Found: C, 45.11; H, 6.56. Reaction with aqueous NaCN released a gas identified as propene by its infrared spectrum. Infrared (KBr wafer) absorption was found at 3000 (m), 2930 (sh), 1630 (sh), 1560 (s), 1520 (s), 1423 (sh), 1388 (s), 1272 (m), 1236 (w), 1203 (w), 1056 (m), 987 (w), and 938 (m) cm^{-1}. The nmr spectrum is described in the following section.

Results

Equilibria. Equilibrium constants for eq 1 corresponding to a variety of olefins are given in Tables III and IV. The values in Table III are the means of 6 to 15 observations covering a 6- to 20-fold variation of initial olefin concentration. The listed probable error is based on the range of values found for K and generally amounts to about 10% of the mean. Further uncertain error is introduced by the use of the ratio of olefin vapor pressures for gas solubility ratios. For the few olefins whose solubilities are recorded (ethylene, propylene, isobutylene) the difference between the ratio of their solubilities and the corresponding ratio of gas vapor pressures is as large as 20% of the solubility ratio. The equilibrium constants in Table IV are based on at least four observations and are believed to have about the same accuracy as those in Table III.

Table IV. Equilibrium Constants[a]

$\text{olefin} + \text{acacRh}(C_2H_4)_2 \rightleftharpoons \text{acacRh}(C_2H_4)(\text{olefin}) + C_2H_4$

Olefin	K_E (25°)	Olefin	K_E (25°)
$CHF{=}CF_2$	88	$CH_2{=}CHC_6H_5$	0.08
$CF_2{=}CF_2$	59	$CH_2{=}CHCN$	>50
$CH_2{=}CCl_2$	No reaction	$CH_2{=}CHN(CF_3)_2$	0.1
cis-$CHCl{=}CHCl$	*Ca.* 0.07	CO	>100
$CCl_2{=}CCl_2$	No reaction		

[a] Based on the following solubilities (ml of gas/ml of toluene at 25°): C_2H_4 (3.02), $CHF{=}CF_2$ (4.31), and $CF_2{=}CF_2$ (1.43). Other olefins are assumed to be concentrated in the liquid phase.

Also included in Table III are calculated values for the enthalpy and entropy change accompanying olefin exchange. Although the probable error is large, these properties appear to be a reasonable basis for qualitative discussion.

The equilibrium constants listed in Table III show that increasing substitution of hydrogen by methyl groups reduces the stability of olefin complexes of rhodium(I). Similar results have been obtained with silver[2,3a,9] and copper(I)[3] compounds. On the other hand, substitution by fluorine increases complex stability. Thus, although the vinyl fluoride complex is less stable than acacRh$(C_2H_4)_2$ ($K = 0.32$), the 1,2-difluoroethylene compounds are about as stable as acacRh$(C_2H_4)_2$, and the trifluoroethylene complex (Table IV) is much more stable.

Stability is also affected by the position of substitution. Complexes of disubstituted ethylene are less stable if the substituents are at the same carbon. Thus, the isobutylene complex ($K = 0.00035$) is less stable than

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(9) R. J. Cvetanović, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Am. Chem. Soc.*, 87, 1827 (1965).

the complexes of *cis*-2-butene ($K = 0.0041$) or *trans*-2-butene ($K = 0.0020$). Similarly, complexes of 1,1-difluoro- or 1,1-dichloroethylene are less stable than those of the corresponding 1,2-dihaloethylenes.

The enthalpy increments listed in Table III indicate that displacement of ethylene by propene or a butene is endothermic, but reaction with vinyl fluoride is slightly exothermic. Entropy decreases in all ethylene displacements. (Enthalpy and entropy increments were not calculated for 1,2-difluoroethylenes because the probable error in the equilibrium constants was prohibitively large, possibly as a consequence of partial displacement of the second ethylene ligand.)

Kinetics. Displacement of C_2H_4 in acacRh(C_2H_4)$_2$ by C_2F_4 or C_2F_3H is relatively slow, and only one ethylene ligand is lost. The reaction, which was followed by measuring the rate of release of C_2H_4, has the kinetics of a second-order reaction of the polyfluoroolefin and acacRh(C_2H_4)$_2$. Plots of absorbance$_t$/(absorbance$_\infty$ − absorbance$_t$) against time[8] for reaction with C_2F_4 at 0 and 25° are linear, and the quotient of the slopes when adjusted for the solubility of C_2F_4 in toluene at the two temperatures corresponds to an Arrhenius activation energy of 12 kcal.

If it is assumed that the ratio of solubilities of C_2F_3H in toluene at 0 and 25° is the same as for C_2F_4 at these temperatures, then displacement of ethylene from acacRh(C_2H_4)$_2$ by C_2F_3H has an activation energy of 8 kcal.

Nmr Spectrum of acacRh($CH_2{=}CHCH_3$)$_2$. Another Route to Relative Stabilities of Olefin Complexes. The nmr spectrum of a solution of acacRh(C_2H_4)$_2$ at 25° exhibits coordinated ethylene as a single sharp absorption.[10] Failure of ethylene protons to be resolved may be attributed to rapid intramolecular exchange, since it has been estimated that the average half-life of coordinated ethylene in acacRh(C_2H_4)$_2$ is less than 10^{-4} sec. When ethylene is added to the test solution, exchange of free and coordinated ethylene is so fast that the spectrum has a single ethylene absorption, broadened and displaced from −2.96 toward −5.3 ppm, the nmr resonance frequency for C_2H_4, to an extent which depends on the amount of free ethylene in the sample.[11]

The nmr spectrum of a $CDCl_3$ solution of acacRh($CH_2{=}CHCH_3$)$_2$ has four areas of absorption: (a and b) sharp peaks at −5.32 and −1.99 ppm assigned to protons on the central and terminal carbon atoms, respectively, of coordinated acetylacetonyl; (c) a doublet (split 5 cps) centered at −1.57 ppm attributed to methyl protons of coordinated propylene; and (d) a smeared, irregular quadruplet between −2.65 and −3.40 ppm corresponding to olefinic protons of coordinated propylene. When propylene is added to the solution, the fine structure of the spectrum of uncoordinated propylene is barely changed and nmr absorptions of free and coordinated propylene are clearly distinguishable. Since absorptions of methyl protons of free and coordinated propylene are separated by 14 cps, the half-life of coordinated propylene is estimated[12] to be longer than 0.1 sec.

When propylene is added to a solution of acacRh(C_2H_4)$_2$, a part of the ethylene is displaced according to eq 1, and the nmr absorption corresponding to ethylene shifts downfield (as a consequence of exchange of coordinated and displaced ethylene) by an amount which depends on the concentration of displaced ethylene. The concentration of displaced ethylene can be estimated by reference to spectra of solutions containing acacRh(C_2H_4)$_2$ and varying amounts of ethylene. Methyl protons of coordinated acetylacetonyl provide a convenient internal standard for measuring the shift of ethylene proton absorption.

Calculations based on experiments with solutions of 0.10 g of acacRh(C_2H_4)$_2$ and 1.5, 5.0, 10.0, or 25.0 ml of gaseous propylene in 1.0 ml of $CDCl_3$ gave a value for K_E of 0.07 ± 0.01, agreeing with that listed for propylene in Table III.

Discussion

Equilibria. The increased stability of complexes of highly fluorinated olefins (Table III) and parallel results with other polar olefins (Tables III and IV) apparently reflect stabilization by negative substituents superimposed on steric destabilization. Destabilization by electropositive groups is less obvious but nevertheless demonstrable. Propylene is less strongly bonded than ethylene ($K = 0.078$), and a similar trend in silver–olefin complexes has generally been attributed to steric hindrance. However, if data concerning coordination of olefins by silver(I) are put into the form of eq 1, and compared with the corresponding reactions of rhodium(I), it is found that the effect of an alkyl substituent is about ten times as large for rhodium(I) complexes as for the corresponding silver compounds. Thus, substitution of olefinic hydrogen by CH_3 reduces the stability of olefin–rhodium complexes by a factor of about 0.03 to 0.08 (column 5, Table V), as compared with approximately 0.2 to 0.5 for silver compounds (column 4, Table V). Consequently, it is proposed that steric hindrance, which accounts for behavior of silver compounds, is augmented by electrical effects in hydrocarbon–rhodium complexes.

Table V. Equilibrium Constants, Enthalpies, and Entropies
$C_2H_4 \cdot ANgO_3 + \text{olefin} \rightleftarrows \text{olefin} \cdot AgNO_3 + C_2H_4$[a]

Olefin	ΔH, kcal mole^{-1}	ΔS, eu	K_E (25°)	K_E (25°)-Rh[b]
$CH_2{=}CHCH_3$	−0.1	−1.5	0.43	0.078
$CH_2{=}CHC_2H_5$	−0.3	−2.0	0.50	0.092
cis-C_4H_8	−0.1	−2.2	0.28	0.0041
trans-C_4H_8	0.6	−1.7	0.091	0.0020

[a] Calculated from data of ref 9. [b] Comparable rhodium complex, from Table III.

Accordingly, electronegative groups strengthen and electropositive groups weaken coordination of olefins to rhodium(I). Since this is the manner in which the π-bond part of the olefin coordination bond is expected to respond to these substituents, it is concluded that the

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(10) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(11) Rapid rotation of coordinated ethylene in acacRh(C_2H_4)$_2$ with the coordination bond as axis would lead to a single absorption for coordinated ethylene in solutions of acacRh(C_2H_4)$_2$.[10] However, it would not account for the effect of added ethylene on the spectrum.

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

electrical effect acts principally through the π bond. This might occur either because the π bond is the stronger bond or because it is more susceptible to inductive effects.[13]

If the enthalpy data of Table III are accepted as significant, they can be interpreted as tending to reinforce the proposed importance of the π bond in electronic effects.[14] Displacements of ethylene by alkylated olefins have a positive enthalpy increment because a weaker coordination bond is formed through a combination of steric and electronic factors.

Conversely, in displacement of ethylene by vinyl fluoride enthalpy decreases because of stronger π bonding. The entropy increment is apparently large enough to overcome a negative enthalpy change giving a positive free-energy change for displacement of ethylene by vinyl fluoride.

In accounting for the relative stabilities of silver(I)-olefin complexes most authors,[2a,3a,15] although recognizing the possible importance of electronic factors, have been concerned with steric effects. However, the greater stability of 3-methylcyclopentene as compared with 4-methylcyclopentene was attributed to electronic effects,[16] and this is supported by molecular orbital calculations[17] which indicate that the increased stability of 3-methylcyclopentene complex is due to the higher donor power of the double bond leading to a stronger σ bond.

Quinn and co-workers,[2b,13a] in precise measurements involving solid olefin complexes of $AgBF_4$ and $AgClO_4$, have demonstrated a progressive *enthalpy change favoring coordination as ethylene hydrogen is replaced by methyl.* This is in contrast to results reported here for rhodium complexes. They found that the amount of perturbation of the olefin double-bond stretch frequency as a consequence of complex formation ($\nu_{\text{uncomplexed}} - \nu_{\text{complexed}}$) was linearly related to the olefin ionization potential (equivalent to olefin basicity) and to the enthalpy change accompanying complex formation. These results indicate that in formation of silver complexes, olefin substituents affect the σ bond primarily.

Kinetics. It has been estimated that the half-life of coordinated ethylene in $acacRh(C_2H_4)_2$ is less than 10^{-4} sec at 25°.[10,18] Although displacement of ethylene by C_2F_4 is thermodynamically favored ($K = 59$), the rate is less than 10^{-6} that of ethylene exchange. This behavior conforms with a mechanism in which the rate-determining step is the nucleophilic addition of the olefin to a d^8 square-planar rhodium(I) complex. It further suggests that development of the σ bond (and not the π bond) is of critical importance in the formation of the activated complex.[19]

Acknowledgment. Dr. C. A. Tolman made important suggestions relating to the calculation of equilibrium constants.

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[13] The much stronger coordination of 1,2-dihaloethylene as compared with 1,1-dihalides may be a consequence of the symmetrical development of both lobes of the π bond: (a) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2897 (1965); (b) J. R. Holden and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955).

[14] Another reasonable interpretation is that the entropy and enthalpy changes reflect differences in the solvation of either the olefins or their complexes. The possibility of measuring a series of equilibrium constants for eq 1 in ethylene glycol, the solvent generally used with silver complexes, has been explored. $acacRh(C_2H_4)_2$ is so sparingly soluble in this liquid that the concentration must be reduced by a factor of 10. The solubility of ethylene is also lower in glycol than in toluene. Because of dilution and the high viscosity of the solutions, equilibration is inconveniently slow. A few measurements with propene gave a value for K_E of 0.06.

[15] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962); I. Jardine and F. J. McQuillin, *J. Chem. Soc., Sect. C*, 458 (1966).

[16] E. Gil-Av and J. Herling, *J. Phys. Chem.*, **66**, 1208 (1962).

[17] W. H. Prichard and W. J. Orville-Thomas, *Theoret. Chim. Acta*, **3**, 426 (1965).

[18] R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

[19] In a related reaction, H. G. Schuster-Woldan and F. Basolo (*J. Am. Chem. Soc.*, **88**, 1657 (1966)) noted the importance of σ-bond formation. They found phosphines (better σ donors) displaced CO from π-$C_5H_5Rh(CO)_2$ faster than phosphites (better π acceptors).

Rates and Mechanism of Substitution Reactions of Nitrosyltetracarbonylmanganese(0) and Trinitrosylcarbonylmanganese(0)

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Abstract: Kinetic studies for substitution reactions of the five-coordinated compound $MnNO(CO)_4$ and some of its derivatives are reported. The parent compound reacts by a second-order process, whereas the replacement of CO from $MnNO(CO)_3L$ is largely a first-order reaction. Investigations on the last known member of the pseudonickel carbonyl series, $Mn(NO)_3CO$, show it to be very reactive. Its rate of reaction depends on the nature and concentration of the reagent.

The compound $MnNO(CO)_4$[2] is isoelectronic and presumably isostructural with $Fe(CO)_5$ which has a trigonal bipyramidal structure.[3] Several five-coordinated metal complexes are known,[4] but the kinetics and mechanism of substitution reactions of these systems have not been extensively examined. Three such studies have been reported. One deals with the reactions of $RCOCo(CO)_4$ with $P(C_6H_5)_3$,[5] another with

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[2] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

[3] J. Donohue and A. Caron, *Acta Cryst.*, **17**, 663 (1964).

[4] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).