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Preliminary communication

STABILISATION OF HIGHLY SUBSTITUTED ALKENE COORDINATION BY CHELATION: PREPARATION AND CRYSTAL AND MOLECULAR STRUCTURE OF $[Rh(Ph_2PO_2CC(H)=CMe_2)Cl]_2$

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Summary

Reactions of α,β-unsaturated acids with Ph_2PCl give the esters $[Ph_2PO_2CC(H)=CMe(R)]$ (R = H or Me), which react with $[L_2RhCl]_2$ ($L = C_2H_4$ or cyclooctene) to give the structurally characterised $[Rh(Ph_2PO_2CC(H)=CMe(R))Cl]_2$; the related complex, $[Rh(Ph_2POCH_2C(H)=CMe_2)Cl]_2$ is also reported.

The chemistry of alkenes can be radically altered by coordination to a transition element so that they become susceptible to e.g. attack of nucleophiles or addition of small molecules. These reactions have found extensive use in a variety of important organic transformations [1]. This approach has not, however, been useful for highly substituted alkenes since their complexity constants are rather low. The main exception to this inability of highly substituted alkenes to coordinate is observed in e.g. α-amidoacrylic acids which have been asymmetrically hydrogenated and in which coordination is stabilised by interaction of a remote oxygen atom to form a chelate ring [2,3]. We now report a facile method for the coordination of highly substituted α,β-unsaturated acids and the wider generality of the process is illustrated by coordination of a highly substituted β,γ-unsaturated alcohol.

Reactions of $[Me(R)C=CHCOOH]$ with Ph_2PCl in the presence of Et_3N at low temperatures give $[Ph_2PO_2CC(H)=CMe(R)]$ (R = H (1), or R = Me (2)) in high yield (see Scheme 1 and Table 1). Although similar routes have been employed to synthesise $[Ph_2PO_2CR]$ ($R = Me, CF_3, C_2F_5$ or C_3F_7) [4], the mixed anhydrides of diphenylphosphinous acid and acrylic acids do not appear to have been reported. Indeed, similar reactions of e.g. Et_2PCl with

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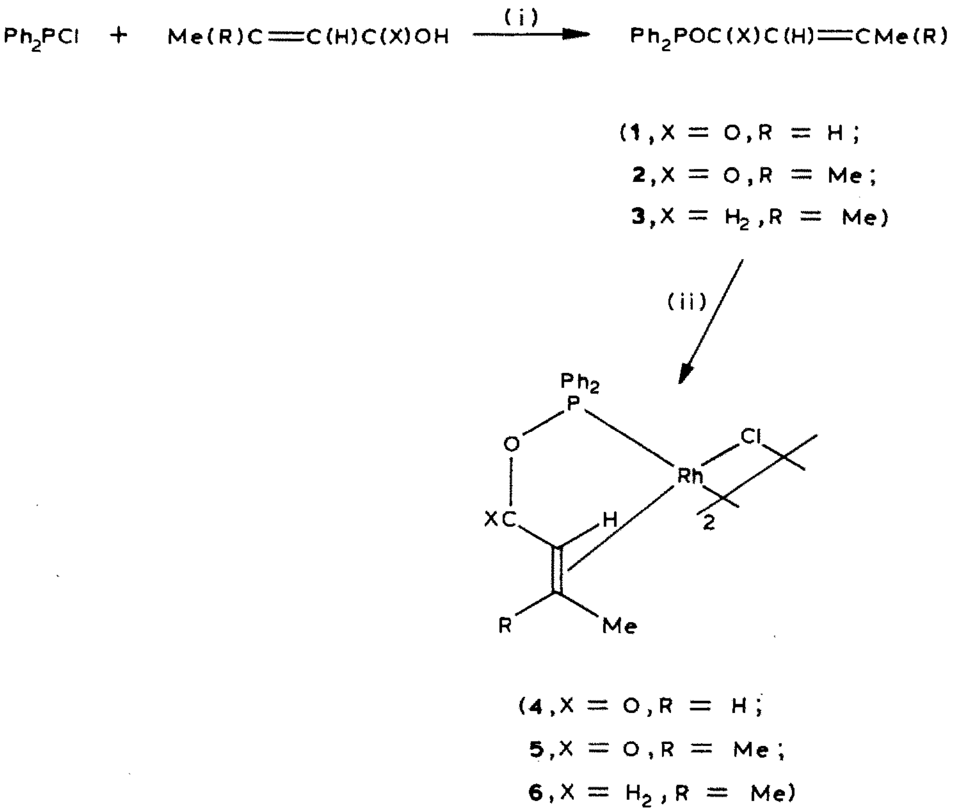

(1, X = O, R = H;
2, X = O, R = Me;
3, X = H_2, R = Me)

(4, X = O, R = H;
5, X = O, R = Me;
6, X = H_2, R = Me)

SCHEME 1. Preparation of compounds 1—6. (i) Et_3N, Et_2O, −10°C; (ii) $[RhL_2Cl]_2$, CH_2Cl_2, 25°C.

TABLE 1

INFRARED AND ^{1}H NMR (25°C in $CDCl_3$) PROPERTIES OF COMPOUNDS 1, 2, 4—6

	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})	δ(*CH*=C)	δ(C*Me*)
1	1700	1640	5.55, 6.72	1.5
2	1687	1636	5.7	1.77, 2.02
4	1758	^{a}	3.53 3.66 ^{b}	1.44 ^{b}
5	1749	^{a}	2.75 ^{c}	1.26, 1.45 ^{c}
6	—	^{a}	3.12 ^{c}	1.36, 1.15 ^{c}

^{a} Not observed. ^{b} In C_6D_6. ^{c} In CD_2Cl_2.

acrylic acids in the absence of base and at higher temperatures give $[Et_2P(O)CH_2CH_2C(O)Cl]$ [5]. $[Ph_2POCH_2C(H)=CMe_2]$ (3) can be prepared from $[Me_2C=CHCH_2OH]$ by a similar reaction.

1, 2 and 3 react with $[RhL_2Cl]_2$ (1 mol equiv. of 1, 2 or 3 per Rh) to give high yields of $[Rh(Ph_2PO_2CCH=CMe(R))Cl]_2$ (R = H (4) or Me (5)) (see Scheme 1) or $[Rh(Ph_2POCH_2C(H)=CMe_2)Cl]_2$ (6). Spectroscopic studies of 4—6 (see Table 1) suggest that 1—3 are coordinated by both the phosphorus atom and the double bond, and this is confirmed by X-ray analysis of 5.

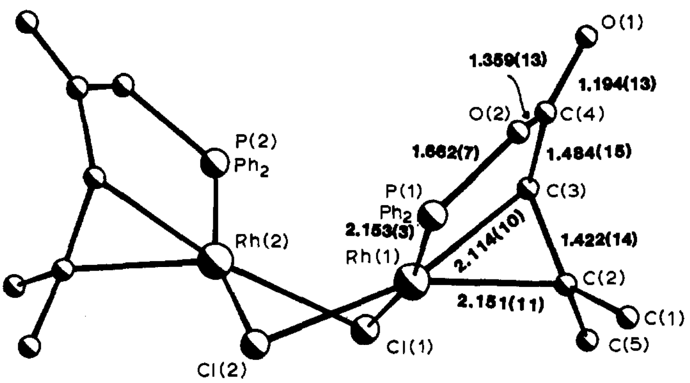

Fig. 1. X-Ray structure, numbering scheme and important bond lengths for 5. Phenyl rings and hydrogen atoms are omitted for clarity. Important bond angles: Cl(1)—Rh(1)—Cl(2) 82.2(1); Rh(1)—Cl(1)—Rh(2) 82.2(1); Cl(1)—Rh(1)—P(1) 94.1(1); Rh(1)—C(2)—C(3) 69.8(6); C(2)—C(3)—C(4) 122.4(9); Rh(1)—C(3)—C(4) 112.4(7); C(3)—C(4)—O(2) 117.9(9); C(4)—O(2)—P(1) 115.2(7); O(2)—P(1)—Rh(1) 107.6(3); C(2)—C(3)—Rh(1) 71.4(6); C(3)—C(4)—O(1) 123.2(10); O(2)—C(4)—O(1) 119.3(10); C(1)—C(2)—C(3) 123.8(9); C(1)—C(2)—Rh(1) 115.8(7); C(1)—C(2)—C(5) 112.0(9); C(5)—C(2)—Rh(1) 111.3(7); C(5)—C(2)—C(3) 117.2(9); C(2)—Rh(1)—C(3) 38.9(4).

Bond lengths and angles for the other half of the molecule are similar to those reported and appear in the supplementary data.

Similar chelate stabilisation of alkene coordination has been reported before for less sterically crowded alkenes, e.g. in $[Rh(Ph_2POCH_2CH{=}CH_2)Cl]_2$ [6].

The structure of 4 is shown in Fig. 1, which also includes important bond lengths and angles.

Crystal data. $C_{34}H_{34}Cl_2O_4P_2Rh_2$, M = 845, Monoclinic, a 8.485(1), b 28.070(3), c 14.253(1) Å, β 93.96(1)°, V 3386.6 Å^3, Z = 4, D_c 1.658 g cm^{-3}, D_f 1.652 g cm^{-3}, space group $P2_1/n$, μ(Cu-K_α) 36.42, λ(Cu-K_α) 1.5419 Å, $F(000) = 1696$.

5740 diffraction intensities were measured to θ_{max} 65° on an Enraf—Nonius CAD4 diffractometer and an empirical absorption correction applied. The structure was solved by Patterson and Fourier methods using SHELX [7] and refined by least-squares procedures. The structure converged to $R(F) = 0.066$ for 4011 reflections $|F_o| > 6\sigma(F_o)$*. The molecule has a non crystallographic C_2 symmetry axis.

The overall structure is similar to that of $[RhCl(CO)_2]_2$ [8] with the relative positions of the dienes being *transoid*. Despite the steric crowding of the alkene, the C(2)—C(3) bond length (1.420 Å) is similar to or slightly longer than those observed in C_2H_4 (1.36 Å) or C_2F_4 (1.4 Å) complexes with rhodium suggesting a strong Rh—alkene interaction [9]. In addition, there is significant pyramidalisation of the substituents around C(2). Finally, the ring angles at C(4) and O(2) are slightly compressed on account of the chelate ring formation.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The ease with which the highly functionalised alkene coordinates in 4—6, suggests that the use of Ph_2P as a protecting group* for the acidic hydrogen atom β to a double bond should allow coordination of a wide range of highly substituted alkenes and greatly increase the range of alkene substrates available for reaction with nucleophiles and small molecules.

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*The Ph_2P group can be removed by e.g. dilute CH_3COOH.