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Synthesis and Characterization of Substituted-Allyl-Rhodium Complexes Incorporating Bidentate Phosphine and Phosphinite Ligands

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The reaction of (1,5-cyclooctadiene)(2-methylallyl)rhodium(I), [η^3-(2-Me-C_3H_4)Rh(COD)], with chelating phosphines and phosphinites results in the smooth displacement of 1,5-cyclooctadiene and the formation of the new (2-methylallyl)rhodium complexes [η^3-(2-Me-C_3H_4)RhL_2], where L_2 = $Me_2PCH_2CH_2PMe_2$, (p-Me-C_6H_4)$_2PCH_2CH_2P(C_6H_4$-p-Me)$_2$, $Ph_2PCH_2CH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, (S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$, $HN(SiMe_2CH_2PPh_2)_2$, $Ph_2PCH_2CH_2AsPh_2$, and $(MeO)_2PCH_2CH_2P(OMe)_2$, in good yields. Similarly, the reaction of a number of the above chelating ligands with the pure syn isomer of (1,5-cyclooctadiene)(1-methylallyl)rhodium(I), [η^3-(1-Me-C_3H_4)Rh(COD)], results in a mixture of the corresponding syn and anti isomers with the syn form predominating. The preparation and spectral characterization of all new compounds are presented together with a discussion of the stereoselectivity of the substitution process.

Since the initial discovery by Wilkinson and others[1] that tris(triphenylphosphine)rhodium(I) chloride, $(Ph_3P)_3RhCl$ (**1**), is an effective and easily prepared *catalyst precursor* for a variety of homogeneous reactions, numerous modifications of this basic rhodium-phosphine system have appeared. For instance, rather than use a *neutral* precursor such as **1**, Schrock and Osborn, in a definitive series of papers,[2] showed that *cationic* diene complexes of the type $[(diene)RhL_2]^+A^-$ (diene = 2,5-norbornadiene or 1,5-cyclooctadiene; L = tertiary phosphine; A^- = noncoordinating anion) would, under suitable conditions, generate active homogeneous hydrogenation catalysts. More recently, it has been shown[3] that allylrhodium phosphite derivatives, [η^3-(C_3H_5)$Rh(P(OR)_3)_x$] (x = 2 or 3), can be activated by reaction with hydrogen to generate a series of exceedingly reactive, neutral clusters of the type $[HRh(P(OR)_3)_2]_n$ (n = 2 or 3).

A more subtle modification was the discovery that chelating *bidentate* phosphines coordinated to rhodium altered[4] the sequence of steps in the catalytic cycle for homogeneous hydrogenation compared with the sequence in similar complexes in which *monodentate* phosphines were used. This was elegantly shown by Halpern,[5] and its impact on the mechanism of asymmetric homogeneous hydrogenation is well documented.[6] The ability of a chelating ligand to affect the reactivity patterns of transition-metal complexes in homogeneous catalysis[7] has prompted us to study the synthesis and reactivity of new potential catalyst precursors incorporating bidentate phosphines and phosphinites. We report here the synthesis and spectral characterization of a variety of substituted-allyl-rhodium(I) diphosphine and diphosphinite complexes.

Results and Discussion

2-Methylallyl Derivatives. The reaction of (2-methylallyl)magnesium chloride with (1,5-cyclooctadiene)chlororhodium(I) dimer, $[(COD)RhCl]_2$, in tetrahydrofuran (THF) produces, in good yield, (1,5-cyclooctadiene)(2-methylallyl)-rhodium(I), [η^3-(2-Me-C_3H_4)Rh(COD)] (**2**), as a yellow, very air-sensitive, volatile solid. **2** is somewhat thermally unstable but less so than the recently reported[3] unsubstituted derivative [η^3-(C_3H_5)Rh(COD)] (**3**).

Addition of 1 equiv of a bidentate phosphine or phosphinite to a benzene or hexane solution of **2** results in the facile displacement[3] of the COD ligand to produce the desired complexes in very high yields (eq 1). For example, when L_2 is

$$[\eta^3\text{-(2-Me-}C_3H_4\text{)Rh(COD)}] + L_2 \rightarrow [\eta^3\text{-(2-Me-}C_3H_4\text{)}RhL_2] + COD \quad (1)$$

1,2-bis(dimethylphosphino)ethane (dmpe), the yellow volatile complex [η^3-(2-Me-C_3H_4)Rh(dmpe)] (**4**) is obtained in nearly quantitative yield. Other derivatives produced by this method are listed in Table I. These complexes are extremely air sensitive, even in the solid state, and with the exception of **4**, are nonvolatile; in addition, they are soluble in most organic solvents, especially aromatic solvents and to some extent hydrocarbon solvents.

From the ^1H and $^{31}P\{^1H\}$ NMR data (Table II), these complexes are formulated as mononuclear, square-planar derivatives with the allyl ligand occupying, formally, two cis sites. The $^{31}P\{^1H\}$ spectra of compounds **4-11** are sharp, temperature-independent doublets indicative of equivalent phosphorus nuclei coupled to rhodium-103 (^{103}Rh, 100% natural abundance, spin $^1/_2$). The rhodium-phosphorus coupling constants ($^1J_{Rh-P}$) are quite similar and range from 180 to 200 Hz for phosphines and slightly higher, 260 Hz, for phosphinites (cf. **11**). The ^1H NMR spectra follow established trends[9-13,15] and are easily interpreted. In addition to the resonances of the bidentate ligands, the 2-methylallyl group displays a low-field singlet due to the syn protons while both the anti protons and the 2-methyl protons appear as doublets at higher field, the former coupled to phosphorus-31 ($^3J_P \approx$ 5.8-7.6 Hz) and the latter coupled to rhodium-103 ($^3J_{Rh} \approx$ 1.8-2.5 Hz). Exceptions to these straightforward spectra are compounds **8** and **9**; in **8**, the chiral chelating phosphine chiraphos[16] transmits its asymmetry, via a rigid chiral array

(1) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. Bennett, M. A.; Longstaff, P. A. *Chem. Ind. (London)* **1965**, 846.
(2) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134, 2143, 4450.
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(11) Nixon, J. F.; Poland, J. S.; Wilkins, B. *J. Organomet. Chem.* **1975**, *92*, 393.
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(13) Nixon, J. F.; Wilkins, B.; Clement, D. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1993.
(14) Fryzuk, M. D., unpublished results.
(15) Vrieze, K.; Volger, H. C. *J. Organomet. Chem.* **1967**, *9*, 537.
(16) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

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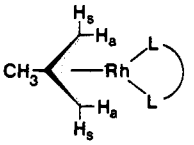
Table I. Analytical Data for the Derivatives $[\eta^3\text{-}(2\text{-Me-}C_3H_4)RhL_2]$

compd no.	L_2	formula	anal. calcd % C	anal. calcd % H	anal. found % C	anal. found % H
4	$Me_2PCH_2CH_2PMe_2$ (dmpe)	$C_{10}H_{23}P_2Ph$	39.0	7.52	39.3	7.54
5	$(p\text{-Me-}C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-Me})_2$ (dptpe)	$C_{34}H_{39}P_2Rh$	66.7	6.42	66.4	6.71
6	$Ph_2PCH_2CH_2CH_2PPh_2$ (dppp)	$C_{31}H_{33}P_2Rh$	65.3	5.83	65.9	5.89
7	$Ph_2PCH{=}CHPPh_2$ (*cis*-dppe)	$C_{30}H_{29}P_2Rh$	65.0	5.27	64.6	5.13
8	$(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2$ (chiraphos)	$C_{32}H_{35}P_2Rh$	65.8	6.04	66.1	6.10
9	$Ph_2PCH_2CH_2AsPh_2$ (arphos)	$C_{30}H_{31}PAsRh$	60.0	5.20	60.3	5.42
10	$HN(SiMe_2CH_2PPh_2)_2$	$C_{34}H_{44}NSi_2P_2Rh$	59.4	6.40	59.0	6.56
11	$(MeO)_2PCH_2CH_2P(OMe)_2$ (dmope)	$C_{10}H_{23}O_4P_2Rh$	32.3	6.23	32.0	6.10

Table II. $^1H^a$ and $^{31}P\{^1H\}^b$ NMR Data[c] for the $[\eta^3\text{-}(2\text{-Me-}C_3H_4)RhL_2]$ Derivatives



compd no.	H_s	H_a (^3J_P)	CH_3 ($^3J_{Rh}$)	δ_P ($^1J_{Rh}$)	ligand[e]
4	3.48 s	2.36 brd (6.0)	1.75 d (2.0)	37.4 (189)	dmpe: $CH_2P(CH_3)_2$, 1.33 m
5	3.90 s	2.71 brd (6.0)	1.90 d (2.0)	66.9 (197)	dptpe: $p\text{-}CH_3C_6H_4$, 2.04 s; PCH_2CH_2P, 2.20 brm
6	3.20 s	*d*	1.87 d (2.2)	27.5 (189)	dppp: PCH_2-, 2.56 t, J_P = 3.4 Hz; $PCH_2CH_2CH_2P$, 2.30 m
7	4.00 s	2.64 brd (6.0)	1.77 d (2.0)	75.6 (196)	*cis*-dppe: $PCH{=}CHP$, 6.9 m[d]
8	3.59 m	2.71 m (6.6)	1.73 d (2.2)	70.7 (193)	chiraphos: $PCH(CH_3)$, 2.17 m; $PCH(CH_3)$, 0.95 m
	3.48 m	2.41 m (6.6)			
9	4.13 m	2.83 s	1.92 d (2.0)	70.6 (198)	arphos: PCH_2CH_2As, 2.00 m
	3.83 m	2.67 d (6.2)			
10	2.80 s	2.35 brd (5.8)	1.82 d (2.0)	26.1 (195)	$HN(SiMe_2CH_2PPh_2)_2$: PCH_2-, 1.62 brm; $-Si(CH_3)_2$-, 0.07 s, 0.03 s
11	3.89 brs	2.31 brd (7.6)	1.60 d (2.2)	204.2 (260)	dmope: PCH_2-, 1.78 m; $P(OCH_3)_2$, 3.51 d, J_P = 13.2 Hz, 3.42 d, J_P = 12.9 Hz

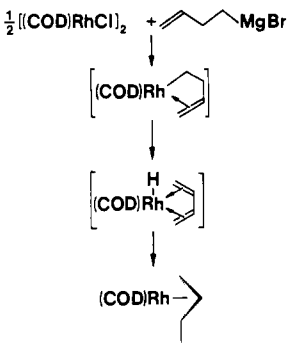
[a] 80 or 400 MHz, in C_6D_6, values in ppm. All coupling constants are in Hz. [b] 32.442 MHz, in C_6D_6, relative to $P(OMe)_3$ at 141 ppm. [c] s = singlet, d = doublet, brd = broad doublet, t = triplet, m = multiplet, brs = broad singlet, brm = broad multiplet, br = broad. [d] Resonances obscured. [e] Phenyl region not listed.

of phenyl groups, to the 2-methylallyl ligand, generating four multiplets, one for each of the diastereotopic syn and anti protons. Complex **9**, the arphos derivative, also generates four multiplets for the nonequivalent syn and anti protons, but in this case it is the different donor atoms in the bidentate ligand that reduce the symmetry; the anti protons of **9** appear as a doublet at 2.67 ppm and a singlet at 2.83 ppm, the former trans to phosphorus (^3J_P = 6.2 Hz) and the latter trans to arsenic.

The spectroscopic data are only consistent with a rigid, symmetric η^3 bonding mode by the 2-methylallyl ligand with very slow η^3–η^1 interconversions. Rotation of the allyl ligand similar to that observed[17] for $[\eta^3\text{-}(C_3H_5)Fe(CO)_3I]$ must also be very slow as this type of internal motion would symmetrize the unsymmetrical derivative **9**. This rigid η^3 bonding mode establishes a "top" (syn to the 2-methyl substituent) and a "bottom" to these square-planar complexes, which can be detected to some extent by the substituents on the phosphorus donors and the backbone of the chelate ring; for example, the silylmethyl protons of **10**[18] appear as two singlets at 0.07 and 0.03 ppm, and the methoxy groups of **11** appear as two doublets at 3.51 ppm (^3J_P = 13.2 Hz) and 3.42 (^3J_P = 12.9 Hz).

The effect of the length and flexibility of the bidentate phosphine backbone was briefly investigated; five-, six-, and eight-membered chelate rings formed easily (cf. **5**, **6**, and **10**). However, attempts to generate a four-membered chelate ring by use of 1,1-bis(diphenylphosphino)methane (dppm) only produced binuclear rhodium complexes whose solution behavior sharply contrasts with that of the mononuclear derivatives described in this study; for this reason they are considered separately.[19]

Scheme I. Proposed Pathway for the Stereoselective Formation of **12**



1-Methylallyl Derivatives. The reaction of excess isopropylmagnesium bromide with $[(COD)RhCl]_2$ in the presence of butadiene is reported[10] to produce, stereoselectively, only the syn isomer of $[\eta^3\text{-}(1\text{-}MeC_3H_4)Rh(COD)]$ (**12**) in 67% yield. Presumably this proceeds by the formation of the unstable intermediate [(COD)RhH(butadiene)], which collapses via hydride addition to one of the double bonds of butadiene to generate **12**. We have modified the synthesis of **12** by the use of 3-butenylmagnesium bromide as the source of both the hydride and the coordinated butadiene (Scheme I). Isolation via sublimation routinely gives **12** in greater than 90% yield. We have verified that **12** exists exclusively as the

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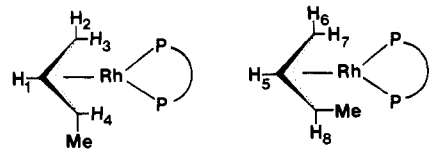
(18) This compound was prepared and characterized by P. A. MacNeil.
(19) Fryzuk, M. D. *Inorg. Chim. Acta* **1981**, *54*, L265.

Table III. ^{1}H NMR (in C_6D_6, ppm)[a] of the Syn and Anti [η^3-(1-Me-C_3H_4)RhL_2] Isomers



compd no.	syn:anti ratio[b]	H_1	H_2 (J_{12})	H_3 (J_{13})	H_4 (J_{14})	H_5	H_6 (J_{56})	H_7 (J_{57})	H_8	syn CH_3 (J_P)	anti CH_3
13	86:14	5.07 m	3.68 m (7.2)	2.32 dd (12.8)	3.39 sep (12.0)	4.98 m	3.82 brd (7.6)	2.58 dd (13.5)	4.69 brm	2.24 m	*c*
14	90:10	5.26 m	4.03 d (7.0)	2.67 dd (13.0, J_P = 6.5)	3.65 sep (12.0, J_{CH_3} = 6.0)	*c*	4.13 brd (7.2)	2.97 dd (13.2, J_P = 6.5)	4.97 brm	*c*	1.31 m
15	80:20	5.07 m	3.25 m	2.39 dd (13.0, J_P = 6.0)	3.25 (*c*)	5.15 m	3.48 brd (7.0)	2.68 dd (12.0, J_P = 6.8)	4.06 brm	1.52 m	1.07 m
16	76:24	5.07 m	3.72 d (7.3)	2.68 dd (12.9, J_P = 6.4)	3.45 sep (12.2, $J_P = J_{CH_3}$ = 6.1)	5.07 m	3.84 brd (7.8)	2.84 dd (13.9, J_P = 6.1)	4.56 m	1.82 m	1.30 m
			3.50 d (7.3)	2.32 dd (12.7)	3.35 sep (12.2, $J_{CH_3} = J_P$ = 6.1)		3.63 brd (6.8)	2.57 dd (13.9, J_P = 6.6)		1.72 m (4.6)	
17	79:21	5.03 m	3.94 m (5.0)	2.15 dd (12.0, J_P = 8.0)	*c*	4.86 m	4.00 brm	2.47 dd (14.0, J_P = 8.0)	5.19 m	2.33 m	1.23 m

[a] All coupling constants are in Hz; sep = septuplet. All spectra were obtained on a Bruker WH-400 instrument operating at 400 MHz. [b] Refers to isolated product. [c] Resonances obscured.

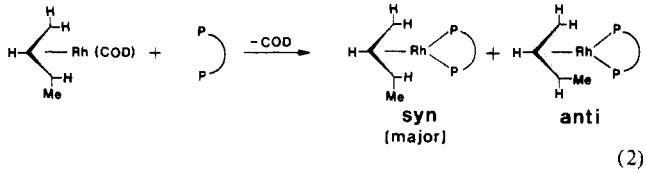
Table IV. $^{31}P\{^1H\}$[a] (C_6D_6) Data and Analyses for (1-Methylallyl)rhodium Phosphine Derivatives

						anal.			
						calcd		found	
compd	L_2	δ_{P_A} ($^1J_{Rh}$)	δ_{P_B} ($^1J_{Rh}$)	$^2J_{P_AP_B}$	formula	% C	% H	% C	% H
syn-13	dmpe	41.6 (192)	39.0 (194)	14.7	$C_{10}H_{23}P_2Rh$	39.0	7.52	39.6	7.56
anti-13		43.0 (189)	40.5 (194)	17.1					
syn-14	dptpe	70.4 (201)	69.0 (201)	17.1	$C_{34}H_{39}P_2Rh$	66.7	6.42	66.6	6.55
anti-14		*b*	*b*	19.5					
syn-15	dppp	29.2 (197)	23.2 (192)	39.7	$C_{31}H_{33}P_2Rh$	65.3	5.83	65.4	5.98
anti-15		29.0 (190)	23.1 (190)	39.7					
syn-16	chiraphos[c]	68.8 (199)	68.8 (199)	0[d]	$C_{32}H_{35}P_2Rh$	65.8	6.04	66.1	5.85
syn'-16		73.2 (195)	65.0 (202)	29.3					

[a] Chemical shifts are relative to $P(OMe)_3$ at 141 ppm; coupling constants are in Hz. [b] Some lines obscured. [c] Only the syn diastereomers could be cleanly observed. [d] Appears as an A_2X pattern.

syn isomer (>99% by 400-MHz ^{1}H NMR).

As with **2**, substitution of the COD ligand by chelating phosphines and phosphinites proceeds smoothly at room temperature but results in a mixture of syn and anti isomers with the syn predominating (eq 2). Ratios of isomers and pertinent



(2)

^{1}H NMR data are given in Table III. Because of the complexity of the ^{1}H NMR spectra of these complexes on routine 80- or 100-MHz instruments, isomer ratios are very difficult to determine; however, the use of high-field instruments (270 or 400 MHz) has allowed accurate integration of syn:anti ratios.

The $^{31}P\{^1H\}$ NMR data are listed in Table IV. By symmetry, the 1-methylallyl derivatives should exhibit ABX $^{31}P\{^1H\}$ spectra due to inequivalent phosphorus nuclei coupled to rhodium-103, and indeed, the majority of the spectra can be analyzed[20] as such. Exceptions are one of the syn diastereomers of **16**, which exhibits a simple A_2X pattern, and **17**, which exhibits a very complicated and as yet unanalyzed pattern; the origin of the discrepancies is not clear.

As already mentioned, the ^{1}H NMR spectra for mixtures of syn and anti isomers are quite complex; although homonuclear and heteronuclear (^{31}P) decoupling experiments establish unambiguously the identity of every resonance, not all the coupling constants are resolvable. Simulations have so far been of marginal assistance in determining coupling constants; rather, they serve to verify couplings already gleaned visually from the spectra. Because the protons of the 1-methylallyl ligand are coupled not only to each other but also to rhodium and phosphorus to some extent as well, the complexity is not surprising.

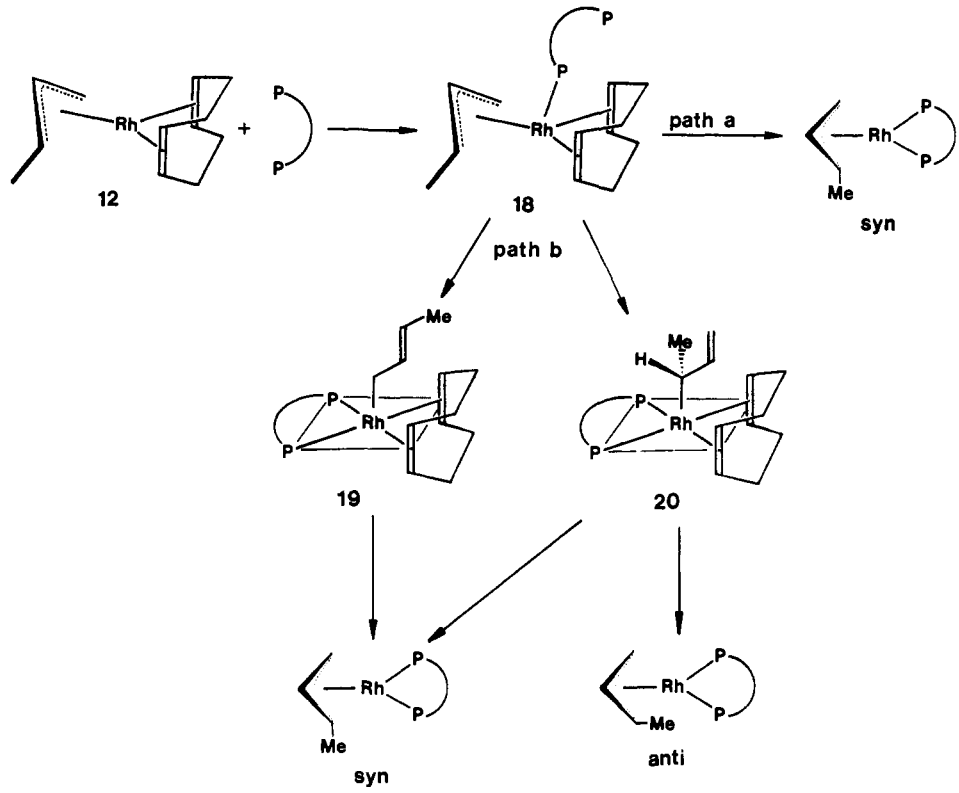
In solution (C_6D_6), the syn:anti ratios do not change measurably with time (2 weeks) or with increasing temperature; above 50 °C, there is noticeable decomposition (darkening of the solution) and butenes can be detected (^{1}H NMR). Addition of CD_3CN (≥10 equiv), a known coordinating solvent, does not affect the initially observed isomer ratio, even after 1 week. Similarly the presence of 1,5-cyclooctadiene does not affect the syn:anti ratio. Addition of more strongly coordinating ligands such as PEt_3, $P(OMe)_3$, or CO[21] generates stable, fluxional adducts with rapid syn–anti exchange.[14]

The chiraphos complex, **16**, is interesting since asymmetric induction at the 1-methyl center is possible. Indeed, all four possible diastereomers can be detected (but not uniquely

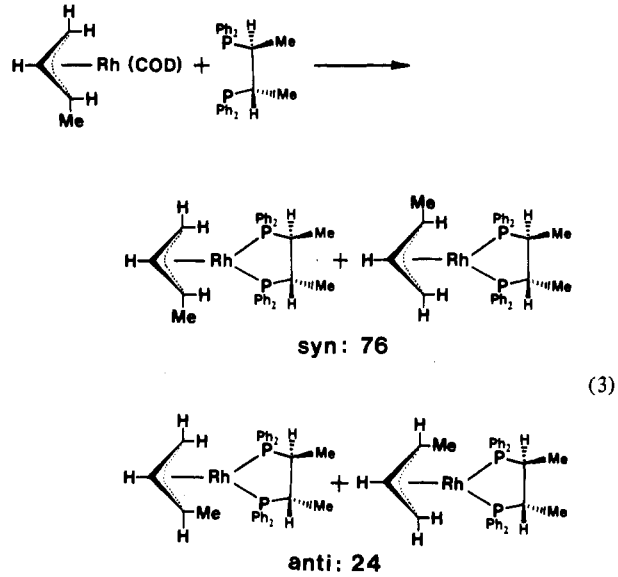
(20) Becker, E. D. "High Resolution NMR"; Academic Press: New York, 1969; pp 149–163.

(21) Addition[14] of excess CO generates the reactive rhodium(I) acyl derivatives [$L_2Rh(CO)_2COR$] (R = 1-Me-C_3H_4 or 2-Me-C_3H_4).

Scheme II. Proposed Pathways for the Substitution of 1,5-Cyclooctadiene by Chelating Phosphines



identified) in the isolated product by ^1H NMR (Figure 1), whereas only the predominant syn diastereomers can be clearly detected by $^{31}P\{^1H\}$ NMR. The total syn:anti ratio is 76:24, the syn diastereomers are obtained in a 56:44 ratio and the anti diastereomers in a 55:45 ratio (eq 3).



(3)

The formation of the anti isomers in all these substitution reactions may be a consequence of the different substitution pathways available since no syn–anti isomerism is observed in the products after substitution of the cyclooctadiene ligand. A reasonable mechanism for the displacement of 1,5-cyclooctadiene by chelating phosphines (or phosphinites) is shown in Scheme II. Initial coordination of one phosphine would generate the saturated (18-electron) complex **18**, which can either lead directly to the desired product with dissociation of 1,5-cyclooctadiene (path a) or undergo conversion of the η^3-1-methylallyl ligand to a mixture of the possible η^1-bonded isomeric intermediates **19** and **20** (path b). Path a, which does not disrupt the η^3 bonding mode, cannot be the exclusive substitution pathway since it does not lead to loss of stereochemistry on the allyl ligand; furthermore, the observed asymmetric induction in **16** is only possible via formation of the η^1-bonded diastereomers **21**, **22**, and **23** (vide infra).

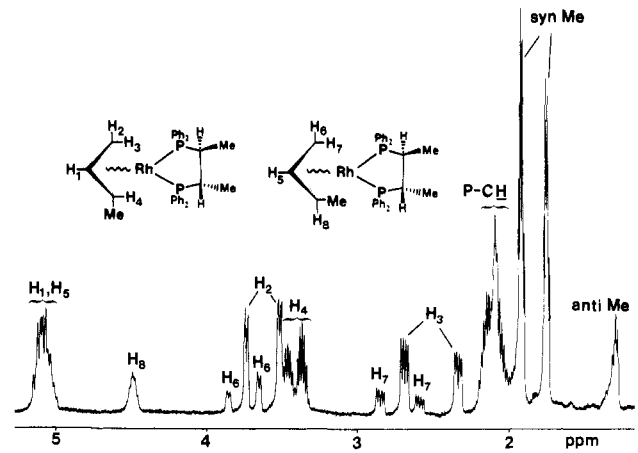
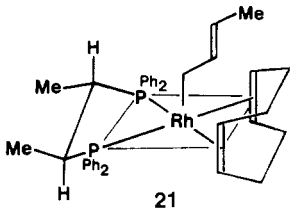


Figure 1. 400-MHz ^1H NMR (C_6D_6) of the mixture of diastereomers of (*S*,*S*)-(1-Me-C_3H_4)Rh(chiraphos).

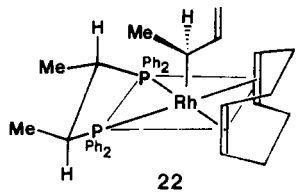
Rearrangement of **18** via path b to **19** and **20** is attractive since analogous complexes of the type [(COD)Rh(Me)L_2] (L_2 = chelating phosphine) have been studied.[22] **19** can only collapse with dissociation of COD to generate the syn isomer. The asymmetric induction observed in the formation of the syn diastereomers of **16** can be rationalized as a slight discrimination of the diastereotopic olefinic faces of the η^1-methylallyl ligand of **21** upon coordination. The situation with the proposed intermediate **20** is more complicated as it can collapse to either a syn or an anti configuration depending on the relative orientation of the 1-methyl substituent and the vinyl group in the transition state. The origin of the asym-

(22) Shapley, J. R.; Osborne, J. A. *Acc. Chem. Res.* **1973**, *6*, 305.

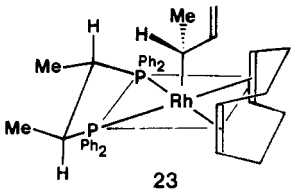


21

metric induction observed for the anti diastereomers of **16** is also not straightforward. Two diastereomeric intermediates, **22** and **23**, epimeric at the η^1-bonded carbon can be envisaged.



22



23

In the absence of any preequilibrium steps in the formation of **22** and **23** from racemic **12**, these diastereomers should be formed in equal amounts. As an excess of one of the diastereomers is observed, it may be that one of the epimeric derivatives **22** or **23** is converted to the appropriate syn diastereomer to a greater extent than the other.

Summary

The displacement of 1,5-cyclooctadiene from [η^3-(2-Me-C_3H_4)Rh(COD)] or [η^3-(1-Me-C_3H_4)Rh(COD)] by chelating phosphines or phosphinites provides a facile, high-yield route to new substituted-allyl–rhodium(I) diphosphine and diphosphinite complexes. The reactivity of these new complexes with H_2 and with H_2–CO mixtures to generate respectively hydrogenation and hydroformylation catalysts[14] will be the subject of future publications.

Experimental Section

General Information. All manipulations were performed under prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purifier or in standard Schlenk type glassware. Hydrated rhodium trichloride was obtained from Johnson-Matthey and used as received to prepare $[(COD)RhCl]_2$ by a literature method.[23] The bidentate ligands $Ph_2PCH_2CH_2CH_2PPh_2$, $Ph_2PCH{=}CHPPh_2$, and $Ph_2PCH_2CH_2AsPh_2$ were obtained from either Strem Chemicals or Pressure Chemical Co. and used as received. $Me_2PCH_2CH_2PMe_2$,[24] $(p\text{-}Me\text{-}C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}Me)_2$,[25] and (S,S)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$[16] were prepared by literature procedures. $(MeO)_2PCH_2CH_2P(OMe)_2$ was prepared from $Cl_2PCH_2CH_2PCl_2$[24] and MeOH in diethyl ether and triethylamine. The synthesis of $HN(SiMe_2CH_2PPh_2)_2$ will be published at a later date.

Methylene chloride (CH_2Cl_2) was purified by distillation from CaH_2 under argon. Toluene, hexanes, and diethyl ether were dried and deoxygenated by distillation from sodium–benzophenone ketyl under argon. Tetrahydrofuran (THF) was predried by refluxing over CaH_2 and then distilling from sodium–benzophenone ketyl under argon.

Melting points were determined on a Mel-Temp apparatus in sealed capillaries under nitrogen and are uncorrected. Carbon and hydrogen analyses were performed by Mr. P. Borda of this department. ^1H NMR measurements were performed on one of the following instruments, depending on the complexity of the particular spectrum: Varian EM-360, Bruker WP-80, Varian XL-100, Nicolet-Oxford 270, and Bruker WH-400. $^{31}P\{^1H\}$ NMR measurements were run at 32.442 MHz on the Bruker WP-80 in 10-mm tubes fitted with inserts for the internal standard, $P(OMe)_3$. C_6D_6 and C_7D_8 were purchased from Aldrich, dried over activated 4-Å molecular sieves, and vacuum transferred.

All Grignard reagents were prepared from the corresponding halide and excess magnesium turnings in THF, filtered through cotton wool, and standardization by titration against 0.10 mol L^{-1} HCl.

[η^3-(2-Me-C_3H_4)Rh(COD)] (2). This procedure follows that of **3** by Sivak and Muetterties.[3] To a cooled (−5 °C) suspension of $[(COD)RhCl]_2$ (3.03 g, 6.15 mmol) in THF (75 mL) was added a THF solution of (2-methylallyl)magnesium chloride (65 mL, 0.21 mol L^{-1}, 13.65 mmol) dropwise over a period of 0.5 h. The resulting clear orange solution was stirred at −5 °C for 1 h and then at room temperature for 1 h. The THF was removed in vacuo and the residue extracted with pentane (3 × 80 mL) and filtered through a medium-porosity frit. Removal of the pentane in vacuo left a yellow to brown solid, which was sublimed under high vacuum (10^{-4} mmHg) at 50 °C to a dry ice–acetone-cooled probe to give yellow crystals of **2** (2.5 g, 75%). Yields are best if the sublimation is carried out as quickly as possible. **2** is somewhat thermally unstable and is best stored at −30 °C under N_2; mp 35 °C. ^1H NMR (C_6D_6, ppm): 4.92, 4.68 (br s, 4 H, COD vinyl protons); 3.16 (s, 2 H, H_{syn}); 2.28, 2.10, 1.74 (m, 8 H, exo and endo methylene protons of COD); 1.86 (s, 2 H_{anti}); 1.58 (d, $^3J_{Rh}$ = 3.2 Hz, 3 H, 2-Me).

[η^3-(2-Me-C_3H_4)Rh(dmpe)] (4). A solution of $Me_2PCH_2CH_2PMe_2$ (dmpe) (0.414 g, 2.76 mmol) in hexane (2 mL) was added dropwise to **2** (0.730 g, 2.74 mmol) in hexane (8 mL) with swirling. The yellow solution was filtered, and the hexane and COD were removed in vacuo. The yellow residue was sublimed at 50 °C under high vacuum (10^{-4} mmHg) to a water-cooled probe to give 0.785 (93%) of yellow plates, mp 41–42 °C.

[η^3-(2-Me-C_3H_4)Rh(dptpe)] (5). Finely ground solid (p-Me-$C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}Me)_2$ (dptpe) (0.454 g, 1.0 mmol) was slowly added to a rapidly stirred solution of **2** (0.266 g, 1.0 mmol) in hexane (5 mL). After 1 h of stirring, the solution was filtered through a coarse frit to remove a small amount of insoluble material and the volatiles were removed in vacuo to generate a yellow-orange oil. This material would not crystallize except at very low temperatures (<−30 °C).

[η^3-(2-Me-C_3H_4)Rh(dppp)] (6). This was synthesized by the procedure outlined for **5**. After removal of the volatiles a yellow, waxy solid was obtained, which was recrystallized from toluene–hexane at low temperatures (−30 °C) to give orange-yellow microcrystals (80%), mp 131–133 °C dec.

[η^3-(2-Me-C_3H_4)Rh(*cis*-dppe)] (7). Finely ground solid *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppe) (0.310 g, 0.782 mmol) was slowly added to a rapidly stirred solution of **2** (0.211 g, 0.793 mmol) in hexane (8 mL); the product precipitated during the addition as a bright yellow solid. After 1 h of stirring the solid was filtered, washed with cold hexane (3 mL), and dried in vacuo. Recrystallization from CH_2Cl_2–hexane gave 0.350 g (81%) of bright yellow microcrystals, mp 183–185 °C dec (darkened at 140 °C).

[η^3-(2-Me-C_3H_4)Rh(chiraphos)] (8). This was synthesized by the same procedure outlined for **7** in 89% yield as bright yellow microcrystals, mp 113–115 °C dec.

[η^3-(2-Me-C_3H_4)Rh(arphos)] (9). A solution of $Ph_2PCH_2CH_2AsPh_2$ (arphos) (0.221 g, 0.5 mmol) in CH_2Cl_2 (1.5 mL) was added to a solution of **2** (0.133 g, 0.5 mmol) in hexane (3 mL). After 0.5 h the volatiles were removed in vacuo to give the product as an orange glass. Dissolution in CH_2Cl_2 (0.5 mL), addition of hexane (5 mL), and cooling to −30 °C gave orange-yellow crystals (0.25 g, 83%), mp 92–95 °C dec.

[η^3-(2-Me-C_3H_4)Rh($HN(SiMe_2CH_2PPh_2)_2$)] (10). A solution of $HN(SiMe_2CH_2PPh_2)_2$ (0.133 g, 0.251 mmol) in hexane (2 mL) was added to a solution of **2** (0.067 g, 0.252 mmol) in hexane (0.5 mL). After the solution stood at 20 °C for 1 h, yellow needles precipitated. Further cooling for 1 h at −30 °C gave 0.120 g (70%, two fractions) of the product, mp 183–185 °C dec (darkened at 130 °C).

[η^3-(2-Me-C_3H_4)Rh(dmope)] (11). A solution of $(MeO)_2PCH_2CH_2P(OMe)_2$ (dmope) (0.107 g, 0.5 mmol) in hexane (2 mL) was added to a solution of **2** (0.133 g, 0.5 mmol) in hexane (1.5 mL) to give a slightly turbid yellow solution. Removal of the hexane and COD in vacuo gave the pure product as an oily yellow solid in quantitative yield.

[η^3-(1-Me-C_3H_4)Rh(COD)][10] (12). To a cooled (−5 °C) suspension of $[(COD)RhCl]_2$ (1.24 g, 2.52 mmol) in THF (50 mL) was added a THF solution of 3-butenylmagnesium bromide (7.1 mL, 0.77 mol L^{-1}, 5.47 mmol) dropwise over a period of 10 min. The resulting clear orange-red solution was stirred at −5 °C for 1 h and then at room temperature for 1 h. The THF was removed in vacuo and the residue extracted with pentane (2 × 50 mL); filtration through a medium-porosity frit and removal of the pentane in vacuo yielded an oily

(23) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.
(24) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.
(25) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079.

orange-red solid which was sublimed at 50 °C under high vacuum (10^{-4} mmHg) to a dry ice–acetone-cooled probe. At −80 °C the sublimate is yellow but upon warming to room temperature changes to orange (1.25 g, 93%). As with **2**, **12** is best stored at −30 °C under N_2.

[η^3-(1-Me-C_3H_4)Rh(dmpe)] (13). This was prepared by the identical procedure used for **4**. Isolation via sublimation at 50 °C under high vacuum (10^{-4} mmHg) to a dry ice–acetone-cooled probe gave a yellow solid, which upon warming to room temperature turned to an orange oil and solidified. The yield was 92%.

[η^3-(1-Me-C_3H_4)Rh(dptpe)] (14). This was synthesized by the procedure outlined for **7** in 82% yield as bright yellow microcrystals.

[η^3-(1-Me-C_3H_4)Rh(dppp)] (15). This was synthesized by the procedure outlined for **6** to give **15** as an orange-yellow waxy solid in 70% yield. An analytical sample was obtained by recrystallization from hexane at low temperatures.

[η^3-(1-Me-C_3H_4)Rh(chiraphos)] (16). This was synthesized by the procedure outlined for **7** in 75% yield as a yellow-orange powder, mp 179–181 °C dec (darkened at 130 °C).

[η^3-(1-Me-C_3H_4)Rh(dmope)] (17). This was synthesized by the procedure outlined for **11** to give **17** as a yellow waxy solid.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada, by the Research Corp., and by the UBC Department of Chemistry. We thank Johnson-Matthey for a generous loan of hydrated rhodium trichloride.

Registry No. **2**, 81177-96-0; **4**, 81177-97-1; **5**, 81177-98-2; **6**, 81177-99-3; **7**, 81178-00-9; **8**, 81178-01-0; **9**, 81178-02-1; **10**, 81178-03-2; **11**, 80105-91-5; *syn*-**12**, 70428-75-0; *syn*-**13**, 81178-04-3; *anti*-**13**, 81204-42-4; *syn*-**14**, 81178-05-4; *anti*-**14**, 81204-43-5; *syn*-**15**, 81178-06-5; *anti*-**15**, 81204-44-6; *syn*-**16**, 81178-07-6; *anti*-**16**, 81244-78-2; *syn*-**17**, 81178-08-7; *anti*-**17**, 81204-45-7; $[(COD)RhCl]_2$, 12092-47-6; 2-methylallyl chloride, 563-47-3; 3-butenyl bromide, 5162-44-7.

Contribution from the Chemistry Division of the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, and the Departments of Chemistry, Carleton College, Northfield, Minnesota 55057, and University of Georgia, Athens, Georgia 30602

Poly(tertiary phosphines and arsines). 18. Preparation and Structure of bis{μ-[(methylamino)bis(dimethoxyphosphine)]}-bis(dicarbonylcobalt), a Binuclear Complex with Approximate Square-Pyramidal and Trigonal-Bipyramidal Coordination of Cobalt Atoms in the Same Molecule[1]

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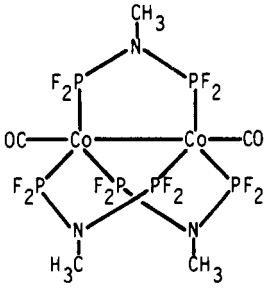
Received November 10, 1981

The ligand $CH_3N[P(OCH_3)_2]_2$ reacts readily with $Co_2(CO)_8$ to form the violet-brown complex $\{CH_3N[P(OCH_3)_2]_2\}_2Co_2(CO)_4$. A single-crystal X-ray diffraction study of this complex shows a structure with a cobalt–cobalt bond 2.698 (1) Å long bridged by two $CH_3N[P(OCH_3)_2]_2$ ligands. The two cobalt atoms are both five-coordinate and have identical sets of ligands, each of the two being bonded to the other cobalt atom, to two carbonyl groups, and to two trivalent phosphorus donors. However, the two cobalt atoms are not equivalent; one has trigonal-bipyramidal coordination and the other has square-pyramidal coordination. The trigonal-bipyramidal cobalt atom has the other cobalt atom and a carbonyl group in the axial positions. The square-pyramidal cobalt atom has a carbonyl group in the apical position. The difference in coordination of the two cobalt atoms probably results from the packing of a fluxional molecule which has a symmetrical average structure in solution. Although the ν(CO) frequencies in the infrared spectrum in solution all appear in the terminal region, the complex in the crystal contains a carbonyl group in a borderline semibridging position with Co–C distances of 1.756 (7) and 2.812 (7) Å, probably as the result of the crystal packing. The atoms of the $Co_2(CO)_4$ unit in the complex are essentially coplanar, and the least-squares best plane through these atoms is an approximate mirror plane for the molecule.

Introduction

The reaction of the small-bite bidentate fluorophosphine $CH_3N(PF_2)_2$ with $Co_2(CO)_8$ gives the binuclear derivative $[CH_3N(PF_2)_2]_3Co_2(CO)_2$, shown by X-ray diffraction analysis to have structure **1**, which contains a cobalt–cobalt bond bridged by three $CH_3N(PF_2)_2$ ligands.[3,4] The $[CH_3N(PF_2)_2]_3Co_2$ structural unit in this complex is chemically very stable; it is retained not only upon substitution of terminal carbonyl groups with Lewis base ligands (phosphines, phosphites, isocyanides, etc.[4]) but also upon reduction to give the radical anion and dianion[5] and upon bromination to give the tetrabromide $[CH_3N(PF_2)_2]_3Co_2Br_4$.[6]



1

These observations on $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ stimulate interest in the cobalt carbonyl derivatives of other small-bite bidentate trivalent phosphorus ligands of the general type $RN(PX_2)_2$. This paper describes the preparation and the X-ray crystal-structure analysis of bis{μ-[(methylamino)bis(dimethoxyphosphine)]}-bis(dicarbonylcobalt), a binuclear cobalt carbonyl complex containing the ligand $CH_3N[P(OCH_3)_2]_2$.

(1) For part 17 of this series see: King, R. B.; Bakos, J.; Hoff, C. D.; Markó, L. *J. Org. Chem.* **1979**, *44*, 3095.
(2) (a) Oak Ridge National Laboratory. (b) Carleton College. (c) University of Georgia.
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