Preparation and Characterization of Rhodium(I) Complexes containing Bidentate Diphenyl(prop-2-enyloxo)phosphine and (But-3-enyl)diphenylphosphine Ligands

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The complexes [LRh(μ-Cl)$_2$RhL] and [RhL(L′)] [L′ = η-cyclopentadienyl (cp) or pentane-2,4-dionato (acac); L = diphenyl(prop-2-enyloxo)phosphine-*P*;*C*^{2},*C*^{3}-η (dppp) or (but-3-enyl)diphenylphosphine-*P*;*C*^{3},*C*^{4}-η (bdpp)] have been prepared and characterized. The strongest metal–olefin bond occurs in the cp complexes and can be recognized by significant changes in spin–spin coupling involving the olefinic protons and a large upfield shift of the terminal olefinic protons (as high as τ 9). Unequal coupling constants ^3J(POCH) of 34 and 6·5 Hz for the complex [Rh(cp)(dppp)] and similar values for [Rh(acac)(dppp)] allow assignment of the configuration of the ligand and of the molecular structures of the complexes in solution.

As an extension of our studies involving ligands of the type PR$_3$, where at least one R group is an alkene,[1-3] a series of new rhodium(I) complexes [(RPh$_2$P)Rh(μ-Cl)$_2$-Rh(PPh$_2$R)] and [RhL′(PPh$_2$R)] [R = $-$CH$_2$CH$_2$CH=CH$_2$ (bdpp) or $-$OCH$_2$CH=CH$_2$(dppp); L′ = η-cyclopentadienyl (cp) or pentane-2,4-dionato (acac)] has been synthesised. Complexes of this type appear to be stabilized by the chelate effect and facilitate the study of metal–olefin interactions since the olefin must remain in the vicinity of the metal by virtue of its attachment to the co-ordinated phosphine.

Previous ^{1}H n.m.r. investigations of metal–olefin complexes indicate that, as a consequence of the change in hybridization of the olefinic carbon atoms, a change in spin–spin coupling constants amongst the olefinic protons accompanies co-ordination, and in most cases the proton resonances are shifted upfield.[4] The complexes of rhodium(I) containing dppp or bdpp permit further study of chemical-shift and coupling-constant data for all three types of olefinic protons, the two terminal and the single vinylic, and the relation of these data with metal–olefin bond strength.

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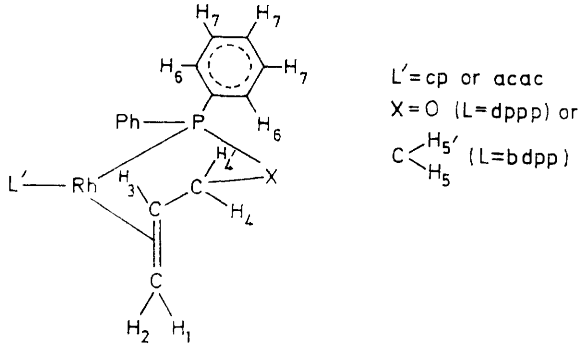
[2] P. E. Garrou and G. E. Hartwell, *J. Organometallic Chem.*, 1973, **55**, 331.

[3] P. E. Garrou and G. E. Hartwell, *J. Organometallic Chem.*, 1974, **71**, 443.

[4] M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometallic Chem.*, 1967, **10**, 301.

RESULTS AND DISCUSSION

The reaction, in diethyl ether, of (but-3-enyl)diphenylphosphine or diphenyl(prop-2-enyloxo)phosphine with the complex [$(H_4C_2)_2Rh(\mu\text{-}Cl)_2Rh(C_2H_4)_2$] or [(cod)Rh($\mu$-Cl)$_2$Rh(cod)] (cod = cyclo-octa-1,5-diene) yielded the



appropriate chelated-phosphine rhodium dimer, [LRh(μ-Cl)$_2$RhL] (L = bdpp or dppp), which may be reacted with η-cyclopentadienylthallium to give [Rh(cp)L]. Reaction between these dimers and (pentane-2,4-dionato)-thallium resulted in a mixture of products including a low yield of [Rh(acac)L]. Good yields of the acac complexes were obtained by reacting [Rh(acac)(C_2H_4)$_2$] or [Rh(acac)(cod)] with the appropriate ligand. The cp complexes, [Rh(cp)L], are formally five-co-ordinate, 18-electron, species and are air stable in the solid state as expected. These complexes function as Lewis bases in solution and undergo oxidative addition in a manner similar to [Rh(cp)(PPh_3)(C_2H_4)].[5] The acac derivatives, however, are four-co-ordinate, 16-electron, complexes which react with air in the solid state and are decomposed by halogens or halogen halides at room temperature in benzene.

N.m.r. data [a]

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	$H_{(cp)}$	$J(H_1-H_3)$	$J(H_2-H_3)$	$\delta(^{31}P)$
dppp	4·72	4·88	4·08	5·68		2·51	2·72		17·0	10·3	−113·0
bdpp	5·06	5·11	4·24	7·91	7·91	2·60	2·70		17·0	10·3	+16·5
[Rh(cp)(dppp)] [b]	8·97	7·58	6·12	5·97 (4′) 5·89 (4)		2·30 2·66	2·66	4·75	10·0	7·5	−169·0
[Rh(cp)(bdpp)] [c]	8·80	7·66	5·96	8·4	8·0	2·31 2·63	2·63 2·74	4·84	10·0	7·5	−77·2
[Rh(cp)(PPh_3)(C_2H_4)] [d]	9·08	7·48						4·91			
[Rh(cp)(C_2H_4)$_2$] [e]	8·97	7·14						4·85	12·2	8·8	
[Rh(cp)(hxd)] [f]	8·20	6·81	5·43 (br)					4·49	11·0	8·5	
[Rh(cp)(cod)]			5·90	8·16 7·84							
[Rh(acac)(dppp)] [g]	7·54	7·01	5·93	6·06 (4) 5·79 (4′)		2·19	2·64		11·5	8·0	
[Rh(acac)(bdpp)] [h]	7·49	7·12	5·81	8·36	7·85	2·21	2·65		11·4	8·0	
[Rh(acac)(C_2H_4)$_2$] [i]	7·51	6·42									
[Rh(acac)(cod)] [j]			6·00	8·18 7·60							
[(hxd)Rh(μ-Cl)$_2$Rh(hxd)]	7·62	6·64	5·46	8·45 7·68					11·8	7·8	
[(cod)Rh(μ-Cl)$_2$Rh(cod)]			5·79	8·25 7·52							

dppp = Diphenyl(prop-2-enyloxo)phosphine, bdpp = (but-3-enyl)diphenylphosphine, cp = η-cyclopentadienyl, hxd = hexa-1,5-diene, cod = cyclo-octa-1,5-diene, and acac = pentane-2,4-dionato.

[a] ^1H N.m.r. spectra of all the complexes prepared in our laboratory were analysed at 220 MHz in $CDCl_3$ with Me_4Si as reference at τ 10·0. ^{31}P Chemical shifts (±0·3 p.p.m.) are relative to 85% H_3PO_4; br = broad. All peak intensities were checked by integration. [b] Additional coupling constants are: J(Rh–P) 214; $J(H_4-P)$ 34; $J(H_4'-P)$ 6·5; $J(H_3-P)$ $\leqslant$1·5; $J(H_2-P)$ *ca.* 1·5; $J(H_1-P)$ 5·0; $J(H_4-H_4')$ 10·0; $J(H_3-H_4)$ 3; $J(H_3-H_4')$ 3; $J(Rh-H_{(cp)})$ 0·5; and $J(P-H_{(cp)})$ 1·1 Hz. [c] Additional coupling constants are: J(Rh–P) 206; $J(P-H_3)$ $\leqslant$1·5; $J(P-H_2)$ *ca.* 1·5; $J(P-H_1)$ 4·5; $J(Rh-H_{(cp)})$ 0·6; and $J(P-H_{(cp)})$ 1·0 Hz. [d] Ref. 5; solvent CD_3COCD_3. [e] R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1971, **5**, 528; solvent $CDCl_3$, −25 °C. [f] Ref. 15; neat. [g] acac Resonances are at τ 4·63 (s) (one), 8·00 (s) (three), and 8·08 (s) (three). $J(P-H_4)$ 33, $J(P-H_4')$ *ca.* 2, $J(P-H_1)$ $\leqslant$1·5, $J(P-H_2)$ $\leqslant$2·0, and $J(H_4-H_4')$ 10 Hz. [h] acac Resonances are at τ 4·62 (s) (one) and 8·00 (s) (six); $J(P-H_1)$, $J(P-H_2)$, and $J(P-H_3)$ $\leqslant$1·5 Hz. [i] Ref. 15; solvent $CDCl_3$, −58 °C. [j] acac Resonances are at τ 4·71 (s) (one) and 8·12 (s) (six).

The C=C stretching frequency for the two free ligands bdpp and dppp occurs at 1 641 and 1 647 cm^{-1} respectively. On formation of the complexes [Rh(cp)L], this band was reduced by *ca.* 170 cm^{-1} to a shoulder at 1 475 ± 5 cm^{-1}, indicating a strong metal–olefin bond.[6] Attempts to refine this assignment using Raman spectroscopy were unsuccessful because of sample decomposition in the laser beam in both the solid state and solution.

N.m.r. spectra of the four complexes [RhL(L′)], can be used to evaluate the rhodium(I)–olefin bond strength and to determine the structures of the complexes. The Table includes several related complexes containing various non-conjugated olefin ligands. The olefinic resonances in each case are shifted upfield on complex formation, the terminal proton H_1 by the greatest and the vinylic proton H_3 by the smallest amount. The terminal protons H_1 and H_2 have a wide range of chemical shifts in chloroform, but can be classified into rather narrow ranges depending on whether the olefin is part of a cp 18-electron complex (H_1, τ 8·80—9·08; H_2, 7·14—7·66) or a 16-electron acac derivative or chloride-bridged dimer

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[5] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1165

[6] R. S. Nyholm, *Soumen Kem.*, 1969, 165.

(H_1, τ 7·49—7·62; H_2, 6·42—7·12). In contrast, the vinylic proton H_3 remains in a rather narrow range for all the complexes, τ 5·46—6·12. These generalizations prompted us to investigate the original assignment of the terminal olefinic proton resonances for [(hxd)Rh(μ-Cl)$_2$Rh(hxd)], one of the few reported rhodium(I) complexes of an olefin containing all three types of olefinic protons.[7] The original assignment of H_1 at τ 8·36, although reasonable for a cp complex, was incorrect and is properly assigned to the resonance at τ 7·62.

^{1}H N.m.r. spectra of the species [LRh(μ-Cl)$_2$RhL] were very complex. For L = dppp, the *cis*- and *trans*-proton coupling constants can be used to identify the terminal olefinic protons and, in conjunction with the intensity of these resonances, it can be concluded that there are three configurations, in nearly equal proportions, for the bonded ligand. The proton-decoupled ^{31}P n.m.r. spectrum had three doublets of nearly equal intensity. Consideration of the many possible isomers of this complex does not allow unambiguous assignment of the spectra to particular structures at the present time. The ^{1}H n.m.r. spectrum of the L = bdpp complex was less well resolved; however, at least two configurations were observed for the ligands. The ^{31}P spectrum showed two doublets in a 2 : 5 ratio, but there are insufficient data for an unambiguous assignment of structures.

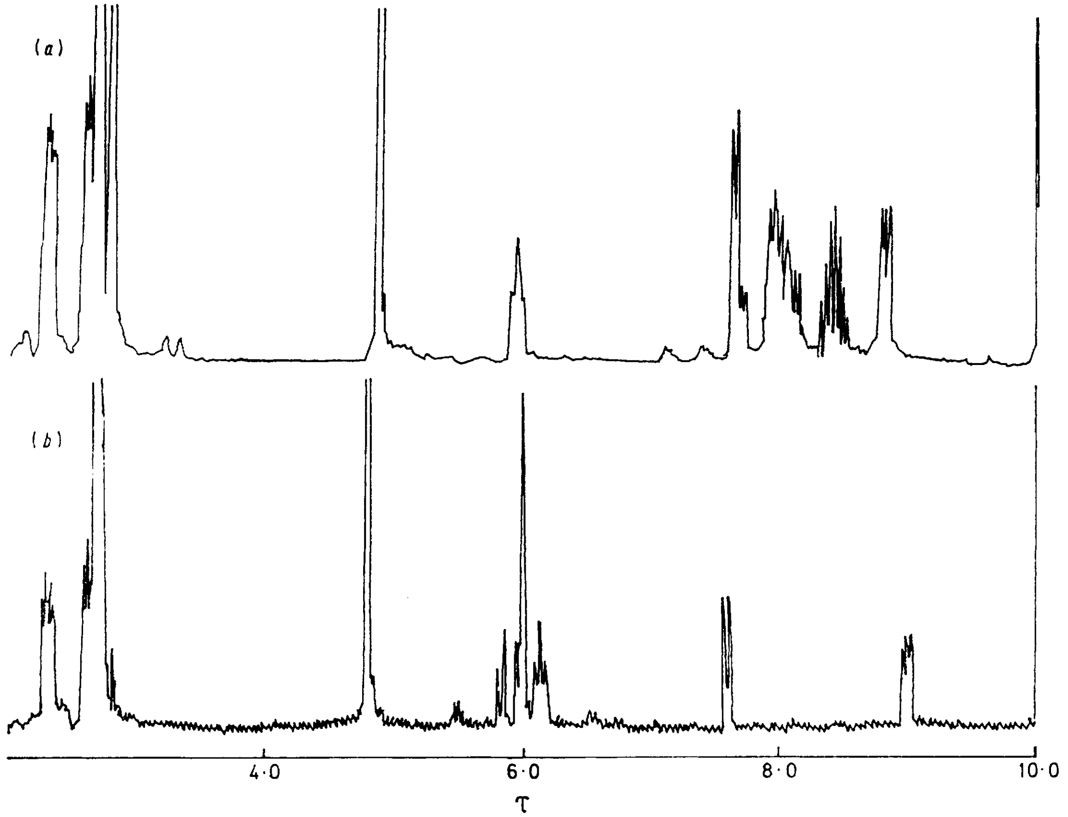

FIGURE 1 ^{1}H N.m.r. spectra in CDCl$_3$ at 220 MHz of the complexes: (*a*) [Rh(cp)(bdpp)]; (*b*) [Rh(cp)(dppp)]

^{31}P N.m.r. spectra of the complexes [Rh(cp)L] showed the expected downfield shift as compared to the free ligand and gave similar rhodium–phosphorus coupling for the two complexes. The principal coupling to the terminal olefinic protons is with H_3 and both $^3J(H_1-H_3)$ and $^3J(H_2-H_3)$ are smaller for these complexes than those of acac, as expected for greater metal–olefin back bonding. The next largest coupling, $^4J(P-H_1)$, was assigned by ^{31}P decoupling of the proton spectra and is considerably larger for the cp complexes [4·5 (bdpp) and 5·0 Hz (dppp)] than for the acac complexes where it is less than 1·5 Hz. The phosphorus coupling to H_2 may be as large as 2·0 Hz for [Rh(acac)(dppp)], but it is less than 1·5 Hz in the other three complexes. For the complexes [Mo(CO)$_4$(bdpp)],[2] [PdCl$_2$(bdpp)],[3] and [PtCl$_2$(bdpp)],[3] ^4J(PH) was not detected. Thus, for terminal protons of a bonded olefin, a larger upfield shift, a larger ^4J(PH), and smaller $J(H_1-H_3)$ and $J(H_2-H_3)$ values are all consistent with a stronger metal–olefin bond for cp complexes of rhodium(I).

Unequal phosphorus–hydrogen coupling constants may be used to determine the most-stable conformation in metal complexes.[8] The assignment of resonances in

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[7] G. Winkhaus and H. Singer, *Chem. Ber.*, 1966, **99**, 3602.

[8] J. Thomson, W. Keeney, M. C. Baird, and W. F. Reynolds, *J. Organometallic Chem.*, 1972, **40**, 205.

cyclic compounds containing P–O–CH linkages has been well documented,[9] and ^3J(POCH) varies from 0 to 33 Hz with the maximum value of the coupling constant occurring at a dihedral angle of 180°.[10] The methylene portion

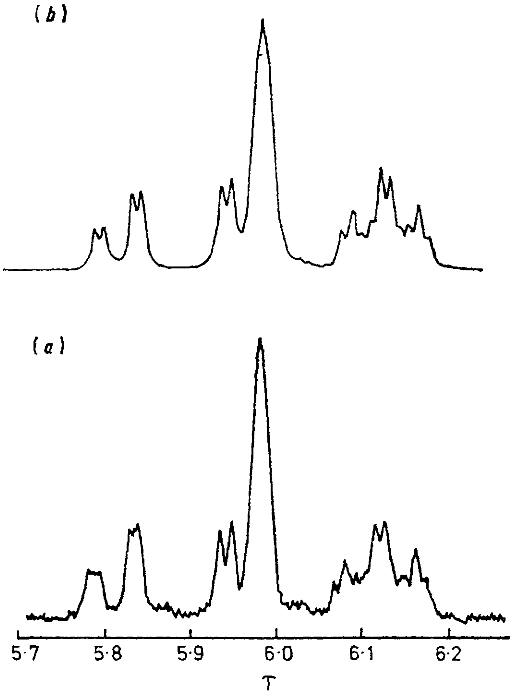

FIGURE 2 ^{1}H N.m.r. spectra in $CDCl_3$ at 220 MHz of the complex [Rh(cp)(dppp)]: (*a*) normal; (*b*) computer simulated

of the spectrum for the complex [Rh(cp)(dppp)] is part of an ABCMNXY spectrum (A = H_4, B = H_4', C = H_3, M = H_2, N = H_1, X = P, and Y = Rh). Rhodium coupling to these methylene protons is expected to be small and was neglected for the computer analysis. Coupling of H_1 and H_2 to H_4 and H_4' is also small and the spectrum is a pseudo-ABCX pattern (A = H_4, B = H_4', C = H_3, and X = P) with $J(H_4–P)$ 34, $J(H_4'–P)$ 6·5, $J(H_4–H_4')$ 10, and $J(H_4–H_3)$ 3 Hz; $\Delta\tau = 0{\cdot}08$ p.p.m. Comparison of the computed spectrum using a six-spin system (ABCMNX) with the actual spectrum (Figure 2) allows assignment of the coupling.

Two possible configurations for the phosphorus–butene portion of the ligand have been established in *X*-ray crystal-structure determinations of the complexes [Rh(bdpp)$_2$Cl][11] and [Rh(tbp)Cl] [tbp = tris(but-3-enyl)phosphine].[12] The configuration (I) appearing in both has the C=C bond axis perpendicular to the rhodium–phosphorus bond (Figure 3). The second configuration (II) also occurs in [Rh(bdpp)$_2$Cl], but the olefin is less strongly bonded to the rhodium. Configuration (I) is consistent with the large differences in $J(P–H_4)$ observed in solution with H_4 at a dihedral angle of 180° relative to the phosphorus. The lack of any temperature dependence (−50 to +50 °C) of the chemical shift of the three olefinic protons indicates that this configuration is stable throughout the range. Rotation about the rhodium–olefin bond axis, as observed for [Rh(cp)(C_2H_4)$_2$], is not possible with bdpp. However, a 90° oscillation is conceivable and has been proposed for Group VI complexes containing bdpp[2] or related olefinic tertiary phosphine ligands. The complex [Rh(cp)(PPh_3)(C_2H_4)], which is closely related to our complexes, [Rh(cp)L], has a non-rotating ethylene ligand even at 40 °C. Unequal phosphorus–hydrogen coupling was also observed in the ^{1}H n.m.r. spectrum of [Rh(acac)(dppp)], and the similarities in CH_2 coupling constants indicate the same configuration for dppp in both complexes. Thus rotation or oscillation on the n.m.r. time scale appears less probable for rhodium(I) than for Mo^0, Pt^{II}, or Pd^{II} bdpp complexes.[2,3]

Further information concerning the configurations of these rhodium(I) complexes was obtained from the phenyl region of the ^{1}H n.m.r. spectra. For the complexes [Rh(acac)L], relative peak intensities of the phenyl protons were 2 : 3, consistent with the usual assignment of the four *ortho*-protons as the multiplet shifted to lower field, τ *ca.* 2·2, and the *meta*- and *para*-protons as the multiplet at higher field, τ *ca.* 2·65. However, the integrals of the two multiplets observed in the phenyl region of the cp complexes, τ *ca.* 2·3 and *ca.* 2·7, were in the ratio of 1 : 4. The equivalence of the four *ortho*-protons in the acac complexes is probably due to rapid rotation about the phosphorus–phenyl bond on the ^{1}H n.m.r. time scale, with similar shielding for each phenyl ring. Although rapid rotation about this bond is also expected for the cp complexes, the inequality of

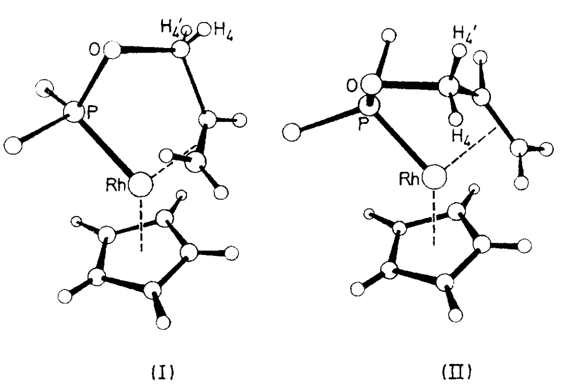

FIGURE 3 Rotational isomers of the complex [Rh(cp)(dppp)]: (I) preferred configuration with the C=C bond axis perpendicular to the metal–phosphorus bond (the methylene protons are non-equivalent with respect to the phosphorus atom; H_4 is at a dihedral angle of *ca.* 180°, H_4' at *ca.* 60°); (II) configuration with the C=C bond axis parallel to the metal–phosphorus bond (the methylene protons are equivalent with respect to the phosphorus atom; H_4 and H_4' at a dihedral angle of *ca.* 120°)

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[12] M. O. Visscher, J. C. Huffman, and W. E. Streib, *Inorg. Chem.*, 1974, **13**, 792.

the two sets of *ortho*-protons is consistent with the location of each of the phenyl rings in a different magnetic environment.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured on a Varian HR220 spectrometer. The ^{31}P n.m.r. spectra were obtained at 40·5 MHz on a Varian XL 100 instrument using Fourier-transform pulse methods with random-noise decoupling of the protons. I.r. spectra (4 000—670 cm^{-1}) were recorded on a Perkin-Elmer 137 spectrometer using a slow scanning rate. M.p.s (uncorrected) were measured on a Fischer–Johns apparatus. Mass spectra were determined at 70 eV using a Varian MAT CH-7 Massenspektrometer. Microanalyses were carried out by Galbraith Industries, Knoxville, Tennessee.

All preparations and reactions were carried out under an argon atmosphere using degassed reagent-grade solvents which had been dried over sodium wire. The complexes $[(H_4C_2)_2Rh(\mu\text{-}Cl)_2Rh(C_2H_4)_2]$,[13] $[(cod)Rh(\mu\text{-}Cl)_2Rh(cod)]$,[14] $[Rh(cp)(cod)]$,[14] $[Rh(acac)(C_2H_4)_2]$,[15] and $[(hxd)Rh(\mu\text{-}Cl)_2Rh(hxd)]$ (hxd = hexa-1,5-diene) [7] were prepared by literature methods; $[Rh(acac)(cod)]$ was prepared in a manner similar to the preparation of $[Rh(acac)(C_2H_4)_2]$ using $[(cod)Rh(\mu\text{-}Cl)_2Rh(cod)]$. The reagent η-cyclopentadienylthallium was prepared by literature methods using $TlNO_3$,[16] and was purified by sublimation at 110 °C and 0·4 Torr. (But-3-enyl)diphenylphosphine was prepared by the reaction of a Grignard reagent with chlorodiphenylphosphine,[17] and diphenyl(prop-2-enyloxo)phosphine by the reaction of allyl alcohol with chlorodiphenylphosphine in diethyl ether containing pyridine.[18]

Di-μ-chloro-bis{[*but*-3-*enyl*)*diphenylphosphine*-P;C^3,C^4-η]*rhodium*(I)}.—The complex $[(H_4C_2)_2Rh(\mu\text{-}Cl)_2Rh(C_2H_4)_2]$ 0·210 g, 0·54 mmol) was suspended in diethyl ether (10 cm^3) heated under reflux, and 5 cm^3 of diethyl ether containing (but-3-enyl)diphenylphosphine (0·25 cm^3, 1·08 mmol) was added dropwise over 2 min with vigorous stirring. An orange-yellow crystalline solid precipitated within 10 min. The suspension was cooled and the solution reduced to *ca.* 5 cm^3. The resulting air-stable *crystals* were collected by filtration, washed twice with diethyl ether, then dried under vacuum for 12 h (yield 0·387 g, 0·51 mmol; 96·3%), m.p. 124—125 °C [Found: C, 50·3; H, 4·70; Cl, 9·55; P, 8·25. *M* (mass spec.), 756. Calc. for $C_{32}H_{34}Cl_2P_2Rh_2$: C, 50·8; H, 4·55; Cl, 9·35; P, 8·20%. *M*, 756]. I.r. spectrum (KBr): 3 100w; 2 980w; 1 480s; 1 435s; 1 100s; 995m; 990m; 962m; 870s; 818s; 747s; 708s; and 692s cm^{-1}.

Di-μ-chloro-bis{[*diphenyl*(*prop*-2-*enyloxo*)*phosphine*-P;-C^2,C^3-η]*rhodium*(I)}.—This complex, a bright yellow crystalline air-stable *solid*, was prepared as above from $[(H_4C_2)_2Rh(\mu\text{-}Cl)_2Rh(C_2H_4)_2]$ or $[(cod)Rh(\mu\text{-}Cl)_2Rh(cod)]$ and diphenyl(prop-2-enyloxo)phosphine (yield 98%), m.p. 205—207 °C [Found: C, 47·45; H, 4·15; P, 8·25. *M* (mass spec.), 760. Calc. for $C_{30}H_{30}Cl_2O_2P_2Rh_2$: C, 47·35; H, 4·00; P, 8·15%. *M*, 760]. I.r. spectrum (KBr): 3 100w; 2 860w; 1 480m; 1 435s; 1 110s; 1 060m; 978m; 788m; 743s; 708s; and 692s cm^{-1}.

[(*But*-3-*enyl*)*diphenylphosphine*-P;C^3,C^4-η](*η-cyclopentadienyl*)*rhodium*(I).—This complex was prepared by suspending $[(bdpp)Rh(\mu\text{-}Cl)_2Rh(bdpp)]$ (0·300 g, 0·85 mmol Rh) with Tl(cp) (0·230 g, 0·85 mmol) in benzene (50 cm^3). After stirring the suspension overnight, it was filtered to remove TlCl and then the filtrate was passed through a 1 in × 3 in column of Florisil. The resulting yellow solution was concentrated to 5 cm^3 and hexane (5 cm^3) was added. Further concentration resulted in formation of a yellow air-stable *solid* (yield 64%), m.p. 94—96 °C {Found: C, 61·8; H, 5·50; P, 7·45. *M* (mass spec.), 408; C_4H_7 fragmentation left $[Rh(cp)(PPh_2)]^+$. Calc. for $C_{21}H_{22}PRh$: C, 61·75; H, 5·45; P, 7·60%. *M*, 408}. This complex is soluble in CH_2Cl_2, $CHCl_3$, C_6H_6, Et_2O, and Me_2CO. I.r. spectrum (KBr): 2 860m; 2 840m; 1 475m; 1 435s; 1 260m; 1 190s; 1 090s; 950m; 858m; 811s; 778s; 750s; and 700s cm^{-1}.

(*η-Cyclopentadienyl*)[*diphenyl*(*prop*-2-*enyloxo*)*phosphine*-P;C^2,C^3-η]*rhodium*(I).—The complex was prepared as above. The yellow air-stable *solid* was collected in 32% yield, m.p. 102—104 °C {Found: C, 58·65; H, 5·05; P, 7·35. *M* (mass spec.), 410; OC_3H_5 fragmentation left $[Rh(cp)(PPh_2)]^+$. Calc. for $C_{20}H_{20}OPRh$: C, 58·55; H, 4·90; P, 7·55%. *M*, 410}. I.r. spectrum (KBr): 3 010w; 2 960w; 2 840w; 1 480m; 1 475sh; 1 435s; 1 345m; 1 260m; 1 235m; 1 100s; 1 090sh; 1 020m; 970s; 945m; 898m; 868m; 794s; 763m; 743s; 708s; and 700s cm^{-1}.

[(*But*-3-*enyl*)*diphenylphosphine*-P;C^3,C^4-η](*pentane*-2,4-*dionato*)*rhodium*(I).—This complex was prepared by dissolving $[Rh(acac)(C_2H_4)_2]$ (0·200 g, 0·78 mmol) in diethyl ether (20 cm^3), chilling the orange solution to −10 °C, and then adding a similarly chilled solution of the phosphine (0·187 cm^3, 0·78 mmol) in diethyl ether (10 cm^3) dropwise over 2 min. The solution was then allowed to warm to 0 °C leading to the precipitation of a small amount of yellow-orange *crystals* over a 45 min period. Additional product was obtained by concentration of the solution while chilling to −80 °C. The air-sensitive complex became an orange oil at room temperature and was characterized by ^{1}H n.m.r. spectroscopy.

[*Diphenyl*(*prop*-2-*enyloxo*)*phosphine*-P;C^2,C^3-η](*pentane*-2,4-*dionato*)*rhodium*(I).—This complex was prepared above as using a 1 : 1 mol ratio of $[Rh(acac)(C_2H_4)_2]$ to the phosphine. The air-sensitive *oil* was isolated under an inert atmosphere and the complex was characterized by ^{1}H n.m.r. spectroscopy.

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