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THE PREPARATION AND SOME CATALYTIC PROPERTIES OF A NUMBER OF RHODIUM(I) DIOLEFIN COMPLEXES

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Summary

The syntheses of the complexes [RhCl(cod)L], $[RhX(cod)]_2$, [Rh(OCOPh)-(cod)(PPh_3)], $[Rh(S_2CNEt_2)(cod)]$ and $[Rh(cod)L_2]PF_6$ (L = a variety of amines or phosphines, X = OCOPh or SPh) are described, together with some exchange reactions of the type

$$[Rh(cod)(PR_3)_2]^+ + [Rh(cod)(pyridine)_2]^+ \rightarrow [Rh(cod)(PR_3)(pyridine)]^+$$

in which the isolable mixed ligand complexes are the only detectable species at equilibrium. Some of these complexes are active homogeneous hydrogenation catalysts for alkenes, alkynes and ketones in non-coordinating solvents such as benzene (in the presence of NEt_3) and dichloromethane (with or without NEt_3). [Rh(OCOPh)(cod)(PPh_3)] selectively reduces 1-alkynes to 1-alkenes.

Introduction

The chemistry of cyclooctadiene complexes of rhodium has continously developed since the discovery by Chatt and Venanzi [1] of the complex [RhCl-(cod)]$_2$. A variety of related complexes of type [RhCl(cod)L] [1,2] and $[Rh(cod)L_2]PF_6$ [2,3] (L = amines and tertiary phosphines) have been isolated. Schrock and Osborn [3] have shown that $[Rh(cod)L_2]PF_6$ are catalyst precursors for the hydrogenation of alkenes, alkynes, alkadienes and ketones in coordinating solvents such as acetone and ethanol. We have prepared further complexes of these types and have found that some of them, in non-coordinating solvents, are active hydrogenation catalysts.

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Results and discussion

The complexes [RhX(cod)]$_2$ (I)

Our modified synthesis of [RhCl(cod)]$_2$ (Ia) from rhodium chloride, (cod) and sodium carbonate by reflux for 18 h in EtOH/H_2O has been described [4]. The benzoato-analogue [Rh(OCOPh)(cod)]$_2$ (Ib) is best prepared by the action of potassium benzoate on Ia in refluxing acetone. The positions of the $\nu(CO_2)$ bands in the IR spectrum of Ib (1545 cm^{-1} (*sym*) and 1410 cm^{-1} (*asym*)) are similar to those found for the analogous acetato complex [1] (1530 and 1419 cm^{-1}) suggesting a similar dimeric structure containing bridging carboxylato groups in both cases.

The dithiocarbamato complex [Rh(S_2CNEt_2)(cod)] (Ic) is obtained in only moderate yield from the complex [Rh(cod)(py)$_2$]PF_6 [2] by the action of [Et_2NH_2][Et_2NCS_2] in ethanol at room temperature. The position of the "thioureide" band in the IR spectrum of Ic ($\nu(NCS_2)$ = 1500 cm^{-1}) suggests [5] that the dithiocarbamate grouping is chelating; the positions of the PMR resonances due to the NEt_2 groups (δ 1.2 and 3.7 ppm) tends to confirm [5b] this structure.

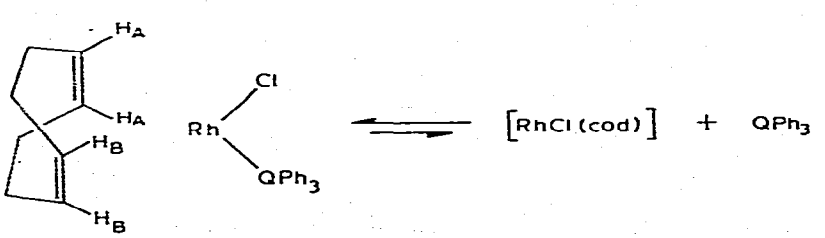
The thiolato complex [Rh(SPh)(cod)]$_2$ (Id) was readily obtained by the action of TlSPh on Ia. These S-containing complexes (Ic and Id) were inactive as hydrogenation catalysts, and did not react with molecular hydrogen.

We were unable to obtain analogous carbonato, oxalato or thiobenzoato complexes by similar methods.

The complexes [RhCl(cod)L] (III)

In non-coordinating solvents, such as benzene or dichloromethane, Ia readily reacts with ligands such as PPh_3; the latter gives [RhCl(cod)(PPh_3)] (IIa) [1]. We were able to synthesise a number of analogues in this way (L = P-n-Bu_3, b; P-i-Pr_3, c; PCy_3, d; 2-picoline, e; imidazole, f). Attempted preparations of similar complexes with the more π-accepting ligands L ($P(OMe)_3$, $P(OPh)_3$, $PPh(OMe)_2$) failed due to loss of (cod), although we have been able to prepare the analogous iridium complexes [6]. This is a further example of the greater lability of olefins bound to rhodium compared with iridium [7], and the greater *trans*-effect associated with the more π-accepting ligands L [6,7].

The ^{1}H NMR spectra of the complexes IIa—IIe show two distinct (cod)vinylic resonances. The protons, H_A, *trans* to L resonate considerably downfield of the protons H_B, *trans* to Cl (see Table 2). We found the same effects [6] for the much wider series of analogous iridium complexes where the position of the H_A



(Q = As, Sb)

resonance correlated well with Tolman's classification of the electronic effects of the ligands L [8].

In the imidazole complex, IIf, the H_A and H_B protons resonated as a single broad peak at room temperature and down to −80°C in CD_2Cl_2. The same behaviour has been observed for the QPh_3 (Q = As, Sb) complexes of type II and has been ascribed to a facile dissociation of QPh_3 [9].

The complex [Rh(OCOPh)(cod)(PPh$_3$)] (III)

[RhX(cod)(PPh_3)] (X = OCOPh, S_2CNEt_2, SPh) could not be obtained by the action of an equivalent of PPh_3 on a dichloromethane solution of Ib—Id; these complexes tended to lose (cod) and gave a complicated mixture.

The required benzoato complex [Rh(OCOPh)(cod)(PPh_3)] (III), which was a selective catalyst for the reduction of 1-alkynes to 1-alkenes (see below), was obtained pure by the action of TlOCOPh on [RhCl(cod)(PPh_3)] for 24 h in THF.

The IR spectrum of III shows $\nu(CO_2)$ bands at 1630 cm^{-1} (*asym*) and 1340 cm^{-1} (*sym*), characteristic [10] of a monodentate carboxylato group. In solution, this complex apparently undergoes an exchange (see below), because the (cod)vinyl protons resonate as a single very broad peak in the PMR spectrum at room temperature; measurements at low temperatures were precluded by solubility limitations.

The complexes [Rh(cod)L$_2$]PF$_6$ (IV) and [Rh(cod)LL']PF$_6$ (V)

A number of complexes of the type [Rh(cod)L_2]PF_6 (IV, L = amines and phosphines) have been reported [2, 3a]. The best procedure seems to be treatment of Ia in acetone with NH_4PF_6 and an excess of L. We have prepared two new complexes by this method [Rh(cod)L_2]PF_6 (IV, L = P-n-Bu_3, a; imidazole, b). The bulky ligands L, having cone angles [8] greater than about 150°, only give the complexes [RhCl(cod)L] (II, L = P-i-Pr_3, c; PCy_3, d) by this procedure.

We find that equimolar mixtures of the bis-phosphine and bis-amine complexes (IV) in CH_2Cl_2 rapidly rearrange in solution to give the new mixed ligand complexes [Rh(cod)LL']PF_6 (V, L = PPh_3, L' = py, a; L' = imidazole, b; L' = py, L = P-i-Pr_3, c; L = PCy_3, d), which were isolated with ether. We have similarly prepared analogous iridium complexes [6]. These complexes show two distinct (cod)-vinylic resonances in the PMR spectrum, but no trace of the (cod)-vinylic resonances of the parent bis-phosphine or bis-amine complexes (see Table 1).

These complexes are also formed by the action of an excess of amine (L') on the complex [RhCl(cod)L] (II, L = PPh_3, P-i-Pr_3, PCy_3) in acetone. They can be crystallised by the addition of ethanolic NH_4PF_6.

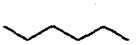
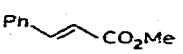
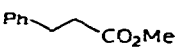
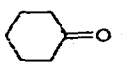
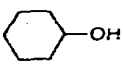
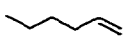
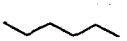
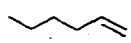
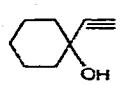
Homogeneous catalysis by the complexes [Rh(cod)L$_2$]PF$_6$ (IV) and [Rh(cod)LL']PF$_6$ (V)

Osborn has described the complexes [$RhH_2L_2S_2$]ClO_4 (VI, L = tertiary phosphine, S = acetone, ethanol) which are formed from [Rh(cod)L_2]ClO_4 in a coordinating solvent under hydrogen. These complexes are catalysts for the hydrogenation of alkenes, ketones and the selective reduction of alkynes and alkadienes to alkenes. Evidence was also found for a deprotonation/protonation equilibrium [3].

In our initial experiments, reported here, we have studied the complexes

TABLE 1

CATALYSTS, CONDITIONS, PRODUCTS AND RATES IN THE HYDROGENATION OF SOME UNSATURATED SUBSTRATES WITH VARIOUS CATALYSTS

Substrate	Catalyst	Conditions [a]	Products [b]	Rate [c]
	IV c	C_6H_6/NEt_3		1500 [d]
$PhCH{=}CH_2$	IV c	C_6H_6/NEt_3	$PhCH_2CH_3$	600 [e]
	IV c	C_6H_6/NEt_3		10
$Me_2C{=}CHMe$	IV c	C_6H_6/NEt_3	Me_2CHCH_2Me	4 [f]
	IV c	C_6H_6/NEt_3		6 [f]
$PhC{\equiv}CMe$	IV c	C_6H_6/NEt_3	$PhCH_2CH_2Me$	2
	IV c	C_6H_6/NEt_3		12
PhCOMe	IV c	C_6H_6/NEt_3	PhCH(OH)Me	12 [g]
Ph_2CO	IV c	C_6H_6/NEt_3	Ph_2CHOH	7
	IV c	CH_2Cl_2		4000
	IV c	CH_2Cl_2/NEt_3		1500 [d]
	V a	CH_2Cl_2		250
	V a	CH_2Cl_2/NEt_3	–	0
$PhC{\equiv}CH$	V a	$C_6H_6/PhCO_2H/NEt_3$	$PhCH{=}CH_2$	3.5 [h]
$HC{\equiv}CCH_2OH$	V a	$C_6H_6/PhCO_2H/NEt_3$	$CH_2{=}CHCH_2OH$	5.5 [h]
	V a	$C_6H_6/PhCO_2H/NEt_3$		2 [f,h]
$PhC{\equiv}CH$	III	$C_6H_6/PhCO_2H/NEt_3$	$PhCH{=}CH_2$	3.7 [h]

[a] Substrate, 0.5 *M*; catalyst, 2 m*M*; H_2, 1 atm (initially); temperature, 20°C (±1°); volume of solution, 16 ml; NEt_3 (where present), 0.1 *M*; $PhCO_2H$ (where present), 10 m*M*. [b] Identity confirmed by PMR and, in most cases, also by GLPC. [c] Maximum rate (mol (mol Rh)$^{-1}$ h^{-1}) of hydrogen uptake measured manometrically and confirmed by PMR and, in most cases, by GLPC of products (±10%). For comparison, the rate of reduction of 1-hexane by $[RhCl(PPh_3)_3]$ was 160 under the same conditions in benzene. [d] Initial rate of formation of 2-hexanes = 300. [e] Some yellow precipitate formed. [f] These slower reactions were not followed to completion. [g] The product alcohol appears to deactivate the catalyst since the rate falls to zero after 250 catalytic cycles. [h] After the absorption of 1 mol of H_2 the product is ca. 95% 1-alkene; subsequent reduction to alkane is about seven times slower.

$[Rh(cod)(PPh_3)_2]PF_6$ (IVc) and $[Rh(cod)(PPh_3)py]PF_6$ (Va) as hydrogenation catalysts in non-coordinating solvents. The use of solvents such as benzene, and especially CH_2Cl_2, of low coordinating power limits the competition between the solvent and the olefin for active sites at the metal and we observe particularly high catalytic activity in these systems.

The yellow complexes IVc or Va dissolve in benzene at 25°C under one atmosphere of hydrogen only in the presence of NEt_3, to give catalytically active solutions and fine precipitates of NEt_3HPF_6. The same complexes dissolve readily in dichloromethane and give catalytically active solutions under hydrogen in the presence or absence of NEt_3. This is largely a solubility effect: only the neutral deprotonated rhodium species are soluble in benzene, while both the cationic and neutral rhodium species are soluble in CH_2Cl_2. Both are excellent hydrogenation catalysts, but the neutral species are also excellent isomerisation catalysts; similar effects were observed by Osborn [3] for the analogous systems in coordinating solvents. The solutions containing NEt_3 had identical activities, within experimental error, for CH_2Cl_2 or benzene as solvents.

The exact nature of the species in solution under our conditions is unknown; certainly, we have found no evidence for the presence of solvates of type VI, such as are found in coordinating solvents. All attempts to crystallize intermediates or observe their PMR spectra at low temperature failed, even though we have been able to observe intermediates of the type $[IrH_2(cod)L_2]PF_6$ in the analogous iridium system [6,11]. Va tends to deposit metallic rhodium after some hours while IVc is apparently indefinitely stable under hydrogen in CH_2Cl_2 or C_6H_6.

Table 1 shows the reaction conditions, substrates, products and rates of reduction of a number of unsaturated compounds by the complexes III, IVc and Va. The rates for IVc are faster than those observed by Osborn [3] but isomerisation of the alkene substrate is a more serious side reaction under our conditions.

The selectivity of IVc or Va for the reduction of alkynes to alkenes is poor, alkane being the sole product, although Schrock and Osborn [3] had success with other complexes of type IV in coordinating solvents. In the presence of benzoate ion, however, Va becomes highly selective for the reduction of 1-alkynes to 1-alkenes. For example, phenylacetylene, which is rapidly polymerised by IVc or Va alone, is slowly reduced with one equivalent of D_2 to *cis*-PhCD=CHD by Va in the presence of an excess of $(NEt_3H)(PhCO_2)$. The reduction therefore occurs via a π-bonded intermediate. Benzoato complexes are probably involved since $[Rh(OCOPh)(cod)(PPh_3)]$ (III) is also a catalyst for the reaction; an excess of $(NEt_3H)(PhCO_2)$ is still necessary, probably to prevent dissociation of the carboxylato ligand. This type of dissociation may also account for the coalescence of the H_A and H_B resonances in the PMR spectrum of III (see above). A *monohapto—dihapto* equilibrium of the benzoato-ligand is a possible alternative explanation; such a process might also account for the selectivity observed in the catalytic reduction of 1-alkynes, described above. On this hypothesis, the 1-alkyne would be better able to open up the chelating benzoato ligand than the 1-alkene, and hence gain access to the metal centre.

Ketones are reduced by IVc in benzene in the presence of NEt_3 but in the case of acetone and acetophenone, the catalyst is soon deactivated, probably by the product alcohol. Cyclohexanone and benzophenone are smoothly reduced, and

the reduction of 4-t-butylcyclohexanone gives a mixture of the *cis* and *trans* alcohols in the molar ratio 37/63.

Some of these results have already been briefly reported [12].

Experimental

The complexes were prepared by standard Schlenk-tube techniques as described in ref. 3. NMR spectra were measured on a Perkin—Elmer R12B instrument.

$RhCl_3$ was a generous loan of the Compagnie des Mètaux Précieux. $(Et_2NH_2)(Et_2NCS_2)$ was prepared by Grodski's method [13]. Other reagents were obtained from Fluka AG and used as received, except PCy_3, which was prepared from CyMgBr and PCl_3 [14] by M. Claude Frajerman. The analyses, PMR data, and yields of the new complexes are shown in Table 2.

Di-μ-benzoatodi-1,5-cyclooctadienehodium(I). $[RhCl(cod)]_2$ (0.25 g) was treated with $PhCO_2K$ (0.5 g) in refluxing acetone (30 ml) for 8 h. Water (20 ml) was added to the cooled solution and the yellow precipitate filtered off, washed with water (2 × 5 ml) then ethanol (2 × 5 ml), and dried in vacuo. The product was recrystallised from CH_2Cl_2/pentane as yellow prisms. Yield 0.25 g.

Dithiocarbamato-1,5-cyclooctadienerhodium(I). $[Rh(cod)(py)_2]PF_6$ [2] (440 mg) in suspension in ethanol (20 ml) was treated with $(Et_2NH_2)(Et_2NCS_2)$ (200 mg) at 20°C for 20 min. The yellow precipitate was filtered off and recrystallised twice from CH_2Cl_2/Et_2O/EtOH (1/1/1) to give a yellow solid. Yield 100 mg.

Phenylthiolatothallium(I). $TlCO_3$ (4 g) was dissolved in water (100 ml) and PhSH (2 ml) added. The mixture was stirred overnight and the yellow microcrystalline precipitate filtered off, and triturated with water (5 × 5 ml), then ethanol (5 ml), then ether (5 ml) and dried in air. Yield 16.5 g (89%) (Found: C, 23.0; H, 1.7. C_6H_6STl calcd.: C, 23.0; H, 1.5%). We thank Dr. K. Turner (Norwich) for this synthesis.

Di-μ-phenylthiolatodi-1,5-cyclooctadienedirhodium(I). $[RhCl(cod)]_2$ (320 mg) was treated with TlSPh (420 mg) in CH_2Cl_2 (10 ml) for 18 h. The product was isolated with ether and recrystallised from CH_2Cl_2/Et_2O to give yellow crystals. Yield 340 mg.

1,5-Cyclooctadiene(t-phosphine)chlororhodium(I). Finely divided $[RhCl(cod)]_2$ (500 mg) in octane (10 ml) was treated with PCy_3 or P-i-Pr_3 (1.2 mol. eq.) or P-n-Bu_3 (1.0 mol-eq.) and stirred. After 20 min at 40°C (L = PCy_3 and P-i-Pr_3) the solid was filtered off and recrystallised from CH_2Cl_2/octane as light yellow prisms. Where L = P-n-Bu_3, the resulting solution deposited large orange crystals of pure complex over 1 month. These were separated by decantation and washed with the minimum volume of octane. L = PCy_3 yield 900 mg; L = P-i-Pr_3 yield 580 mg; L = P-n-Bu_3 yield 350 mg.

1,5-Cyclooctadiene(amine)chlororhodium(I). The following complexes were prepared similarly in CH_2Cl_2 (10 ml) with a 10 mol excess of L. They were isolated with ether and recrystallised as above. L = 2-picoline: yield 620 mg; L = imidazole, yield 570 mg.

Benzoatothallium(I). A saturated aqueous solution of $PhCO_2Na$ (3 g) was added to $TlNO_3$ (4.5 g) in H_2O (15 ml). The white precipitate was filtered off,

TABLE 2

YIELDS, ANALYSES AND PMR DATA FOR THE NEW COMPLEXES

Complex [a]		Yield (%)	Analysis (found (calcd.)(%)			PMR data [b] (δ (ppm))	
			C	H	N	(cod)-vinyl [c]	L resonances
$[Rh(OCOPh)(cod)]_2$	Ib	80	54.4 (54.2)	5.0 (5.2)		4.28	7.2, c, and 7.8, c, Ph.
$[Rh(S_2CNEt_2)(cod)]$	Ic	15	43.3 (43.5)	5.9 (6.1)	4.3 (3.9)	4.45	1.2, t (7), Me; 3.7 q (7), CH_2.
$[Rh(SPh)cod)]_2$	Id	82	52.3 (52.5)	5.4 (5.4)		4.25	7.1—7.6, c, Ph.
$[RhCl(cod)(P\text{-}n\text{-}Bu_3)]$	IIb	40	53.8 (53.5)	8.6 (8.7)		5.30 3.50	1.95, c, Me; 2.5 c, CH_2.
$[RhCl(cod)(P\text{-}i\text{-}Pr_3)]$	IIc	65	50.5 (50.2)	8.3 (8.2)		5.29 3.72	1.3, dd (6 and 12), Me; 2.0, c, CH.
$[RhCl(cod)(PCy_3)]$	IId	80	59.7 (59.3)	8.6 (8.6)		5.32 3.60	0.8—2.1, c, Cy.
[RhCl(cod)(pc)]	IIe	90	49.3 (49.5)	5.6 (5.6)	4.1 (4.1)	4.75 3.50	3.25, s, Me; 7.2—7.8, c, and 8.8—9.0, c, Ar.
[RhCl(cod)(imid)]	IIf	90	41.7 (42.0)	5.5 (5.1)	8.9 (8.9)	4.18 [d]	6.9, c, and 7.8, c, imid.
$[Rh(OCOPh)(cod)(PPh_3)]$	III	56	66.5 (66.7)	5.2 (5.4)		~4.4 [e]	7.0—8.0, c, Ph.
$[Rh(cod)(P\text{-}n\text{-}Bu_3)_2]PF_6$	IVa	60	50.9 (50.5)	8.7 (8.7)		4.95	1.95, c, Me; 2.5, c, CH_2.
$[Rh(cod)(imid)_2]PF_6$	IVb	75	34.2 (34.2)	4.0 (4.1)	11.2 (11.4)	4.05	6.9, c, and 7.2, c; imid.
$[Rh(cod)(PPh_3)(py)]PF_6$	Va	85	53.5 (53.5)	4.7 (4.6)	2.2 (2.0)	4.92 3.85	6.9—7.8, c and 8.4—8.6, c, Ar.
$[Rh(cod)(PPh_3)(imid)]PF_6$	Vb	80	50.7 (50.8)	4.4 (4.6)	4.0 (4.1)	4.90 3.73	6.9—7.8, c, Ar
$[Rh(cod)(P\text{-}i\text{-}Pr_3)(py)]PF_6$	Vc	80	44.5 (44.3)	6.4 (6.4)	2.4 (2.4)	4.45 [f]	1.3, dd, (6 and 12), Me; 2, c, CH; 7.5—8.0 and 8.8—9.0, c, Ar.
$[Rh(cod)(PCy_3)(py)]PF_6$	Vd	90	52.0 (52.2)	7.0 (7.1)	1.9 (2.0)	4.45 4.25	0.9—2.0, c, Cy; 7.5—7.9 and 8.8—9.0, c, Ar.

[a] cod = 1,5-cyclooctadiene, Cy = cyclohexyl, pc = 2-methylpyridine, imid = imidazole. All the complexes were yellow crystalline or microcrystalline solids. [b] in $CDCl_3$ at 35°C. Resonances reported as follows: position (δ, ppm, multiplicity, coupling constant (Hz)), assignment, s = singlet, d = doublet, c = complex resonance, Ar = aromatic group. In all cases satisfactory integrals were obtained. All complexes had a broad unresolved resonance at δ 1.8—2.6 ppm assigned to (cod)CH_2 protons and those complexes containing PPh_3 groups had a complex resonance from δ 7.0—7.9 ppm assigned to the aromatic protons. [c] Broad unresolved resonances: $\omega(1/2) \sim 10$ Hz. In some cases the inequivalent (cod) vinyl protons were distinguished (see text). [d] Only one (cod)vinyl peak is observed probably due to an exchange process (see text). [e] The (cod)vinyl resonance is very broad at room temperature probably due to an exchange process. [f] A broad resonance $\omega(1/2) \sim 20$ Hz; the inequivalence of the (cod)vinyl protons is insufficient for the resonances to be distinguished.

washed with water (5 × 5 ml) and dried in air. Yield 3.7 g (68%) (Found: C, 26.0; H, 1.4. $C_7H_5O_2Tl$ calcd.: C, 25.8; H, 1.6).

Benzoato-1,5-cyclooctadienetriphenylphosphinerhodium(I). [RhCl(cod)-(PPh_3)] [1] (350 mg) in THF (5 ml) was treated with TlOCOPh (350 mg) for 24 h and the mixture centrifuged decanted and filtered. The solvent was evapor-

ated and the residue was twice recrystallised from CH_2Cl_2/octane to give a yellow powder. Yield 260 mg.

1,5-Cyclooctadienebis(tri-n-butylphosphine)rhodium(I) hexafluorophosphate. $[RhCl(cod)]_2$ (500 mg) was treated with P-n-Bu_3 (0.45 ml) and NH_4PF_6 (70 mg) in aqueous acetone (1/10, 10 ml). The solvent was removed and the residue treated with CH_2Cl_2/H_2O (1/1, 10 ml). The organic layer was separated, dried over $MgSO_4$, and the product crystallised by addition of octane (5 ml) with partial removal of the solvents in vacuo. Yield 940 mg.

1,5-Cyclooctadienediimidazolerhodium(I) hexafluorophosphate. $[RhCl(cod)]_2$ (500 mg) in acetone (20 ml) was treated with imidazole (500 mg) and NH_4PF_6 (400 mg). Water (20 ml) was added and the solid formed was filtered off, washed with water (2 ml), dried in vacuo and recrystallised from CH_2Cl_2/Et_2O to give light yellow prisms. Yield 740 mg,

1,5-Cyclooctadiene(amine)triphenylphosphinerhodium(I) hexafluorophosphate. Method A. $[Rh(cod)(PPh_3)_2]PF_6 \cdot CH_2Cl_2$ [3] (190 mg) and $[Rh(cod)(py)_2]PF_2$ [2] (100 mg) were dissolved in CH_2Cl_2 (5 ml) and ether (10 ml) added. The crystals of $[Rh(cod)(PPh_3)(py)]PF_6$ formed were filtered off, washed with ether (2 ml) and dried in air. Yield 250 mg.

Method B. $[RhCl(cod)(PPh_3)]$ [1] (500 mg) in aqueous acetone (1/10, 10 ml) was treated with pyridine (2 g) and NH_4PF_6 (200 mg). The solvent was removed in vacuo, the residue washed with water, the methanol, and recrystallised from CH_2Cl_2/Et_2O/EtOH (5/4/1) to give yellow crystals. Yield 620 mg.

The corresponding imidazole complex was obtained similarly by both methods in comparable yields (80—85%). The corresponding complexes $[Rh(cod)L(py)]PF_6$ (L = P-i-Pr_3 and PCy_3) were obtained in a similar way, but the reaction mixture must be refluxed 5 min (L = P-i-Pr_3) or 20 min (L = PCy_3) to effect substitution.

Method C. $[Rh(cod)(py)_2]PF_6$ [2] (500 mg) in acetone was treated with 1.5 mol-eq. of tertiary phosphine (L = P-i-Pr_3, and PCy_3). The crude products were precipitated with water washed with methanol, dried, and recrystallised as yellow-orange prisms from CH_2Cl_2/Et_2O. L = P-i-Pr_3 yield 480 mg; L = PCy_3 yield 650 mg.

Hydrogenation experiments. The hydrogenations were performed in a closed three-necked flask (volume: 358 ml) equipped with a manometer, a magnetic stirrer and taps connected to the hydrogen supply and a vacuum line. The solution to be studied was made up, except for the catalyst, and degassed by two freeze-thaw cycles in vacuo. The solid catalyst was added to the frozen solution under nitrogen the vacuum reestablished and the contents of the flask brought to 20°C with a water bath. The hydrogen, previously equilibrated with the appropriate solvent, was admitted. Hydrogen absorption began upon starting the stirrer and the pressure changes with time were recorded. The products were observed by PMR spectroscopy of the solutions and determined by GLC analysis. For good repeatability of the curves (a) the catalysts had to be freshly prepared, Va in particular having a tendency to give variable results with time, although the appearance of the catalyst was unaltered; (b) the olefin, or its benzene or dichloromethane solution, was passed through a short column of alumina (Merck Grade I) to deperoxidize it immediately prior to use. The alkynes and ketones were distilled or recrystallised as appropriate; (c) the benzene should be thio-

phene free and the CH_2Cl_2 should be freshly distilled from CaH_2 prior to use. The rate of reduction is quoted in mol H_2 absorbed (mol Rh)$^{-1}$ h^{-1} and refers to the fastest rate observed during a run; this was normally attained in the first minute or so. The catalyst solutions were yellow, except those involving 1-alkynes, which became deep red on addition of the substrate, but lightened somewhat when this had all been reduced to alkene.

The observation of cis-deuteriation of phenylacetylene. The reduction of phenylacetylene with an equivalent of D_2 by the method described above (see also Table 1) gave a solution which was passed through an alumina column to remove the substrate, catalysts and co-catalysts. The solvent was largely removed in vacuo and the PMR spectrum of the resulting colourless liquid recorded. This showed no peaks in the vinylic proton region other than a 1/1/1 triplet ^3J(H—D) *trans* 2.7 Hz. at δ 5.9 ppm which can only be due to *cis*-PhCD=CHD. In PhCH=CH_2, ^3J(H—H) *trans* 17.5 Hz and $^2J(H—H)_{gem}$ 0.3 Hz for the corresponding signal at δ 5.9 ppm. The ratio $^3J(H—H)/^3J(H—D) = 6.5$ is, within experimental error and as expected [15], the ratio of the magnetogyric ratios $\gamma_H/\gamma_D = 6.52$, confirming the correctness of the assignment.

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References

1 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
2 B. Denise and G. Pannetier, J. Organometal. Chem., 63 (1973) 423.
3 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 91 (1971) 2816; 98 (1976) 2134, 2143 and 4450.
4 G. Giordano and R.H. Crabtree, Inorg. Syn., in press.
5 (a) J. Chatt, L.A. Duncanson and L.M. Venanzi, Nature, 177 (1956) 1042; (b) T.A. Stephenson and J.M.C. Alison, J. Chem. Soc. Dalton, (1973) 254.
6 R.H. Crabtree, H. Felkin and G.E. Morris, J. Organometal. Chem., in press.
7 L.M. Haines and E. Singleton, Inorg. Chem., 10 (1971) 1685 and 1696; J. Chem. Soc. Dalton, (1972) 1891.
8 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2953 and 2956.
9 H.C. Volger, K. Vrieze and A.P. Praat, J. Organometal. Chem., 14 (1968) 185 and 429.
10 S.D. Robinson, J. Chem. Soc. Dalton, (1973) 1912.
11 R.H. Crabtree, H. Felkin and G.E. Morris, Chem. Commun., (1976) 716.
12 R.H. Crabtree, Chem. Commun., (1975) 647.
13 M. Grodski, Ber., 14 (1881) 2754.
14 M.J. Smith, D. Ph. Thesis, Oxford, 1971, p. 99.
15 J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959.