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Preliminary communication

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cis-DICHLORO{BIS-1-*anti*,3-*syn*-(*o*-DIPHENYLPHOSPHINO)PHENYL-1-METHALLYL(1-3η)}RHODIUM(III): A CHELATE π-ALLYLIC COMPLEX FORMED BY PROTON ABSTRACTION FROM AN OLEFINIC DI-TERTIARY-PHOSPHINE)

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Summary

The preparation, properties, and single crystal X-ray structure of the title complex, $RhCl_2[o\text{-}Ph_2PC_6H_4CH{\cdots}CH{\cdots}C(CH_3)C_6H_4PPh_2\text{-}o]$ are described.

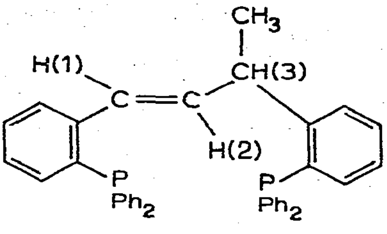
We have reported previously [1] that *o*-styryldiphenylphosphine [(*o*-vinylphenyl)diphenylphosphine), $o\text{-}CH_2{=}CHC_6H_4PPh_2$], is dimerized by rhodium(III) chloride in refluxing 2-methoxyethanol to give a planar rhodium(I) complex RhCl(1-Bdpb), from which the tridentate olefinic ligand bis-1,3-[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene, $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o$, 1-Bdpb (I) can be readily displaced. This ligand is deprotonated at the tertiary carbon atom, with concomitant isomerization of the configuration of the olefinic protons from *trans* to *cis*, on reaction with salts of palladium(II) or platinum(II) to give planar, chelate σ-alkyls such as II [2], which are similar to recently reported complexes derived from the ligands $o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4\text{-}PPh_2\text{-}o$ and $o\text{-}Ph_2PC_6H_4CH\overset{t}{=}CHC_6H_4PPh_2\text{-}o$ [3]. However, reaction of I with rhodium(III) chloride in 1/1 mole ratio results in both deprotonation and coordination of the double bond. The product, which is formed in 60% yield based on rhodium, is an orange crystalline solid of empirical formula $RhCl_2$(1-Bdpb-H) and has been shown by NMR spectroscopy and single crystal X-ray analysis to be the chelate 1-3η-allylic complex III. The singlet resonance for the methyl group in the ^1H NMR spectrum (Table 1) indicates loss of the methine proton from the ligand, and the two doublets in the ^{31}P-decoupled spectrum (J 8.0 Hz) can be readily assigned to the allylic protons. The chemical shifts of the latter are similar to those given

TABLE 1

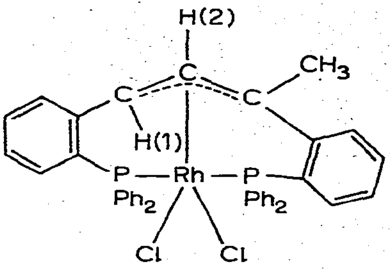
^{1}H AND ^{31}P NMR DATA [a] FOR Rh AND Ir COMPLEXES DERIVED FROM 1-Bdpb

Complex	δ(H) [b]				J(H—H)		J(P—H)	δ(P)	J(P—P)	J(Rh—P)
	H(1)	H(2)	H(3)	CH_3						
III [c]	2.05m	4.82m	—	1.70s	$J_{3,2}$	8.0	PH(1) 4.0, 2.0	33.6, 18.2	493	75, 98
							PH(2) 8.0, 2.0			
IV [c]	6.41d	5.01m	3.82m	1.82d	$J_{1,2}$	12.0	PH(2) 3.0, 0	10.2, −23.8	430	
					$J_{2,3}$	8.5	PH(3) sum ~2.5			
					$J_{3,Me}$	7.0				

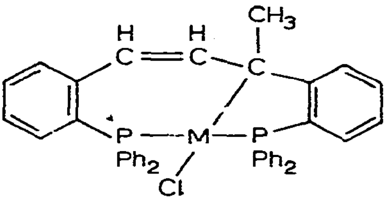
[a] Solutions in CD_2Cl_2. ^{1}H shifts in ppm from internal tetramethylsilane. ^{31}P shifts in ppm from external H_3PO_4, downfield defined as positive in both cases. Couplings from ^{31}P spectra ± 5 Hz. [b] m, multiplet; d, doublet; s, singlet. Aromatic signals in range 6.9 — 8.5 ppm.
[c] Recrystallised from CH_2Cl_2/MeOH. III contains 1 mole of MeOH (δ 3.38). Analysis III. Found: C, 63.2; H, 4.3; Cl, 9.7; P, 7.8. $C_{40}H_{35}Cl_2P_2Rh{\cdot}CH_3OH$ calcd.: C, 63.0; H, 4.8; Cl, 9.1; P, 7.9%. Molecular weight: found 766 ($CHCl_3$, V.P.O., 37°) calc. (unsolvated) 750. Analysis IV. Found: C, 53.4; H, 4.4; Cl, 14.1; P, 7.1. $C_{40}H_{34}Cl_3P_2Ir{\cdot}0.3CH_2Cl_2$ calcd.: C, 53.7; H, 3.9; Cl, 14.2; P, 6.9%. Molecular weight: found 969 ($CHCl_3$, V.P.O., 37°) calc. (unsolvated) 875.



(I)



(III)



(II)

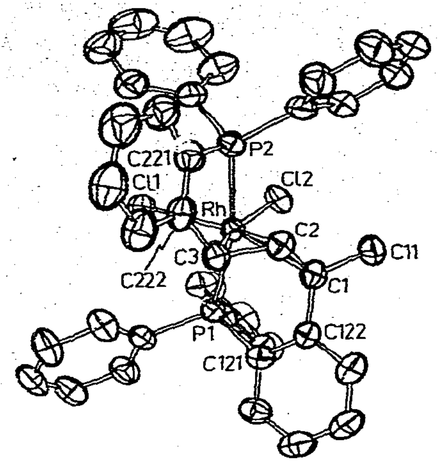
as typical [4] of π-allylic metal complexes, with H(1) in an *anti*-position with respect to H(2), as in III. The magnitude of the coupling would have suggested a *cis* arrangement for these protons by analogy with published work on 1-3η-allylic complexes [4], but the X-ray work (see below) contradicts this.

Generally, in planar palladium(II)-π-allyl(phosphine) complexes, strong ^{31}P coupling is observed only to the *anti* protons. In III, the larger ^{31}P coupling is to H(2) rather than H(1) but this observation is readily accounted for by the different orientation of the metal—phosphorus bond to the π-allylic moiety.

The ^{31}P NMR spectrum comprises 8 lines, *i.e.* an AB quartet arising from inequivalent phosphorus atoms split into doublets by coupling with ^{103}Rh. The magnitude of $J(P—P)$ suggests that the phosphorus atoms are mutually *trans*, in agreement with the X-ray result.

Crystals of $RhCl_2\{o\text{-}Ph_2PC_6H_4CH \overset{\cdots}{-} CH \overset{\cdots}{-} C(CH_3)C_6H_4PPh_2\text{-}o\}\cdot CH_3OH$ are monoclinic, space group C_c, with $a = 9.833(2)$, $b = 19.430(5)$, $c = 18.898(5)$ Å, $\beta = 93.18(2)°$, $Z = 4$. Using data which had been corrected for absorption effects, the structure is fully refined, and has converged to a conventional R factor of 0.023. [3811 reflections with $I/\sigma(I) \geqslant 3.0$, collected by counter methods using graphite-crystal monochromated Cu-K_α radiation; anisotropic thermal parameters for Rh, Cl, P, O, and C; refined positional and isotropic thermal parameters for π-allyl hydrogen atoms; fixed parameters for phenyl hydrogen atoms.]

The overall stereochemistry of the molecule, which is essentially octahedral about the central Rh^{III} atom, is shown in Fig. 1. Important features of the geometry of the coordinated π-allylphosphine ligand are: (1) There is considerable steric strain in the tridentate ligand, as shown by the angles



ATOMS	DISTANCE, Å
Rh-Cl(1)	2.391(1)
Rh-Cl(2)	2.456(1)
Rh-P(1)	2.311(1)
Rh-P(2)	2.354(1)
Rh-C(1)	2.281(4)
Rh-C(2)	2.105(3)
Rh-C(3)	2.140(3)
P(1)-C(121)	1.805(4)
C(121)-C(122)	1.395(5)
C(122)-C(1)	1.505(5)
C(1)-C(2)	1.427(4)
C(1)-C(11)	1.497(5)
C(2)-C(3)	1.425(5)
C(3)-C(222)	1.465(5)
C(222)-C(221)	1.411(5)
C(221)-P(2)	1.823(4)

Fig. 1. The overall stereochemistry of the molecule.

P(1)—Rh—P(2) [167.28(3)°], Rh—P(1)—C(121) [105.4(1)°], and Rh—P(2)—C(221) [99.9(1)°], which differ significantly from their expected values of 180, 116, and 116° respectively. In addition, in contrast to the situation in $[(\pi\text{-}C_4H_7)RhCl_2(AsPh_3)_2$ [5], where the Rh—C(π-allyl) distances are equal within experimental error (average 2.24 Å), the Rh—π-allyl bonding in the present complex is asymmetric [6] with the Rh—C distances varying from 2.105(3) to 2.281(4) Å ($\Delta/\sigma \doteqdot 44$);

(2) The distances C(1)—C(2) and C(2)—C(3) are equal within experimental error (average 1.426 Å), and are very similar to π-allyl carbon—carbon distances found for $[(\pi\text{-}C_4H_7)RhCl_2(AsPh_3)_2]$ (1.43(2) and 1.46(2) Å) [5];

(3) The angle C(1)—C(2)—C(3) is 123.9(3)°, *cf.* 119.8° for $[(\pi\text{-}C_3H_5)PdCl]_2$ [7], and 129.8° for $[(\pi\text{-}C_3H_5)Pd(PPh_3)(SnCl_3)]$ [8].

In contrast with Rh^{III}, Pd^{II} and Pt^{II}, iridium(III) chloride reacts with I in refluxing 2-methoxyethanol to give a yellow, crystalline chelate olefin complex $IrCl_3$(1-Bdpb) (IV), in which the methine proton remains intact. NMR spectra (Table 1) indicate that the *trans* arrangement about the double bond of (I) is preserved on coordination and that the phosphorus atoms are mutually *trans* in the complex.

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