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Preliminary communication

STERIC EFFECTS IN SUBSTITUTION REACTIONS AND ISOMERISATIONS IN SQUARE PLANAR CARBENE AND DICARBENE COMPLEXES OF RHODIUM(I)

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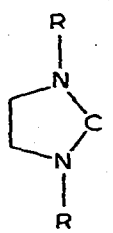
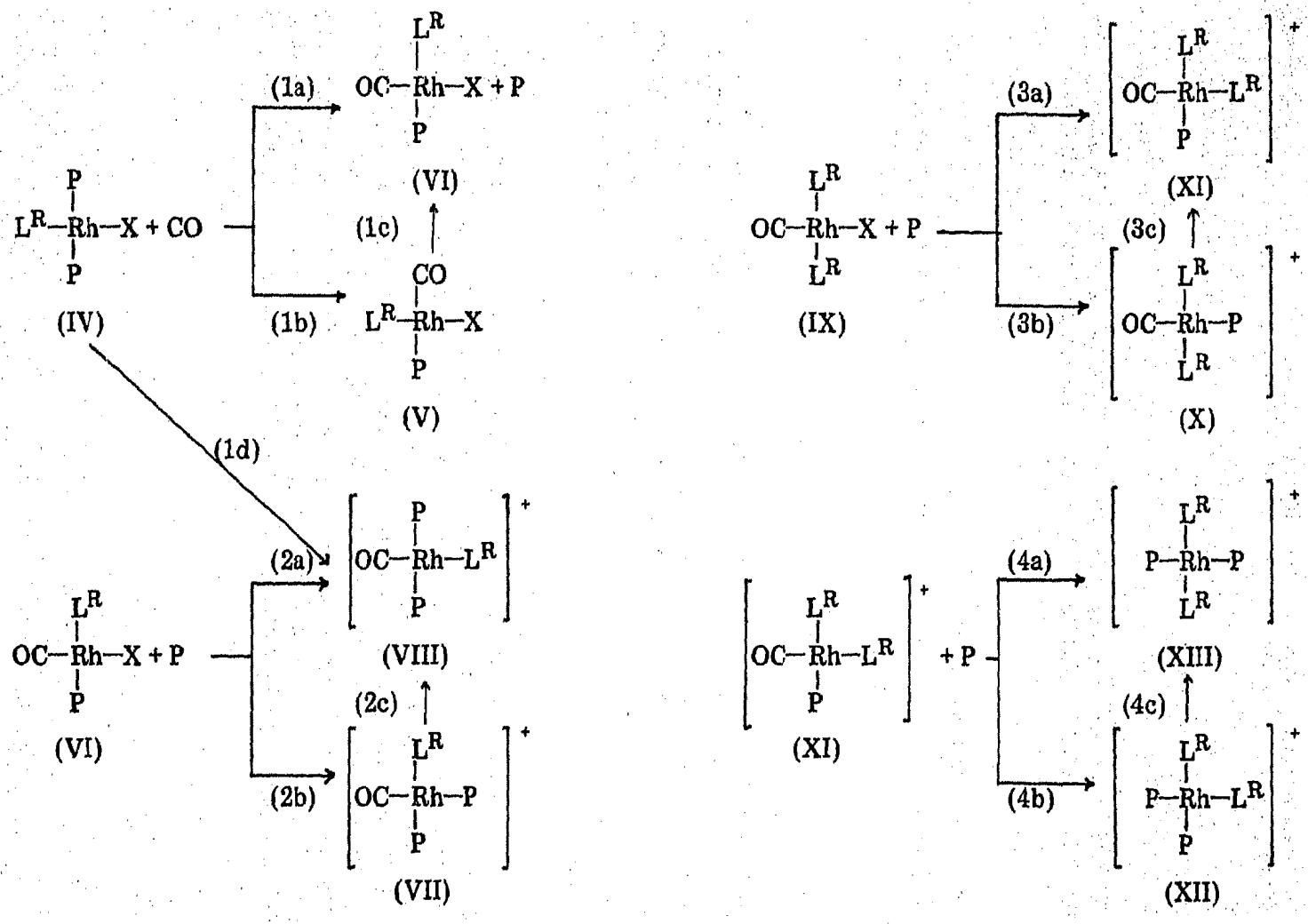
Summary

Substitution reactions of square planar complexes of type $[RhL^R_nP_{2-n}(CO)X]$ (n = 1, 2; P = tertiary phosphine; L^R = tertiary carbene) with tertiary phosphines to give cationic carbene complexes of type $[RhL^R_nP_{3-n}(CO)X]$ (n = 1, 2) with change of configuration at the metal, are shown to proceed by a two step process: substitution with retention and subsequent isomerisation, each of which is sensitive to steric effects; a *cis*-influence and *cis*-effect for the carbene is demonstrated.

Ligand substitutions at square planar d^8 metals have been studied most intensively for Pt^{II}; in general the product is obtained with retention of configuration about the metal [1]. We now report data on the systems (1a)-(4a) for Rh^I complexes in which the opposite steric course prevails. For the Rh^I substrates the ligands include 1,3-disubstituted-imidazolidin-2-ylidenes (carbenes) L^R, (I), tertiary phosphines P, and halides X^-. Reactions (1a)-(4a) were examined serially by changing successively the bulk of L^R, P and X^-. The results are especially sensitive to variations in R, probably because this substituent (for R > Me) in some conformations lies above and below the metal centre. The

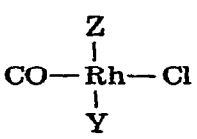


(I) = L^R

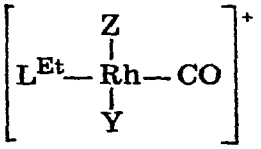


Scheme 1. Scheme of the reaction carried out at 25°C in $CHCl_3$. (1) and (2) P = PPh_3; R = Ph, *p*-Tol, Me. (3) P = PPh_3, PPh_2Me, $PPhMe_2$; R = Me, Et. (4) P = $PPhMe_2$; R = Me, Et.

following features emerge: (i) Reactions (1a)-(4a) are composites of two elementary processes: a stereospecific substitution with retention of configuration about the metal centre [eqn. (1b)-(4b)], and an isomerisation [eqn. (1c)-(4c)]. (ii) Both of these processes (c) and (b) are subject to steric constraints, for example, for the former this is demonstrated by the markedly reduced rate of isomerisation with large R groups and small phosphines in (3), and for the latter by the lack of reactivity of the larger phosphines PPh_3 and $PMePh_2$ (although less basic) with (XI) in (4). Complexes (XIII) are formed with these phosphines under more forcing conditions. (iii) A *cis*-effect is evident, because substitution of X^- by P is facile for some complexes [e.g., eqn. (2), P = PPh_3] but not for others in which the only difference is the replacement of a *cis*-L^R by PPh_3 [2]. (iv) A *cis*-influence is demonstrated, for example, by trends in ν(CO) (cm^{-1} for dilute solutions in $CDCl_3$) in the series of neutral complexes (II): Z, Y = $2PPh_3$, 1980; Z, Y = L^{Me}, PPh_3, 1958; Z, Y = $2L^{Me}$, 1938; and cationic complexes (III): Z, Y = $2PPh_3$, 2010; Z, Y = L^{Et}, PPh_3, 1995; Z, Y = $2L^{Et}$, 1978.



(II)



(III)

Some data on representative compounds (IV)-(XIII) are in Table 1. Analysis of salts (VIII), (XI), and (XIII) are consistent with the presence of coordinated solvent molecules of crystallisation. At present only intermediate complexes of type (X), with a suitable choice of R and P have been detected, and they have not yet been isolated free from the corresponding *cis*-isomers (XI). The pathway via intermediates (V) and (VII), from reactions (1) and (2) respectively, is predicted by the steric course of square planar d^8 substitution reactions in general. These complexes have not yet been observed spectroscopically under the conditions employed.

TABLE 1

^{1}H NMR DATA FOR L^R (τ)[a]

Compound	—CH_2—CH_2—	N—()—CH_3	N—CH_2—	M.p. (°C)[c]
trans-[$RhL^{Me}(PPh_3)_2Cl$]	6.90s[b]	7.60s		183-184 (dec.)
[$Rh(CO)L^{Me}(PPh_3)Cl$]	6.34s[b]	6.48s		147-148 (dec.)
trans-[$Rh(CO)L^{Me}(PPh_3)_2$]Cl	7.17s	7.38s		155-157 (dec.)
trans-[$Rh(CO)L^{Et}_2Cl$]	6.43s	8.74t	5.94c	184-186 (dec.)
trans-[$Rh(CO)L^{Et}_2(PPh_3)$]Cl	5.8 - 7.0c	8.94t	5.8 - 7.0c	[d]
cis-[$Rh(CO)L^{Et}_2(PPh_3)$]Cl	5.5 - 7.2c	8.71t; 9.21t	5.5 - 7.2c	120-121
trans-[$RhL^{Me}_2(PPh_3)_2$]Cl	7.20s	6.97s		165-167 (dec.)

[a]Spectra recorded in $CDCl_3$ solution, with TMS as internal reference, except where noted. [b]TMS used as an external reference. [c]Melting points were taken in air, and are uncorrected. [d]Complex was not isolated. s, singlet; t, triplet; c, overlapping complex multiplets.

Evidence for the participation of (X) in the reaction sequence rests on changes in ^{1}H NMR spectra during the course of reaction (see Table 1). Changes in ν(CO) in the IR spectrum for reaction (1) show initial formation of (VI) followed by (VIII), with subsequent loss of (VI). It is probable that (VIII) is formed via reaction (2), but L^R may have a labilising effect on the Rh—X bond, as for complexes (II), so that pathway (1d) may also be operative. Complex (VI) has been isolated from (1) under different reaction conditions.

The stereochemical assignments of complexes (IV) - (XIII) were deduced from the ^{1}H NMR resonances of the protons of the carbene ligands [(X), (XI), (XIII)], and phosphine methyl protons (XIII) [3], ^{31}P NMR [(IV) and (VIII)] and IR spectra (VI). A detailed discussion will appear elsewhere.

Acknowledgments

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