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Synthesis and characterization of mono- and bimetallic complexes with phosphine-salicylaldimine ligands. The X-ray crystal structure of *trans*-PdCl₂{Ph₂P(CH₂)₃N=CHC₆H₄-o-OH}₂

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Abstract

Complexes of the type $M{Ph_2P(CH_2)_nN=CHC_6H_4-o-OH}_2$ (n = 3, 4 and M = cis- and trans-PdCl₂, cis-PtCl₂, cis,cis,trans-RuCl₂(CO)₂) have been synthesized by the reactions of the ligands with the appropriate metal precursors. All of the complexes are obtained in high yields, and, in all of the complexes, the ligands are coordinated solely through the phosphorus. Attempts to form bimetallic complexes by reaction of these complexes with either nickel acetate or diethylzinc give incomplete reactions and mixtures of products. A bimetallic Pd(II)–Ni(II) complex has been obtained by the reaction of $\{Ph_2P(CH_2)_4N=CHC_6H_4-o-O\}_2Ni$ and Pd(cod)Cl₂. Crystals of this complex are yellow–brown but yield a green powder when ground. NMR spectra of the complex suggest that it is monomeric in solution. The X-ray crystal structure of trans-PdCl₂ $\{Ph_2P(CH_2)_3N=CHC_6H_4-o-O\}_2$ has been determined. The coordination geometry of the Pd is a nearly perfect, trans square plane containing two phosphines and two chlorides. The Pd–Cl bonds are nearly parallel to the P–CH₂ bond, and the salicylaldimine groups lie on opposite sides of the plane formed by Pd, P and Cl. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phosphine complexes containing two different metal centers are of interest because they can exhibit unusual catalytic activities and selectivities [1,2]. We have earlier reported that ligands containing both a P-donor group and a salicylaldiminato N/O-donor group can be used to prepare the bi- and trinuclear heterometallic complexes in Fig. 1 [3–5]. Unfortunately, none of these complexes are useful as catalysts due to the inertness of the Group VIB metal centers.

Complexes of the types shown in Fig. 1 in which a Ru(II), Rh(I), Pd(II) or Pt(II) center replaces the group VI metal center could exhibit interesting catalytic properties, however, no such complexes have been reported.

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The reactions used to prepare group VI complexes with X = NH ligands cannot be used to prepare related Pt-group metal complexes because chlorodiphenylphosphine complexes of these metals analogous to the $M(CO)_{6-n}(Ph_2PCI)_n$ (n = 1, 2) are not available [3]. It should be possible to prepare Pt-group metal complexes with the $X = (CH_2)_n$ ligands because the ligands are first synthesized and then coordinated to the metal centers. However, this route is complicated by the fact that the P-donor ligand/salicylaldiminato ligands can chelate to Pt-group metals centers [4–7]. This is particularly true for ligands that contain relatively short spacers between the P-donor and salicylaldiminato groups.

In this paper, we report the synthesis of several Pt-group metal complexes containing P-coordinated $Ph_2P(CH_2)_nN=CHC_6H_4$ -o-OH (n = 3, 4) ligands. The X-ray crystal structure of one of these complexes, *trans*-PdCl₂[Ph₂P(CH₂)₃N=CHC₆H₄-o-OH] has been determined and is discussed. We also describe our attempts

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to prepare bimetallic complexes containing a Pt-group metal center and either Ni²⁺ and Zn²⁺ and compare our results with those obtained previously with the related Group VI metal complexes, *cis*-M(CO)₄[Ph₂P(CH₂)_nN=CHC₆H₄-o-OH]₂ (M = Cr, Mo; n = 3-5) [4] and M(CO)₅[Ph₂P(CH₂)₄N=CH-C₆H₄-o-OH] (M = Cr, W) [5].

2. Experimental

All reactions were carried out under dry N₂. The $Ph_2P(CH_2)_nN=CHC_6H_4$ -o-OH, (n = 4, 1) and (n = 3, 2) [5], trans-[Ph_2P(CH_2)_4N=CHC_6H_4-o-O]₂Ni (3) [5], Pd(PhCN)_2Cl_2 [8], M(cod)Cl_2 (M = Pd, Pt) [9], and RuCl_2(CO)_3THF [10] precursors were synthesized by literature methods. All other reagents and solvents were reagent grade and were used as received.

Both ³¹P and ¹³C nuclear magnetic resonance spectra of approximately 0.1 *M* chloroform- d_1 solutions of the complexes were run on a Nicolet 300MHz, wide-bore, FT NMR spectrometer. The ¹³C NMR spectra were referenced to internal TMS, and the ³¹P NMR spectra were referenced to external 40% phosphoric acid with downfield considered positive. IR spectra of dichlormethane solutions of the complexes in the 1700– 1500 cm⁻¹ region were run on a Perkin–Elmer 283B infrared spectrometer.

2.1. $PdCl_2[Ph_2P(CH_2)_4N=CHC_6H_4-o-OH]_2$ (4)

A solution of 0.54 g (1.4 mmol) of $Ph_2P(CH_2)_4$ -N=CHC₆H₄-o-OH (1) and 0.25 g (0.7 mmol) of Pd(PhCN)₂Cl₂ in 25 ml of dichloro-methane was stirred at ambient temperature for 2 h. The solution was then evaporated to dryness, and the residue was washed with diethyl ether to yield 0.59 g (95%) of the crude product. Precipitation of the crude product from a dichloromethane solution with diethyl ether yielded pure PdCl₂[Ph₂P(CH₂)₄N=CHC₆H₄-o-OH]₂·0.5H₂O (m.p. 188-194°C). Anal. Found: C, 60.82; H, 5.56; N, 2.91. C₄₆H₄₉Cl₂N₂O₂ ₅P₂Pd Calc.: C, 60.77; H, 5.43; N, 3.08%. ³¹P NMR (chloroform- d_1): δ 28.52 (minor cis isomer, s), 16.89 (major trans isomer, s). ¹³C NMR of major *trans* isomer (chloroform- d_1): δ 164.89 (C=N, s); 161.25 (C-OH, s); 133.63 (ortho P-phenyl, aq, $|{}^{2}J(PC) + {}^{4}J(PC)| = 11$ Hz); 130.45 (para P-phenyl, s); 129.99 (*ipso* P-phenyl, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 46$ Hz); 128.26 (meta P-phenyl, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 9$ Hz); 132.00, 131.21, 118.77, 118.34, 116.94 (other salicylaldiminato aromatic carbons, all s); 58.60 (N- CH_2 , s); 31.90 (N-CH₂-CH₂, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 14$ Hz); 24.94 (P-CH₂, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 30$ Hz); 21.71 $(P-CH_2-CH_2, s)$. IR (dichloromethane): 1635, 1585 cm^{-1} (C=N, C-O stretches).

2.2. $PdCl_2[Ph_2P(CH_2)_3N=CHC_6H_4-o-OH]_2$ (5)

Using the procedure for the synthesis of 4, 1.39 g (4.00 mmol) of $Ph_2P(CH_2)_3N=CHC_6H_4-o-OH$ (2) and 0.71 g (2.0 mmol) of Pd(PhCN)₂Cl₂ yielded 1.68 g (96%) of crude product. This material was identified by comparison of its ³¹P and ¹³C NMR spectra with those of 4. ³¹P NMR (chloroform- d_1): δ 29.27 (minor *cis* isomer, s), 17.30 (major trans isomer, s). ¹³C NMR of major *trans* isomer (chloroform- d_1): δ 165.37 (C = N, s); 161.16 (C-OH, s); 133.71 (ortho P-phenyl, aq, $|{}^{2}J(PC) + {}^{4}J(PC)| = 7$ Hz); 130.64 (para P-phenyl, s); 129.88 (*ipso* P-phenyl, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 47$ Hz); 128.43 (meta P-phenyl, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 7$ Hz); 132.21, 131.31, 118.75, 118.54, 116.99 (other salicylaldiminato aromatic carbons, all s); 60.20 (N-CH₂, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 16$ Hz); 25.85 (N-CH₂-CH₂, s); 23.14 (P-CH₂, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 30$ Hz). IR (dichloromethane): 1635, 1584 cm⁻¹ (C=N, C-O stretches).



Fig. 1. Bi- and trinuclear complexes with phosphorus-donor/salicylaldiminato ligands.

2.3. $cis-PtCl_2[Ph_2P(CH_2)_4N=CHC_6H_4-o-OH]_2$ (6)

A solution of 1.5 g (4.1 mmol) of Ph₂P(CH₂)₄-N=CHC₆H₄-o-OH (1) and 0.78 g (2.0 mmol) of Pt(cod)Cl₂ in 25 ml of dichloromethane was stirred at ambient temperature for 2 h. The solution was then evaporated to dryness, and the residue was washed with diethyl ether to yield 1.9 g (96%) of crude product. Precipitation of this material from dichloromethane with diethyl ether yielded pure cis-PtCl₂[Ph₂P(CH₂)₄-N=CHC₆H₄-o-OH]₂·0.5H₂O (m.p. 180-181°C). Anal. Found: C, 55.16; H, 5.03; N, 2.70. C₄₆H₄₉Cl₂N₂O_{2.5}-P₂Pt; Calc.: C, 55.36; H, 4.95; N, 2.81%. ³¹P NMR (chloroform- d_1): δ 8.22 (s and d, $|{}^{1}J(PtP)| = 3655$ Hz). ¹³C NMR (chloroform- d_1): δ 165.05 (C=N, s), 161.24 (C-OH, s); 133.29 (ortho P-phenyl, aq, $|^2J(PC) +$ $|{}^{4}J(PC)| = 9$ Hz); 130.96 (*para* P-phenyl, s); 129.13 (*ipso* P-phenyl, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 64$ Hz); 128.25 (meta P-phenyl, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 10$ Hz); 132.09, 131.34, 118.71, 118.46, 116.88 (other salicylaldiminato aromatic carbons, all s); 58.35 (N-CH₂, s); 31.58 (N- $CH_2 - CH_2$, s); 30.01 (P-CH₂, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| =$ 46 Hz); 22.64 (P-CH₂-CH₂, s). IR (dichloromethane): 1635, 1555 cm⁻¹ (C=N, C-O stretches).

2.4. $cis, cis, trans-RuCl_2(CO)_2$ -[$Ph_2P(CH_2)_4N=CHC_6H_4-o-OH$]₂ (7)

A solution of 0.91 g (3.2 mmol) of $Ph_2P(CH_2)_4$ -N=CHC₆H₄-o-OH, 1, and 0.40 g (1.6 mmol) of RuCl₂(CO)₃THF in 100 ml of dichloromethane was stirred at ambient temperature for 4 days. The solution was then evaporated to dryness to yield 1.2 g (94%) of the crude product. Trituration of this material with a 1:1 mixture of diethyl ether and hexanes yielded analytcis, cis, trans-RuCl₂(CO)₂[Ph₂P(CH₂)₄ically pure N=CHC₆H₄-o-OH]₂. Anal. Found: C, 60.83; H, 5.40; N, 3.08. C₄₈H₄₈N₂O₄P₂Cl₂Ru Calc.: C, 60.63; H, 5.05; N, 2.95%. ³¹P NMR (chloroform- d_1): δ 19.09 (s). ¹³C NMR (chloroform- d_1): δ 192.46 (CO, t, $|^2 J(PC) = 10$ Hz); 164.95 (C=N, s); 161.18 (C-OH, s); 133.72 (ortho P-phenyl, aq, $|{}^{2}J(PC) + {}^{4}J(PC)| = 10$ Hz); 130.63 (para P-phenyl, s); 130.06 (*ipso* P-phenyl, aq, $|^{1}J(PC) +$ ${}^{3}J(PC) = 66$ Hz); 128.48 (meta P-phenyl, aq, ${}^{3}J(PC) +$ ${}^{5}J(PC) = 9$ Hz); 131.97, 131.25, 118.61, 118.30, 116.80 (other salicylaldiminato aromatic carbons, all s); 58.02 $(N-CH_2, s); 31.10 (N-CH_2-CH_2, aq, |^3J(PC) +$ ${}^{5}J(PC) = 13$ Hz); 30.01 (P-CH₂, aq, $|{}^{1}J(PC) +$ $^{3}J(PC) = 27$ Hz); 20.09 (P-CH₂-CH₂, s). IR (dichloromethane solution): 2058, 1996 (carbonyl stretches), 1636, 1553 cm⁻¹ (C=N, C-O stretches).

2.5. trans- $PdCl_2[Ph_2P(CH_2)_4N=CHC_6H_4-o-O]_2Ni$ (8)

A solution of 0.11 g (0.38 mmol) of $Pd(cod)Cl_2$ and 0.30 g (0.38 mmol) of $[Ph_2P(CH_2)_4N=CHC_6H_4-o-O]_2Ni$

(3) in 50 ml of dichloromethane was stirred at ambient temperature for 4 days. The solution was then evaporated to dryness to yield 0.41 g (100%) of the crude product. Recrystallization of this material by diffusion of diethyl ether into a THF solution of the crude mixture yielded analytically pure trans-PdCl₂[Ph₂P(CH₂)₄N=CHC₆H₄-o-O]₂Ni·THF (m.p. 195-196°C). Anal. Found: C, 58.32; H, 5.17; N, 2.92. C₅₀H₅₄Cl₂N₂NiO₃P₂Pd; Calc.: C, 58.30; H, 5.24; N, 2.72%. ³¹P NMR (chloroform- d_1): δ 16.72 (s). ¹³C NMR (chloroform- d_1): δ 163.40 (C=N, s); 162.54 (C-OH, s); 133.66 (ortho P-phenyl, aq, $|^2J(PC) +$ ${}^{4}J(PC) = 10$ Hz); 133.40 (ortho P-phenyl, bs); 130.50 (para P-phenyl, s); 130.25 (ipso P-phenyl, aq, $|{}^{1}J(PC) +$ $^{3}J(PC) = 46 \text{ Hz}$; 129.81 (*para* P-phenyl, s); 129.45 (*ipso* P-phenyl, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 47$ Hz); 128.48 (meta P-phenyl, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 10$ Hz); 127.78 (meta P-phenyl, aq, $|{}^{3}J(PC) + {}^{5}J(PC)| = 9$ Hz); 132.33, 128.66, 121.53, 120.77, 114.95 (other salicylaldiminato aromatic carbons, all s); 58.78 (N-CH₂, s); 35.81 (N-CH₂-CH₂, bs); 25.22 (P-CH₂, aq, $|{}^{1}J(PC) + {}^{3}J(PC)| = 25$ Hz); 22.73 (P-CH₂-CH₂, s). IR (dichloromethane): 1617, 1545 cm⁻¹ (C=N, C-O stretches).

2.6. X-ray crystal structure of trans- $PdCl_2[Ph_2P(CH_2)_3N=CHC_6H_4$ -o-OH] (5)

A yellow, plate-like crystal of *trans*-PdCl₂[Ph₂P-(CH₂)₃N=CHC₆H₄-o-OH] (**5**) was obtained by cooling a dichloromethane/hexanes solution of the complex to -5° C. The crystal was mounted on a glass fiber with epoxy cement, and the cell constants were obtained from least-squares refinement of 25 reflections with $25 \le \theta \le 35^{\circ}$. All measurements were taken on an Enraf-Nonius CAD4 diffractometer at 23°C using graphite-monochromated Cu K α radiation ($\lambda = 1.5418$ Å). Data were collected by ω -2 θ scans, and an empirical absorption correction was applied.

The structure was solved by heavy-atom methods and refined by a full-matrix least squares procedure that minimized $w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$ using the MOLEN package of programs from Enraf-Nonius. The hydrogen atoms bonded to carbons were placed in calculated positions (C-H = 0.96 Å, $U_{iso}(H) = 1.3 \times$ $U_{iso}(C)$) and were ridden on the carbons. The hydrogen on the salicylaldimine oxygen was located in a difference Fourier map, and its positional parameters were refined. The data was weighed using a non-Poisson scheme. A secondary extinction correction was applied to the data [11], and the extinction coefficients were refined. In the last stage of the refinement for the structure, no parameter varied by more than 0.01 of its standard deviation, and the final difference Fourier map had no interpretable peaks. Heavy atom scattering factors were taken from the compilations of Cromer and Weber [12], and those for hydrogen were taken

Table 1

Data collection and structure solution and refinement parameters for trans-PdCl₂[Ph₂P(CH₂)₃N=CHC₆H₄-o-OH]₂ (**5**)

Formula	$C_{44}H_{44}Cl_2N_2O_2P_2$
$M_{\rm eff}$ (Da)	Pu 872 11
Space group	P2 /n
$a(\dot{\Lambda})$	$1 2_1/n$ 0 060(1)
$u(\mathbf{A})$ $h(\mathbf{\hat{A}})$	9.2662(8)
$c(\dot{A})$	22.188(2)
$\mathcal{E}(\mathbf{A})$	100.251(0)
p() $V(\dot{A}^3)$	2015(1)
7 (A)	2013(1)
$D_{\rm c}$ (g cm ⁻³)	1 437
Crystal dimensions (mm)	$0.13 \times 0.34 \times 0.40$
h h	$0.13 \times 0.34 \times 0.49$
n_{\max}, n_{\min}	12, -12
$\kappa_{\max}, \kappa_{\min}$	11, 0
l_{\max}, l_{\min}	27, 0 Cu V (1.54184)
λ (A)	$Cu K\alpha (1.34164)$
$\frac{1}{2} = \frac{1}{2}$	22
Absorption coefficient (mm ⁻¹)	6.1209
θ limits (°)	0.1 - /4
Decay correction	none
Absorption correction	analytical
$T_{\rm max}, T_{\rm min}$	0.5346, 0.1752
Reflections measured	4256
Scan width (°)	1.3
Reflections with $I > n\sigma I$ (n_o)	3595 $(n = 3)$
No. of variables (n_v)	242
Function minimized	$w(F_{\rm o} - F_{\rm c})^2$
Weighing scheme	non-Poisson ^a
Instrumental uncertainty factor (p)	0.05
Secondary extinction correction type	Zachariesen
Minimized extinction coefficient	7.5×10^{-7}
R (%) ^b	3.52
R _w (%) ^c	5.24
GOF ^d	1.38
Max., min. residual electron density (e $Å^{-3}$)	0.615, -0.674
Max. shift/error	0.01

$$\begin{split} ^{\mathrm{a}} & w = (2F_{\mathrm{o}})^{2} / |\sigma(I)^{2} + (pF_{\mathrm{o}}^{2})^{2}|. \\ ^{\mathrm{b}} & R = \Sigma ||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma |F_{\mathrm{o}}|). \\ ^{\mathrm{c}} & R_{\mathrm{w}} = (\Sigma w ||F_{\mathrm{o}}| - |F_{\mathrm{c}}||^{2} / \Sigma w |F_{\mathrm{o}}|^{2})^{0.5}. \\ ^{\mathrm{d}} & \mathrm{GOF} = [\Sigma w (||F_{\mathrm{o}}| - |F_{\mathrm{c}}||)^{2} / (n_{\mathrm{o}} - n_{\mathrm{v}})]^{0.5}. \end{split}$$

from the International Tables for X-ray Crystallography, vol. IV [13]. Corrections for anomalous dispersion were taken from the compilations of Cromer and Lieberman [14] and applied to chlorine, phosphorus

Table 2

Selected bond lengths	Å) for	trans-PdCl2[Ph2	$P(CH_2)_3N=$	CHC ₆ H ₄ -0-0	$OH]_2$	(5)
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and palladium. Data for the X-ray structure analysis are given in Table 1. Values of selected bond lengths are given in Table 2, and values of selected bond angles are given in Table 3. Tables of atomic positional parameters, thermal parameters, torsion angles and least squares planes are available as supplementary material. An ORTEP [15] drawing of the structure is given in Fig. 2.

3. Results and discussion

3.1. Syntheses of mono- and bimetallic complexes

Platinum-group metal complexes with phosphoruscoordinated $Ph_2P(CH_2)_nN=CHC_6H_4-o-OH$ (*n* = 4, 1; and n = 3, 2), ligands were prepared by the reactions of the appropriate metal precursors with the free ligands as shown in Eqs. (1)-(3). These reactions were run at ambient temperatures and gave high yields of the desired products. This is in contrast to the reaction of $Rh(acac)(CO)_2$ with 1, which gives exclusively the chelated product, $Rh(CO)(Ph_2P(CH_2)_nN=CHC_6H_4-o-$ O), under similar conditions [4]. This difference is most likely due to the fact that the acetylacetonate (acac) ligand in Rh(acac)(CO)₂ is sufficiently basic to be protonated by the salicylaldimine and allow coordination of the salicylaldiminato group to occur. The chloride ligands in the Pd(II), Pt(II) and Ru(II) precursors used in this study will not do this.

 $Pd(PhCN)_{2}Cl_{2} + 2Ph_{2}P(CH_{2})_{n}N=CHC_{6}H_{4}-o-OH \rightarrow cis-PdCl_{2}[Ph_{2}P(CH_{2})_{n}N = CHC_{6}H_{4}-o-OH]_{2} + trans-PdCl_{2}[Ph_{2}P(CH_{2}) = N(CHC_{2}H_{4}-o-OH]_{2}$ (1) cis-4 (n = 4), cis-5 (n = 3) trans-4 (n = 4), trans-5 (n = 3) $Pt(cod)Cl_{2} + 2Ph_{2}P(CH_{2})_{4}N=CHC_{6}H_{4}-o-OH \rightarrow d$

$$cis-PtCl_{2}[Ph_{2}P(CH_{2})_{4}N = CHC_{6}H_{4}-o-OH]_{2}$$
(2)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Pd	Cl	2.2949(8)	C14	C15	1.516(5)
Pd	Р	2.3354(6)	C16	C17	1.460(5)
Р	C1	1.820(3)	C17	C18	1.402(5)
Р	C7	1.820(3)	C17	C22	1.374(5)
Р	C13	1.828(3)	C18	C19	1.387(6)
01	C18	1.329(4)	C19	C20	1.360(6)
N1	C15	1.452(6)	C20	C21	1.369(7)
N1	C16	1.258(4)	C21	C22	1.372(8)
C13	C14	1.523(5)			

Table 3 Selected bond angles (°) for trans-PdCl₂[Ph₂P(CH₂)₃N=CHC₆H₄-o-OH]₂ (5)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl	Pd	Р	89.32(2)	C13	C14	C15	110.2(3)
Pd	Р	C1	108.81(8)	N1	C15	C14	112.7(3)
Pd	Р	C7	118.64(9)	N1	C16	C17	123.0(3)
Pd	Р	C13	116.9(1)	C16	C17	C18	121.6(3)
C15	N1	C16	118.3(3)	01	C18	C17	121.8(3)
Р	C13	C14	113.9(2)				

(3)

fac-Ru(CO)₃Cl₂(THF) + 2Ph₂P(CH₂)₄N= CHC₆H₄-o-OH → cis, cis, trans-RuCl₂(CO)₂[Ph₂P(CH₂)₄N = CHC₆H₄-o-OH]₂ 7

The reactions shown in Eqs. (1)–(3) yield complexes with a variety of coordination geometries. The palladium, 4 and 5, and platinum, 6, complexes are square planar. Both the cis and trans isomers of 4 and 5 are formed as indicated by ³¹P NMR resonances at approximately 28 ppm for the cis isomers and at approximately 17 ppm for the *trans* isomers. The cis:trans ratio is approximately 7:93 for 4 based on the integration of these resonances. In contrast, only the cis isomer of 6 is observed as indicated by the large $|^{1}J(PtP)|$ of 3655 Hz. The ruthenium complex, 7, is octahedral and can have a number of possible isomers. Only a single isomer is obtained and appears to contain cis carbonyl and chloride ligands and trans phosphines based on the observations of a single ³¹P NMR resonance, a single 1:2:1 triplet ¹³C NMR resonance for the carbonyls and two equally intense IR carbonyl stretching absorptions [10a]. The coordination geometries observed for the complexes of 1 and 2 are similar to those reported for related complexes of less complex phosphine ligands suggesting that the salicylaldimine group does not significantly affect the manner in which the phosphine group coordinates to the metals [10a].

Although the monometallic complexes, 4-7, were readily synthesized, they could not be cleanly converted into bimetallic complexes by reaction either with nickel acetate or with a solution of diethylzinc in toluene. Invariably, these reactions were incomplete and also gave mixtures of products. Attempts to separate the various components in these mixtures by fractional recrystallization were unsuccessful.

The bimetallic complex, trans-PdCl₂[Ph₂P(CH₂)₄. N=CHC₆H₄-o-O]₂Ni (8) was prepared by the reaction of [Ph₂P(CH₂)₄N=CHC₆H₄-o-O]₂Ni (3) and PdCl₂(cod). This gave a single compound that could be recrystallized by slow evaporation of a THF/diethyl ether solution to give golden-brown crystals. Complex 8 was not sufficiently soluble in common organic solvents to allow its molecular weight to be obtained by either cryoscopy or vapor phase osmometry. However, the facts that the complex did crystallize and that it exhibited a sharp and symmetric ³¹P NMR resonance suggest that it is monomeric. This suggestion is further supported by the fact that the phenyl rings of the phosphine groups are inequivalent. The constrained and helical orientation of the ligands in bimetallic complexes of the type shown in Fig. 1 could result in inequivalent phenyls. The ligand orientation in an oligomeric complex would be less constrained should not result in inequivalent phenyls. Both the fact that **8** is diamagnetic and its d–d transition at 623 nm (dichloromethane solution) are consistent with a square planar coordination geometry for the Ni [3c].

In contrast to the clean reaction of **3** and $Pd(cod)Cl_2$ to yield **8**, the reaction of **3** and $Pt(cod)Cl_2$ gave a mixture of products including *cis*- $PtCl_2[Ph_2P-(CH_2)_4N=CHC_6H_4-o-OH]_2$ (**6**). Complex **3** used in this reaction did not contain any free ligand, and thus **6** must be formed by decomplexation of the Ni²⁺ after coordination of the phosphines of **3** to the platinum. This suggests that bimetallic complexes with *cis*-coordinated phosphines are more strained and less stable than those with *trans*-coordinated phosphines. This conclusion is consistent with the fact that the closely related



Fig. 2. ORTEP drawing [15] of the molecular structure of *trans*- $PdCl_2[Ph_2P(CH_2)_3N=CH-C_6H_4-o-OH]_2$ (5). The thermal ellipsoids are drawn at the 25% probability level and the hydrogen atoms are omitted for clarity.

cis-Mo(CO)₄[Ph₂P(CH₂)₄N=CHC₆H₄-o-O]₂Ni complex isomerizes upon standing [4].

3.2. X-ray crystal structure of trans- $PdCl_2[Ph_2P(CH_2)_4N=CHC_6H_4-o-OH]_2$ (5)

Although 5 exists in solution as a mixture of cis and trans isomers, crystals of the pure trans isomer could be obtained by slowly cooling a saturated dichloromethane/hexanes solution of 5 to -5° C. The complex crystallizes in the $P2_1/n$ space group with the Pd located on an inversion center so that the asymmetric unit is one half of the molecule. An ORTEP drawing of the molecule is shown in Fig. 2.

The coordination geometry of the Pd is an almost perfect square plane with Cl-Pd-P angles of $89.32(2)^{\circ}$ and Cl-Pd-Cl and P-Pd-P angles of $90.68(2)^{\circ}$. The Pd-Cl and Pd-P distances of 2.2949(8) and 2.3354(6), respectively, are well within the ranges expected for these bonds. The Pd-Cl bonds are nearly parallel to the P-C13 bond (the C13-P-Pd-Cl torsion angle is $168.1(1)^{\circ}$) and split the angle between the two P-phenyl bonds.

The presence of the center of symmetry in the molecule means that the two salicylaldimine groups are located on opposite sides of the plane formed by Pd, P and Cl and are coplanar. This orientation would not allow chelation of both salicylaldimine groups to a single metal dication without significant reorganization of the structure. If this type of orientation is also favored in solution, it could explain why the reactions of 4 or 5 with either nickel acetate or diethylzinc are incomplete and give mixtures of products. The route that was successfully used to prepare trans- $PdCl_2[Ph_2P(CH_2)_4N=CH-C_6H_4-o-O]_2Ni$ (8) avoids this problem by first coordinating the salicyaldimine groups to the Ni^{2+} to form 3 and then reacting the free phosphine groups in this complex with Pd- $(cod)Cl_2$.

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