Synthesis, Structure, and Reactivity of RhCl(PhP{$CH_2CH_2PPh_2$}$_2$)

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Introduction

A large number of polydentate phosphine complexes of transition metals have been synthesized and characterized over the past 20 years for possible applications in homogeneous catalysis.[1] Indeed, while RhCl(TRIPHOS) (**1**; TRIPHOS = PhP{$CH_2CH_2PPh_2$}$_2$) was prepared initially in 1971,[2] it was later believed that one of the phosphine appendages bridged to another rhodium atom, generating polynuclear rhodium complexes.[3] More recently, however, a complex formulated as **1** was reported to be an active catalyst precursor for the hydrogenation of cyclohexene.[4] We present herein the preparation and characterization of **1** by NMR spectroscopy and X-ray crystallography, confirming that **1** is indeed monomeric both in solution and in the solid-state and that all three of the phosphorus atoms are coordinated to the rhodium center. The reactivity of **1** with Na[C_5H_5] and Na[C_9H_7] is also addressed, as is the reaction of TRIPHOS with (C_9H_7)Rh(C_2H_4)$_2$.

Experimental Section

General Procedures. NMR spectra were recorded on Bruker WM250 (^{1}H at 250 MHz, ^{13}C at 63 MHz, ^{31}P at 101 MHz) and AMX500 (^{1}H at 500 MHz, ^{13}C at 126 MHz, ^{31}P at 202 MHz) spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to external TMS and were referenced to residual protons in the solvent; coupling constants are in hertz. Multiplicities are reported as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, and (ov) overlapping. ^{31}P chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4. ^{13}C chemical shifts are reported in ppm relative to external TMS using solvent carbon resonances as an internal standard. Methylene chloride was freshly distilled from CaH_2, while THF and toluene were freshly distilled from sodium benzophenone ketyl. TRIPHOS was purchased from Aldrich Chemical Co. and used as received. [Rh(μ-Cl)(COD)]$_2$,[5] (C_9H_7)Rh(C_2H_4)$_2$,[6] Na[C_5H_5],[7] and Na[C_9H_7][8] were prepared by established methods.

Preparation of RhCl(TRIPHOS) (1). Method A. A solution of TRIPHOS (PhP{$CH_2CH_2PPh_2$}$_2$) (534 mg, 1.0 mmol) in 20 mL of toluene was added dropwise to a suspension of [Rh(μ-Cl)(COD)]$_2$ (246 mg, 0.5 mmol) in 20 mL of toluene. After being heated at reflux for 12 h, the solution was concentrated *in vacuo* to 10 mL and cooled at −30 °C for 48 h. The resulting yellow crystals were collected by filtration, washed with cold pentane (2 × 10 mL), and dried *in vacuo* to yield 590 mg (88%) of **1**.

Table 1. Crystallographic Data for **1**

formula	$C_{34}H_{33}ClP_3Rh$
color	yellow
fw	672.92
cryst dimens (mm^3)	0.32 × 0.28 × 0.27
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	10.314(1)
b (Å)	17.136(2)
c (Å)	17.383(2)
β (deg)	97.32(1)
V (Å^3)	3047.2(7)
d_{calc} (g cm^{-3})	1.467
Z	4
radiation	Mo Kα
tot. no. of reflcns	5408
no. of tot. reflcns obsd	4083
σ test	$I > 3.0\sigma(I)$
R^a	0.0284
$R_w{}^b$	0.0323

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Method B. A solution of TRIPHOS (PhP{$CH_2CH_2PPh_2$}$_2$) (800 mg, 1.5 mmol) in 10 mL of THF was added dropwise to a solution of [Rh(μ-Cl)(COD)]$_2$ (370 mg, 0.75 mmol) in 10 mL of THF. After being stirred for 16 h, the solution was concentrated *in vacuo* to 10 mL, and hexane (40 mL) was added. The resulting yellow solid was collected by filtration, washed with hexane (10 mL), and dried *in vacuo* to yield 817 mg (81%) of **1**. Complex **1** was characterized spectroscopically by ^{1}H and ^{31}P NMR. NMR spectroscopic data (in CD_2Cl_2): ^{31}P{^{1}H} δ 44.2 (d d, J_{PRh} = 145, $^2J_{PP}$ = 32 Hz), 112.6 (d t, J_{PRh} = 163 Hz); ^{1}H δ 1.63 (m, J = 7 Hz, 4H, CH_2), 1.92 (ov m, 4H, CH_2), 6.88 (ov m, 15H, Ph), 7.15 (ov m, 10H, Ph).

Addition of Na[C_5H_5] to 1. A suspension of Na[C_5H_5] (14 mg, 0.16 mmol) in 5 mL of THF was added dropwise to a suspension of **1** (67 mg, 0.1 mmol) in 20 mL of THF. The reaction mixture was stirred for 24 h, after which the solvent was removed *in vacuo* and the resulting red solid was stirred with 5 mL of toluene, filtered out, and dried *in vacuo* to yield 55 mg (79%) of **2**. NMR spectroscopic data (AMX500 spectrometer; in C_6D_6): ^{31}P{^{1}H} δ −12.4 (d, $^2J_{PP}$ = 38 Hz, P_a), 83.5 (d d, J_{PRh} = 220, $^2J_{PP}$ = 46 Hz, P_c), 86.8 (d d d, J_{PRh} = 220, $^2J_{PP}$ = 46, 38 Hz, P_b); ^{1}H δ 1.25 (m, 1H, CH_2), 1.44 (m, 1H, CH_2), 1.67 (m, 1H, CH_2), 1.98 (ov m, 3H, CH_2), 2.30 (m, 1H, CH_2), 2.59 (m, 1H, CH_2), 5.40 (s, 5H, C_5H_5), 7.10 (ov m, 15H, Ph), 7.51 (m, 4H, Ph) 7.63 (m, 2H, Ph), 7.83 (m, 4H, Ph); selected ^{13}C{^{1}H} NMR data δ 24.9 (d d, J = 5, 14 Hz, CH_2), 28.8 (d d, J = 28, 33 Hz, CH_2), 30.4 (d d, J = 16, 23 Hz, CH_2), 31.1 (d d, J = 23, 33 Hz, CH_2), 84.7 (s, C_5H_5), some aromatic peaks overlapping with solvent resonances. Anal. Calcd for $C_{39}H_{38}RhP_3$: C, 66.68; H, 5.45. Found: C, 66.61; H, 5.48.

Addition of Na[C_9H_7] to 1. A solution of Na[C_9H_7] (22 mg, 0.16 mmol) in 5 mL of THF was added dropwise to a suspension of **1** (67 mg, 0.1 mmol) in 20 mL of THF. The reaction mixture was stirred for 1 h, after which the solvent was removed *in vacuo* and the resulting red mixture was dissolved in 1 mL of CD_2Cl_2 and characterized spectroscopically by ^{1}H and ^{31}P NMR. NMR spectroscopic data (WM250 spectrometer; in CD_2Cl_2): ^{31}P{^{1}H} δ 22.6 (app d d q, J_{PRh} = 128, $^2J_{PP}$ = 257, 33 Hz, P_c), 44.2 (d d, J_{PRh} = 145, $^2J_{PP}$ = 32 Hz, **1**), 52.9 (app d t, J_{PRh} = 142, $^2J_{PP}$ = 33 Hz, P_e), 76.1 (d d d, J_{PRh} = 220, $^2J_{PP}$ = 38, 33 Hz, P_b), 76.9 (d d, J_{PRh} = 220, $^2J_{PP}$ = 38 Hz, P_a), 111.1 (d d t, J_{PRh} = 125, $^2J_{PP}$ = 257, 33 Hz, P_d), 112.3 (d t, J_{PRh} = 163 Hz, **1**); ^{1}H δ 1.63 (br), 1.67 (ov m), 1.90 (br), 2.46 (br), 2.63 (br), 2.84 (br), 3.32 (d d, J = 19, 9 Hz), 3.67 (br), 4.61 (br d, J = 21 Hz), 5.32 (br d, J = 8 Hz), 6.01 (br m), 6.62 (br), 6.89 (br), 7.32 (br, major, Ph), 7.98 (ov m, major, Ph), 8.11 (ov m, major, Ph). Note that the ^{1}H spectrum is extremely complex owing to the presence of **1** and other

(1) For a recent review on polydentate phosphines and their metal complexes see: Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179 and references therein.
(2) (a) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1971**, *93*, 4158. (b) King, R. B.; Kapoor, P. N.; Kapoor, R. N. *Inorg. Chem.* **1971**, *10*, 1841.
(3) Nappier, T. E., Jr.; Meek, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 306.
(4) Taqui Khan, M. M.; Taqui Khan, B.; Begum, S.; Mustafa Ali, S. *J. Mol. Catal.* **1988**, *49*, 43.
(5) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.
(6) (a) Eshtiagh-Hosseini, H.; Nixon, J. F. *J. Less-Common Met.* **1978**, *61*, 107. (b) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648.
(7) Lucas, C. R. *Inorg. Synth.* **1990**, *28*, 267.
(8) Na[C_9H_7] was prepared via a method similar to that described in ref 7. See also: Schade, C.; Schleyer, P. v. R.; Gregory, P.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1988**, *341*, 19.

0020-1669/94/1333-4589$04.50/0

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Rh(1)	546.5(2)	1382.6(1)	2297.5(1)	36.2
Cl(1)	−826.1(9)	2490.2(5)	1885.0(6)	52.1
P(1)	−1082.6(8)	637.2(5)	2686.7(5)	35.2
P(2)	1700.6(8)	339.9(5)	2566.0(5)	37.2
P(3)	2526.1(8)	1989.2(5)	2415.8(5)	40.7
C(1)	−438(4)	−339(2)	2995(2)	48
C(2)	1021(3)	−272(2)	3273(2)	45
C(3)	3406(3)	550(2)	2955(2)	49
C(4)	3824(4)	1251(2)	2498(2)	50
C(5)	−2601(3)	393(2)	2071(2)	40
C(6)	−3289(4)	−295(2)	2174(2)	51
C(7)	−4398(4)	−477(3)	1676(2)	57
C(8)	−4817(4)	13(3)	1079(2)	59
C(9)	−4152(4)	683(3)	968(2)	62
C(10)	−3037(3)	886(2)	1472(2)	51
C(11)	−1602(3)	1018(2)	3588(2)	41
C(12)	−2821(4)	874(3)	3803(2)	56
C(13)	−3141(5)	1152(3)	4511(3)	73
C(14)	−2248(5)	1562(3)	5001(2)	62
C(15)	−1047(5)	1710(3)	4785(2)	63
C(16)	−718(4)	1442(2)	4081(2)	55
C(17)	1812(3)	−310(2)	1741(2)	40
C(18)	1506(4)	−15(2)	995(2)	51
C(19)	1583(4)	−485(3)	355(2)	62
C(20)	1940(4)	−1260(3)	451(3)	65
C(21)	2252(4)	−1555(2)	1190(3)	61
C(22)	2190(4)	−1086(2)	1833(2)	53
C(23)	2746(3)	2511(2)	3342(2)	45
C(24)	1702(4)	2951(2)	3541(2)	56
C(25)	1811(5)	3352(3)	4235(3)	72
C(26)	2954(5)	3312(3)	4743(3)	71
C(27)	3976(5)	2876(3)	4561(3)	72
C(28)	3881(4)	2479(2)	3862(2)	57
C(29)	3119(3)	2702(2)	1756(2)	49
C(30)	2229(4)	3050(2)	1199(2)	58
C(31)	2631(5)	3618(3)	707(3)	78
C(32)	3914(6)	3831(3)	767(3)	83
C(33)	4816(5)	3485(3)	1301(3)	83
C(34)	4427(4)	2921(3)	1802(3)	67

[a] Equivalent isotropic *U* defined as $(U_{11}U_{22}U_{33})^{1/3}$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Rh(1)-Cl(1) 2.4212(9)	Rh(1)-P(1) 2.2808(8)
Rh(1)-P(2) 2.1646(8)	Rh(1)-P(3) 2.2770(8)
Cl(1)-Rh(1)-P(1) 95.84(3)	Cl(1)-Rh(1)-P(2) 174.65(3)
Cl(1)-Rh(1)-P(3) 98.78(3)	P(1)-Rh(1)-P(2) 83.08(3)
P(1)-Rh(1)-P(3) 156.19(3)	P(2)-Rh(1)-P(3) 83.98(3)

unidentified degradation products in solution. Reactions carried out in other solvents, such as toluene and pyridine, led to an even more complex mixture of products.

Addition of $(C_9H_7)Rh(C_2H_4)_2$ (4) to TRIPHOS. A solution of **4** (55 mg, 0.2 mmol) in 20 mL of THF was added dropwise to a solution of TRIPHOS (107 mg, 0.2 mmol) in 20 mL of THF. The reaction mixture was stirred for 1 h, after which the solution was concentrated *in vacuo* to 10 mL and cooled at −30 °C for 48 h. The resulting orange-red precipitate was collected by filtration, washed with cold pentane (2 × 10 mL), and dried *in vacuo* to yield 141 mg (47%) of **3**. A $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed only resonances due to **3** and a small amount of **1**. The amount of **1** increased with time until only **1** was present (see Results and Discussion).

Synthesis of $[(\eta^5\text{-}C_5H_5)Rh\{\mu\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}\text{-}Rh(TRIPHOS)]^+[BPh_4]^-$ (6). A solution of **2** (41 mg, 0.06 mmol) in 5 mL of CH_3CN was added to a suspension of **1** (39 mg, 0.06 mmol) in 5 mL of CH_3CN with stirring. To this mixture was added as a solid $NaBPh_4$ (20 mg, 0.06 mmol). After being stirred for 16 h, the orange solution was evaporated to dryness, the resulting solid was extracted into THF, and the extract was filtered. Precipitation with hexane and drying *in vacuo* yielded 51 mg (50%) of **6** as a yellow solid. $^{31}P\{^1H\}$ NMR spectroscopic data (AMX500 spectrometer; the labeling scheme used for **6** is the same as that for **3** shown in Figure 3; in C_6D_6): δ 22.1 (d d q, $J_{PRh} = 128$, $^2J_{P_d-P_c} = 256$, $^2J_{P_e-P_c} = {}^3J_{P_b-P_c} = 34$ Hz, P_c), 52.7 (app d d t, $J_{PRh} = 143$, $^2J_{P_d-P_e} = {}^2J_{P_c-P_e} = 31$ Hz; an additional splitting is due to the fact that the two phosphorus atoms labeled P_e are actually diastereotopic due to the chiral center at P_b. The small difference in chemical shifts was only observed on the 500 MHz spectrometer, P_e), 82.6 (d d, $J_{PRh} = 218$, $^2J_{P_b-P_a} = 46$ Hz, P_a), 85.5 (d t, $J_{PRh} = 222$, $^2J_{P_a-P_b} = {}^3J_{P_c-P_b} = 34$ Hz, P_b), 110.0 (d d t, $J_{PRh} = 122$, $^2J_{P_c-P_d} = 256$, $^2J_{P_e-P_d} = 31$ Hz, P_d).

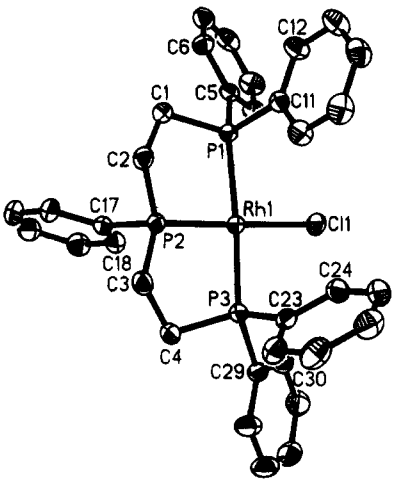
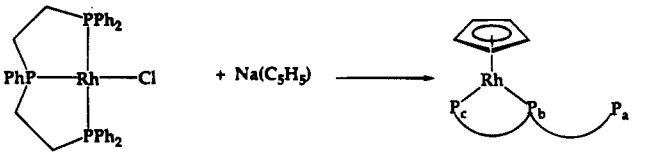


Figure 1. Molecular Structure of RhCl(TRIPHOS) (**1**) with hydrogens omitted for clarity.

Scheme 1



1 *2*

X-ray Crystal Structure of 1. Crystals of **1** suitable for X-ray diffraction studies were grown from a CH_2Cl_2 solution at room temperature. A summary of the crystal data and parameters for data collection is given in Table 1. Data were collected at room temperature on a Syntex $P2_1$ diffractometer using graphite-filtered Mo Kα radiation ($\lambda = 0.71073$ Å) and $2\theta-\theta$ scan methods. The data were reduced in the usual fashion for Lorentz–polarization effects. Solution and refinement of **1** were performed on an IBM 4341 computer using a package of programs which has been described previously.[9] The structure was solved using Patterson and Fourier techniques, and refinement was performed using full-matrix least-squares methods on *F*, with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, *w*, assigned as $(1.72 - 0.0165F + 0.00025F^2)^{-1}$. The atomic scattering factors were taken from the tabulations of Cromer and Waber.[10] Final atomic coordinates are given in Table 2, and selected bond distances and angles are given in Table 3. Complete tables of bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and hydrogen atom positions and isotropic thermal parameters are available as supplementary material.

Results and Discussion

The reaction of $[Rh(\mu\text{-}Cl)(COD)]_2$ with the tris(phosphine) TRIPHOS either in refluxing toluene or in THF at ambient

(9) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.
(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

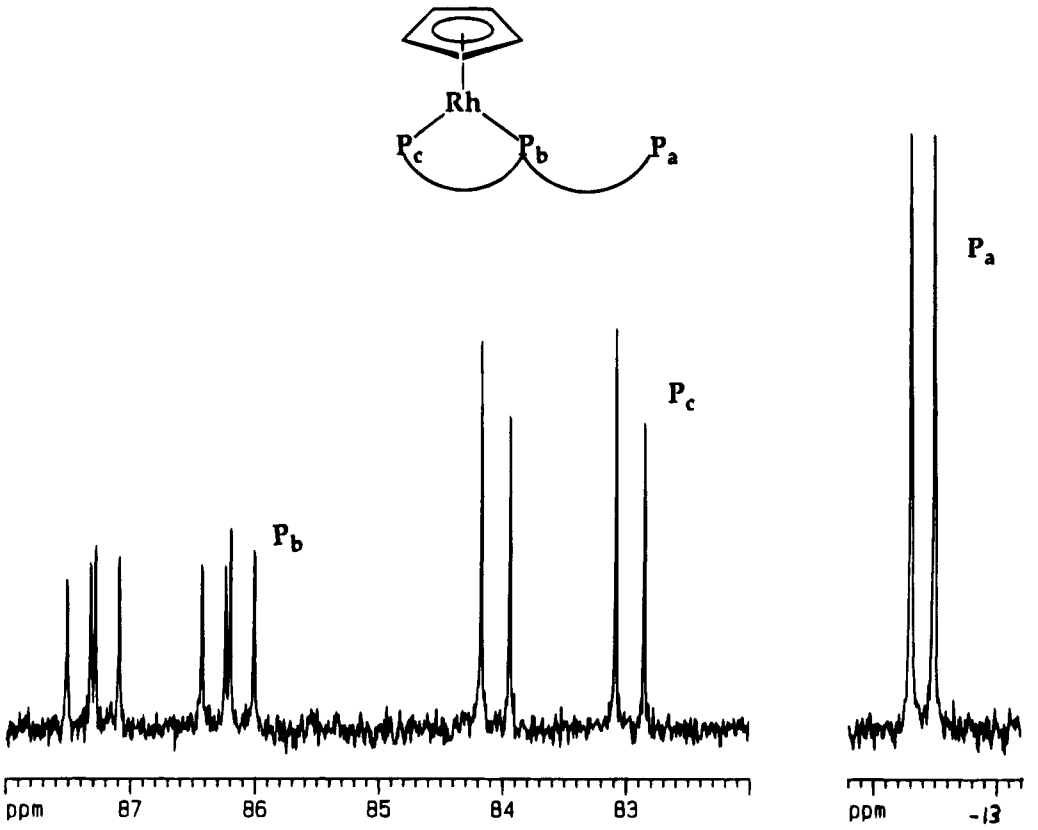
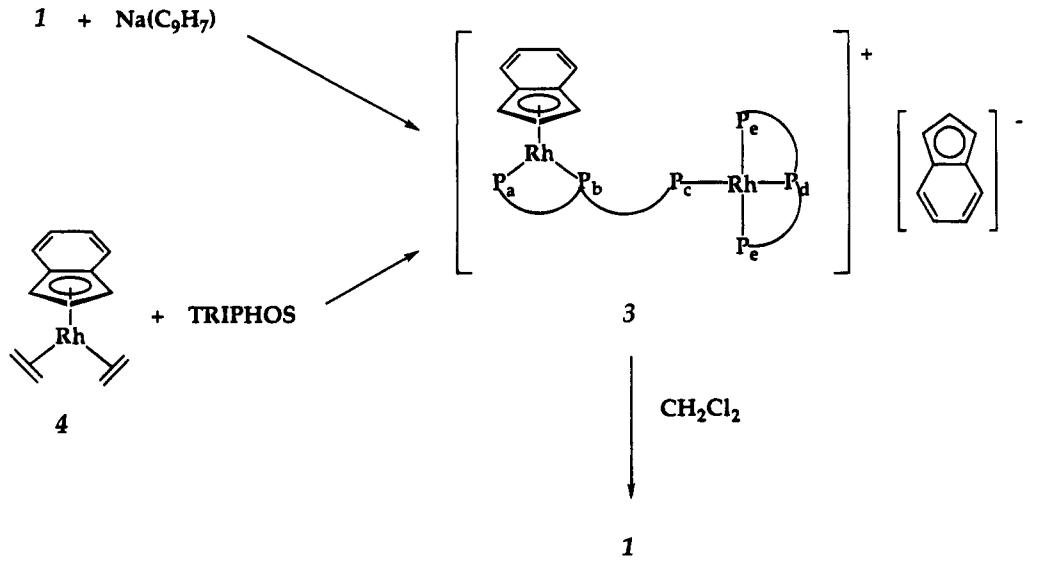


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of (η^5-C_5H_5)Rh(TRIPHOS) (**2**) in C_6D_6.

Scheme 2



temperature provides an excellent route for the synthesis of RhCl(TRIPHOS) (**1**; TRIPHOS= PhP{$CH_2CH_2PPh_2$}$_2$).[11] Compound **1** is air-stable in the solid state. The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 consists of a simple first-order AM_2X splitting pattern producing a doublet of triplets for the unique central phosphorus atom and a doublet of doublets for the two magnetically equivalent terminal P atoms of the TRIPHOS ligand. The ^{31}P NMR spectrum is consistent with a square-planar structure in which the chloride atom and the central phosphorus atom lie *trans* to one another. This structure was confirmed by single-crystal X-ray diffraction (Figure 1).

The structure of **1** consists of a discrete mononuclear species in which the rhodium atom is in a distorted square-planar environment being coordinated by all three phosphorus atoms of the TRIPHOS ligand as well as the chloride ligand. The P—Rh—P_{cis} angles (83.08(3) and 83.98(3)°) are somewhat smaller (*cf.* 90 ± 1°) than those found in analogous Rh(ttp) (ttp = PhP{$CH_2CH_2CH_2PPh_2$}$_2$) complexes[12] which contain sterically less-imposing six-membered chelate rings. Puckering

(11) A few Co, Rh, and Ir complexes containing a TRIPHOS ligand have been reported previously: (a) Taqui Khan, M. M.; Martell, A. E. *Inorg. Chem.* **1974**, *13*, 2961 ([M(CO)(TRIPHOS)]Cl and [M(CO)$_2$-(TRIPHOS)]Cl where M = Rh or Ir). (b) DuBois, D. L.; Meek, D. W. *Inorg. Chim. Acta* **1976**, *19*, L29 ("[Rh(BH_3)(TRIPHOS)]"). (c) Arpac, E.; Dahlenburg, L. *J. Organomet. Chem.* **1984**, *277*, 127 ([IrR-(CO)(TRIPHOS)] where R = CH_2SiMe_3 or 4-MeC_6H_4). (d) Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 85 ([Rh(NO)-(TRIPHOS)]). (e) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979 ([Rh(PPh_3)-(TRIPHOS)]$^+$[*nido*-7,8-(μ-*o*-xylylene)-7,8-$C_2B_9H_{10}$]$^-$).

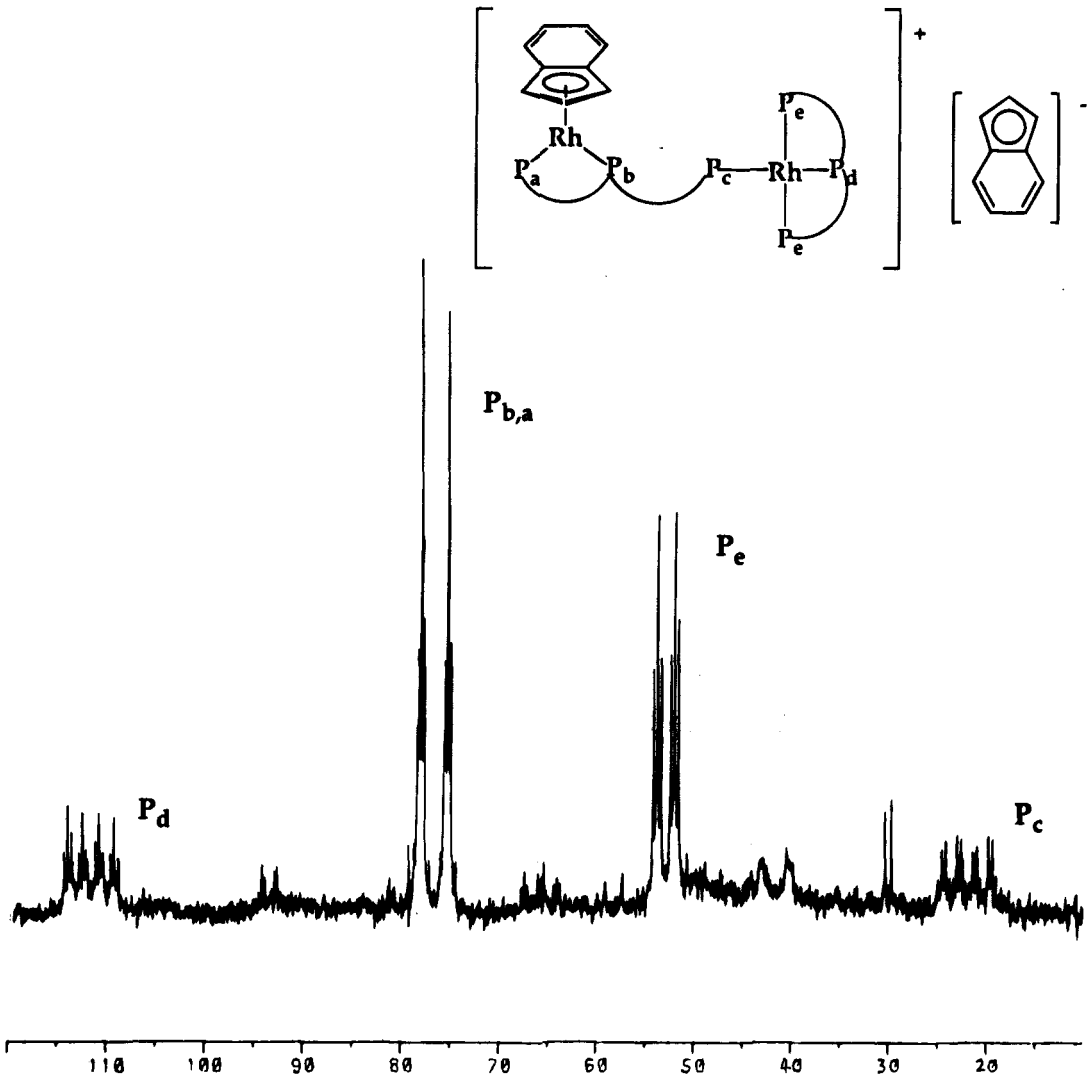


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[(\eta^5\text{-}C_9H_7)Rh\{\mu\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}Rh(TRIPHOS)]^+[C_9H_7]^-$ (**3**) in pyridine-d_5.

of the five-membered rings in **1** is further exemplified by the reduced P(1)—Rh(1)—P(3) angle of 156.19(3)° (*cf.* 180°). The P(2)—Rh(1)—Cl(1) angle is 174.65(3)°.

As part of our ongoing investigation into transition metal indenyl chemistry,[13] we decided to prepare both the cyclopentadienyl and indenyl Rh(TRIPHOS) compounds. While no reaction was observed when **1** was treated with excess $Li[C_5H_5]$, the analogous metathetical reaction with $Na[C_5H_5]$ gave red-pink $(C_5H_5)Rh(TRIPHOS)$ (**2**) (Scheme 1) in 79% isolated yield. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a typical AMQX spin system with three signals of intensity 1:1:1. The low-frequency resonance (Figure 2) appears as a doublet assigned to P_a due to coupling to *only* the central P atom. The central phosphorus atom, assigned as P_b, appears as a doublet of doublet of doublets while the terminal P atom (P_c), coordinated to Rh, appears as a doublet of doublets. In the ^1H NMR spectrum, only one resonance is observed for the equivalent Cp protons. In order for the Cp ring to adopt an η^5-bonding mode while maintaining an 18-electron count at Rh, one of the arms of the phosphine ligand is required to dissociate from the metal center.

In contrast, the indenyl ring can stabilize an η^3-bonding mode under certain circumstances owing to a resonance stabilization gained from a rearomatization of the six-membered ring.[14] However, in an attempt to prepare $(\eta^3\text{-}C_9H_7)Rh(TRIPHOS)$ by treatment of $Na[C_9H_7]$ in THF with **1**, we observed the formation of the novel dinuclear compound formulated on the basis of ^{31}P NMR spectroscopy as $[(\eta^5\text{-}C_9H_7)Rh\{\mu\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}Rh(TRIPHOS)]^+[C_9H_7]^-$ (**3**) (Scheme 2). Thus, for the indenyl compound, one Rh center employs an $\eta^5\text{-}C_9H_7$ ligand and obtains an 18-electron count by using two arms of the bridging TRIPHOS ligand, while the second Rh center is a 16-electron square-planar cation composed of a tridentate TRIPHOS ligand as well as the pendent arm of the bridging TRIPHOS ligand. This requires an "η^{0}"-bonding mode for the second indenyl moiety, as has been observed previously in the $[(dmpe)_2Rh]$ salt[15] of the indenyl anion. The ^{31}P NMR spectrum of **3** (Figure 3) is quite similar to a composite of the

(12) (a) Christoph, G. G.; Blum, P.; Liu, W.-C.; Elia, A.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 894 ([RhCl(ttp)], $[Rh(pyridine)(ttp)]^+$, $[Rh(ttp)(PEt_3)]^+$). (b) Dahlenburg, L.; Arpac, E. *J. Organomet. Chem.* **1983**, *241*, 27 ($[Rh(2\text{-}MeC_6H_4)(ttp)]$).

(13) (a) Frankcom, T. M.; Green, J. C.; Nagy, A.; Kakkar, A. K.; Marder, T. B. *Organometallics* **1993**, *12*, 3688. (b) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198–200*, 219. (c) O'Hare, D.; Green, J. C.; Marder, T. B.; Collins, S.; Stringer, G.; Kakkar, A. K.; Kaltsoyannis, N.; Kuhn, A.; Lewis, R.; Mehnert, C.; Scott, P.; Pugh, S. *Organometallics* **1992**, *11*, 48. (d) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777 and references therein.

(14) (a) Merola, J. S.; Kacmarcik, R.-T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329. (b) Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *Organometallics* **1987**, *6*, 889. (c) Nesmeyanov, A. W.; Ustynyuk, N. A.; Makarova, L. G.; Andrianov, V. G.; Struchkov, Yu. T.; Andrae, S.; Ustynyuk, Yu. A.; Malyugina, S. G. *J. Organomet. Chem.* **1978**, *159*, 189.

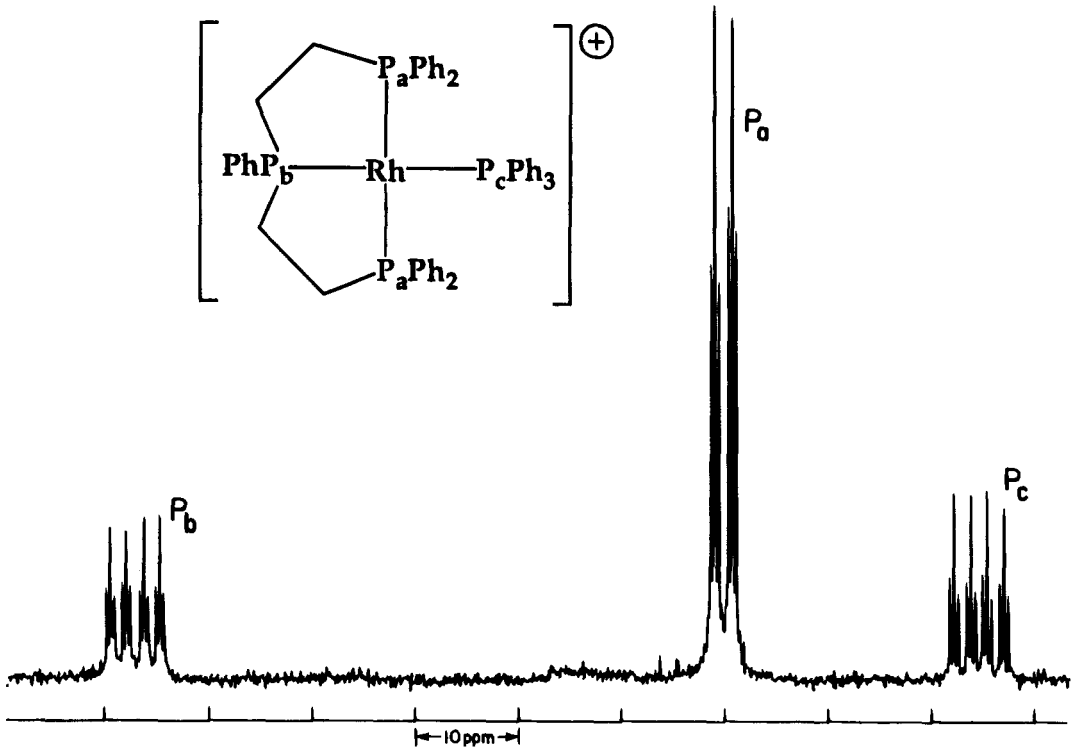


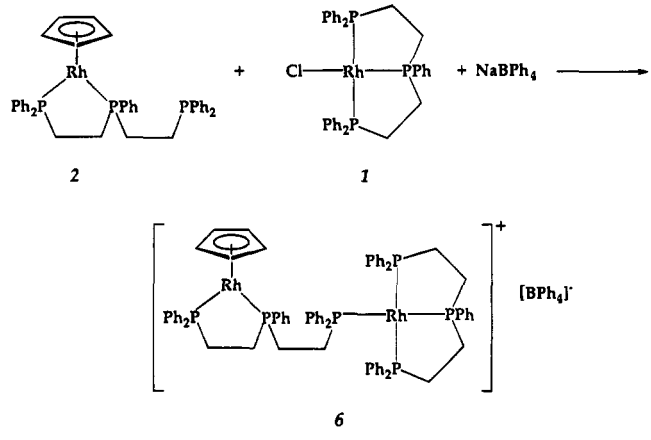
Figure 4. $^{31}P\{^1H\}$ NMR spectrum of $[Rh(PPh_3)(TRIPHOS)]^+$ (**5**) in 10% C_6D_6/THF at 200 K.

spectrum of **2** and that of the $[Rh(PPh_3)(TRIPHOS)]$ cation **5** (Figure 4),[11e] with the dangling arm of the TRIPHOS ligand in **2** replacing the PPh_3 ligand in **5**. Clearly, in this case, the indenyl ligands prefer to adopt an η^5/η^0 arrangement rather than the expected η^3 coordination mode.

Monitoring the reaction mixture by ^{31}P NMR spectroscopy showed that **3** was the major (phosphine)rhodium species in solution (*ca.* 80%). Interestingly, complex **3** could also be prepared by addition of $(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2$ (**4**) to TRIPHOS via loss of both ethylene ligands. Unfortunately, unlike **1**, **3** decomposed rapidly (*ca.* 1 h) in solution to give a mixture of unidentified products. Indeed, when **3** was dissolved in CH_2Cl_2, quantitative conversion to **1** was observed to occur within 48 h, and partial conversion was observed within 15 min. Activation of C—Cl bonds in CH_2Cl_2 was recently reported for rhodium complexes containing chelating bidentate methyl-[16] and phenylphosphine derivatives.[17] However, it seems more likely, in this case, that the uncoordinated indenyl anion reacts with CH_2Cl_2, releasing chloride ion, which can subsequently attack the metal center. The instability of **3** in CH_2Cl_2, compared with that of **1**, **2**, and **6** (*vide infra*), provides evidence for the presence of free indenide moieties. Attempts to observe η^3 or η^1 intermediates in the reaction of **4** with TRIPHOS, by conducting the reaction at low temperature in an NMR tube, led to a complex series of ^{31}P NMR spectra which were uninterpretable due to considerable peak overlap.

In order to obtain additional data to substantiate the formulation of complex **3**, we carried out the reaction of **2** with **1** in the presence of $NaBPh_4$. We reasoned that the uncoordinated phosphine arm in **2** would displace chloride from **1** and that this would be enhanced by the presence of a noncoordinating anion and the formation of NaCl. This reaction was entirely successful, generating the analogous complex $[(\eta^5\text{-}C_5H_5)Rh\{\mu\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}Rh(TRIPHOS)]^+[BPh_4]^-$ (**6**) (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **6** (Figure 5) is virtually identical to that of **3**, with only minor shifts in the positions of the resonances due to the two phosphorus atoms coordinated to the $(\eta^5\text{-}C_5H_5)Rh$ center in **6** *vs* the related phosphorus atoms complexed to the $(\eta^5\text{-}C_9H_7)Rh$ center in **3**. The shifts and complex coupling patterns observed for both **3** and **6** are unique, and provide unambiguous evidence for their formulations. Interestingly, **6** is stable in CD_2Cl_2 solution, providing further support for the instability of **3** being due to the presence of the free indenyl anion.

Scheme 3



Conclusions

Reaction of TRIPHOS with $[Rh(\mu\text{-}Cl)(COD)]_2$ gives RhCl(TRIPHOS) (**1**) in high yield. The structure of **1** was confirmed by X-ray diffraction; **1** is monomeric with all three P atoms coordinated to Rh. Reaction of **1** with $Na[C_5H_5]$ gave (C_5H_5)-Rh(TRIPHOS) (**2**), in which one arm of the phosphine ligand

(15) Marder, T. B.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1987** 1478. See also: Kakkar, A. K.; Taylor, N. J.; Marder, T. B. *Organometallics* **1989**, *8*, 1765.
(16) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543.
(17) (a) Fennis, P. J.; Budzelaar, P. H. M.; Frijns, J. H. G.; Orpen, A. G. *J. Organomet. Chem.* **1990**, *393*, 287. (b) Ball, G. E.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Rettig, S. J. *Organometallics* **1991**, *10*, 3767.

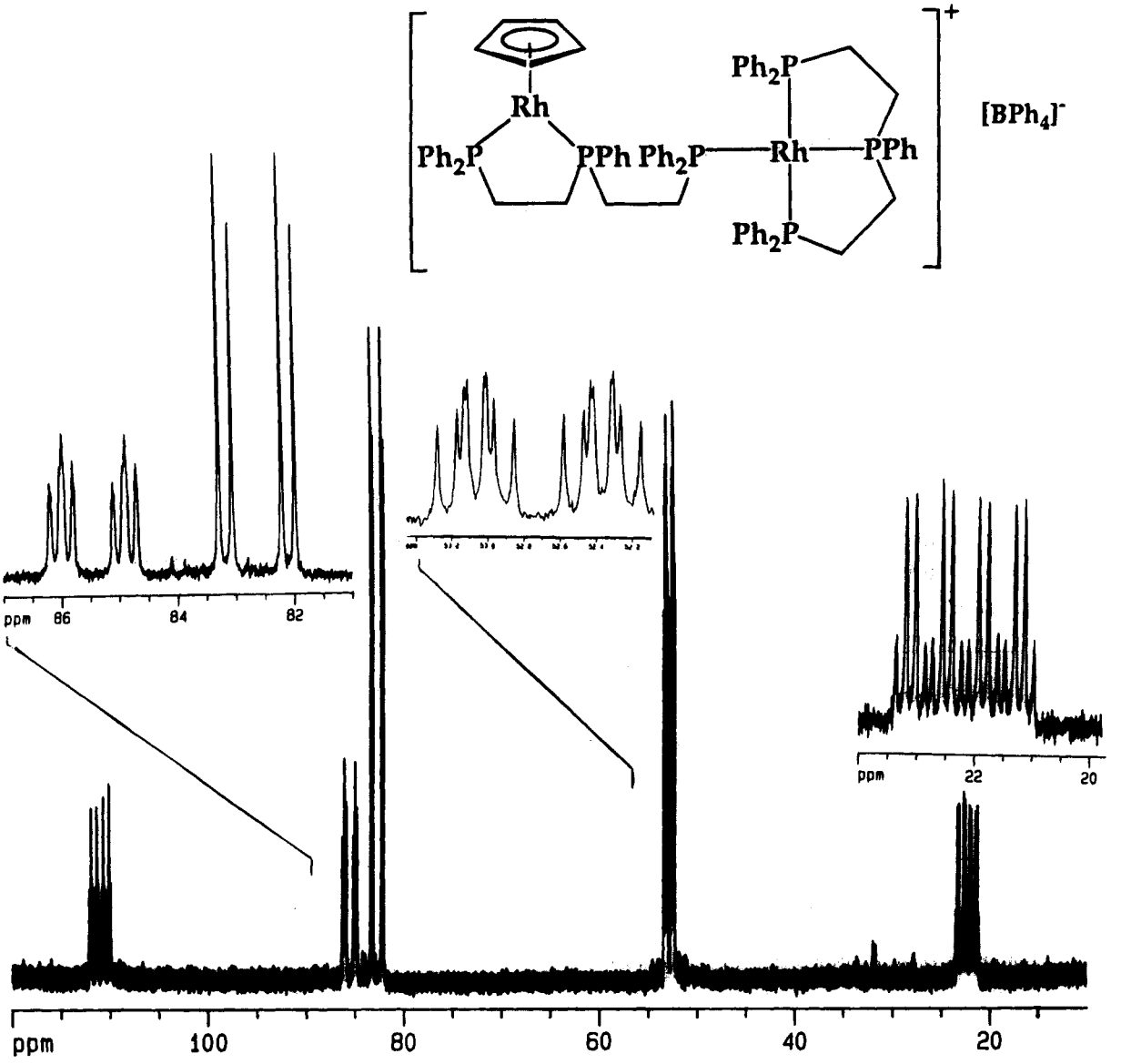


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $[(\eta^5\text{-}C_5H_5)Rh\{\mu\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}Rh(TRIPHOS)]^+[BPh_4]^-$ (**6**) in 10% C_6D_6/THF. Insets show expansions of the regions around 22, 52, and 84 ppm, respectively.

is not coordinated to Rh. In contrast, reactions of **1** with Na[C_9H_7] or of $(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2$ (**4**) with TRIPHOS gave an unusual dinuclear complex **3** containing a bridging TRIPHOS ligand and η^5- and η^0-indenyl groups. This novel compound decomposed in or reacted with solvents in which it was soluble, making elemental analysis or X-ray diffraction studies impossible. However, it was characterized unambiguously by comparison of its ^{31}P NMR spectra with those of **2**, $[Rh(PPh_3)(TRIPHOS)]^+$ cation **5**, and the related compound $[(\eta^5\text{-}C_5H_5)Rh\{\mu\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}Rh(TRIPHOS)]^+$ $[BPh_4]^-$ (**6**). The latter species was prepared cleanly via reaction of **1** with **2** in the presence of $NaBPh_4$. That **2** does not dimerize to produce an analog of **3** is consistent with the enhanced lability of the indenyl ligand *vs* a coordinated cyclopentadienyl group.

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Supplementary Material Available: Tables of crystallographic data, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters and a figure depicting the distorted square-planar coordination environment around Rh in **1** (8 pages). Ordering information is given on any current masthead page.