

Complexation of Olefins with Planar Rhodium(I) Co-ordination Compounds

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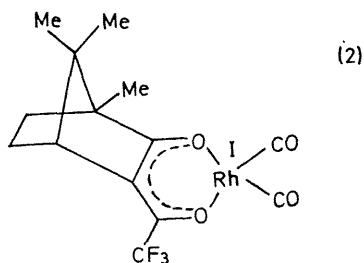
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Summary Complexation of lower olefins with $\text{Rh}(\text{CO})_2(\text{acac})$ and $[\text{Rh}(\text{CO})_2(3\text{-trifluoroacetylcamphorate})]$, presumably through a five-co-ordinate bond, has been detected by g.l.c. and applied to selective olefin separations.

STABLE pentaco-ordinate Rh^{I} compounds with olefinic

ligands have been isolated recently, *e.g.* with potentially quadridentate groups such as trialkenyl- or triarenylphosphines.¹ An intermediate five-co-ordinate species has also been suggested to explain the kinetics of the exchange of stibines by amines in Rh^{I} derivatives.² We therefore investigated the complexation of simple olefins with planar Rh^{I} complexes, which has been detected by g.l.c.

The increase in retention volume of a solute, v , resulting from the addition of a complex-forming reagent to the stationary phase, permits the determination of the stability



constant involved.³ Data obtained at 30° for C₂–C₄ olefins with 0.1M-solutions of Rh(CO)₂(acac) (1) and the newly prepared [Rh(CO)₂(3-trifluoroacetylcamphorate)]⁴ (2) are given in the Table.

Relative retention volumes of C₂–C₄ olefins with squalane and 0.1M-solutions of (1) and (2) in squalane as stationary phases.^a

Compound	Rh Complex	
	Squalane	(1) (2)
Ethylene	0.01	1.13 10.0
Propene	0.07	0.79 7.95
Isobutene	0.25	0.31 1.08
But-1-ene	0.25	3.40 30.4
Buta-1,3-diene	0.25	12.50 140 ^b
n-Butane	0.30	0.31 0.31
<i>trans</i> -But-2-ene	0.33	0.64 4.7
<i>cis</i> -But-2-ene	0.37	1.36 12.0

^a Reference compound is n-pentane ($v = 1$) with corrected retention time of 5 min.

^b Estimated by extrapolation of data for 0.01M-solution of (2).

Complexation of olefins with (1), and particularly with (2), is apparent from the ratios of retention volumes, v/v_0 , being greater than unity. In contrast, where no interaction occurs, as with [Rh(acac)(1,5-cyclo-octadiene)] (3) and n-butane, the retention volumes are the same as for pure squalane (v_0). Steric and electronic effects appear to influence interaction of olefins with Rh^I, as observed³ for Ag^I. Thus, substitution on the double bond reduces retention, and *trans*-but-2-ene is eluted before the *cis*-isomer. Furthermore, C₂D₄ emerges after C₂H₄ with $v_{C_2D_4}/v_{C_2H_4} = 1.20$ (1.11⁵ for Ag^I), indicating predominant olefin-metal σ -bonding. However, Rh^I is more sensitive to steric hindrance, as can be seen from the weak interaction with isobutene ($v_{iso}/v_{trans} < 1$ for Rh^I and > 1 for Ag^I). On the other hand, for olefins with little steric hindrance, e.g. but-1-ene, interaction is more pronounced than with Ag^I and is readily detected even in 0.01M-solutions of (2) (see Figure). Acetylene, which is retained irreversibly by Ag^I, does not interact with Rh^I, whereas for allene the situation is reversed.

The analytical applications of this approach are obvious. Of particular interest is the large effect of deuterium substitution and the considerable difference in the retention

of isobutene and but-1-ene and of acetylene and ethylene, which have identical values on squalane, respectively. Solubility in apolar solvents is another advantage of these reagents.

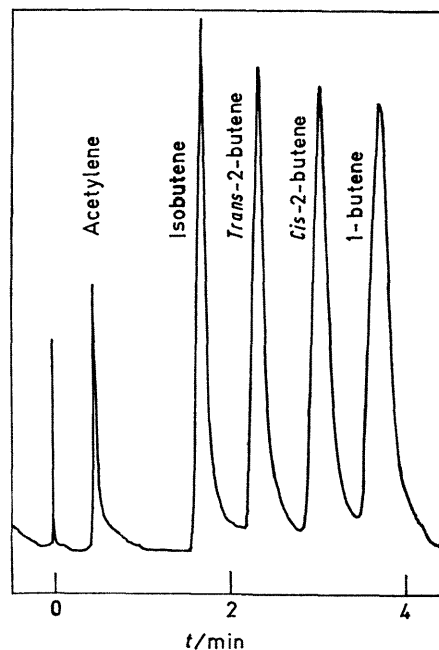


FIGURE. Separation of butenes with 0.01M-solution of (2) (1.4 mg) in squalane.

The g.l.c. experiments were carried out with a glass column of 2 m \times 1.75 mm, filled with 80–100 mesh Chromosorb P, AW-DMCS, coated with a 15% solution of the complex in squalane. In order to reach maximum activity, the columns were conditioned for 2–7 days, depending on complex concentration.

Reversible formation of a fifth co-ordination bond, which is favoured by attainment of noble gas configuration of Rh^I, is believed to be involved in these interactions. The olefin complex may have trigonal bipyramidal geometry, with the CO groups in apical and the olefin and β -diketonate in equatorial positions. Formation of such a geometry might be difficult in the presence of two bidentate ligands, and this could account for the lack of interaction observed with (3).

A five-co-ordinate trigonal bipyramidal transition state has been assumed to occur in exchange reactions of CO with Rh^I carbonyl complexes.⁶ Formation of a true intermediate of CO with (1) and (2) is evident from the observation that introduction of excess of CO into a column coated with (1) or (2) reversibly blocks complexation with olefins.

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¹ P. W. Clark and G. E. Hartwell, *Inorg. Chem.*, 1970, **9**, 1948; D. I. Hall and R. S. Nyholm, *Chem. Comm.*, 1970, 488.

² L. Cattalini, A. Orio, R. Ugo, and F. Bonati, *Chem. Comm.*, 1967, 48; *J. Amer. Chem. Soc.*, 1968, **90**, 4800.

³ E. Gil-Av and J. Herling, *J. Phys. Chem.*, 1962, **66**, 1208; M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697.

⁴ V. Schurig, to be published.

⁵ R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Canad. J. Chem.*, 1963, **41**, 2095; *J. Amer. Chem. Soc.*, 1965, **87**, 1827.

⁶ A. Wojcicki and F. Basolo, *J. Amer. Chem. Soc.*, 1961, **83**, 525; A. Wojcicki and H. B. Gray, Abstracts, 141st National Meeting of the American Chemical Society, 1962, 32M.