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The Aryl Group Transfer Process from a Triarylphosphine to a Chlorotetrakis(amidato)diruthenium(II,III) Species: Syntheses and Molecular Structures of $Ru_2(R)_2(R'CONH)_2[R_2POC(R')N]_2$ ($R = C_6H_5$, $R' = 3,5\text{-}(OCH_3)_2C_6H_3$; $R = p\text{-}C_6H_4CH_3$, $R' = C_6H_5$)

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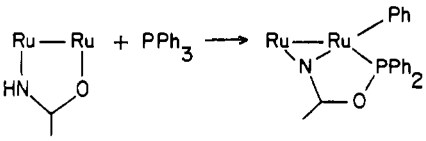
The syntheses and structures of the two diruthenium complexes $Ru_2(C_6H_5)_2[3,5\text{-}(OCH_3)_2C_6H_3CONH]_2[(C_6H_5)_2POC(3,5\text{-}(OCH_3)_2C_6H_3)N]_2$ (**1**) and $Ru_2(p\text{-}C_6H_4CH_3)_2(C_6H_5CONH)_2[(p\text{-}C_6H_4CH_3)_2POC(C_6H_5)N]_2$ (**2**) are reported. Compound **1** was obtained by reacting $Ru_2Cl(3,5\text{-}(OCH_3)_2C_6H_3CONH)_4$ and $P(C_6H_5)_3$ in Me_2SO–MeOH in the presence of $[N(C_4H_9)_4]ClO_4$. Compound **2** was prepared in a similar way by reacting $Ru_2Cl(C_6H_5CONH)_4$ and tri-*p*-tolylphosphine $[P(C_7H_7)_3]$. Both compounds have been fully identified and characterized by X-ray crystallography. They crystallize in the triclinic space group $P\bar{1}$ with the following unit cell dimensions. Compound **1**: $a = 12.716$ (3) Å, $b = 15.301$ (3) Å, $c = 18.003$ (4) Å, $\alpha = 90.67$ (2)°, $\beta = 98.47$ (2)°, $\gamma = 105.50$ (2)°, $V = 3334$ (1) Å^3, $Z = 2$. Compound **2**: $a = 11.855$ (4) Å, $b = 13.134$ (5) Å, $c = 11.603$ (4) Å, $\alpha = 113.28$ (2)°, $\beta = 90.25$ (3)°, $\gamma = 114.42$ (3)°, $V = 1480$ (2) Å^3, $Z = 1$. The compounds are brown crystalline solids, insoluble in common solvents. X-ray structure determinations of compounds **1** and **2** showed that the molecules are centrosymmetric diruthenium(III) complexes having two pseudooctahedra sharing a common edge. X-ray studies also show that an aryl group migration from triarylphosphine onto the metal center has taken place along with a synergic joining of an oxygen atom from a bridging amide ligand to the phosphorus atom, thereby forming a chelate cum bridging ligand, $R_2POC(R')N$, with an essentially planar $P\text{–}Ru(\mu\text{-}N)_2Ru\text{–}P$ unit during the syntheses of the compounds **1** and **2**. Compound **1** crystallizes with two independent molecules each residing on an inversion center. The average Ru–Ru distance in **1** is 2.567 [1] Å. The Ru–Ru distance in **2** is 2.570 (2) Å. The ground electronic configuration of the $Ru(III)(t_{2g}{}^5)\text{–}Ru(III)(t_{2g}{}^5)$ dimers is proposed to be $(\sigma)^2(\pi)^2(\delta,\delta^*)^4(\pi^*)^2(\sigma^*)^0$, and the formal bond order is 1.0. The Ru–P, Ru–N, Ru–O, and Ru–C distances in **1** and **2** lie in the ranges 2.287 (3)–2.309 (2), 2.006 (6)–2.103 (5), 2.091 (5)–2.137 (6), and 2.093 (7)–2.097 (8) Å, respectively.

Introduction

In the chemistry of metal–metal multiple bonds, mono(tertiary phosphines) have been used extensively as ligands.[1] The usual mode of ligation of these phosphines is the conventional coordination through phosphorus to the axial and/or equatorial sites of the dimetallic core. Previous reports[2-4] have shown that triphenylphosphine can also be transformed via ortho metalation into a three-atom bridging ligand, as in $Os_2Cl_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2$ and $Rh_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2L$ (L = pyridine or CH_3CO_2H). Though ortho metalation is not uncommon among monomeric complexes in which the ortho-metalated tertiary phosphine acts as a chelating ligand with a four-membered ring, examples are rare among metal–metal multiply bonded complexes. The first example of this sort of complexation was seen[5,6] in $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$, where the ortho-metalated ligand has an unusual tridentate mode of coordination. Recently, we have shown[7] that PPh_3, when reacted with a diruthenium(II,III) tetraamidato species, engages in a displacive transfer of a phenyl group from PPh_3 onto the metal center along with a synergic transfer of the amido oxygen atom to the phosphorus atom. The total effect of both processes is to change the amido nitrogen atom from a unidentate to a μ_2-bridging mode, as shown in eq 1. Theoretical aspects of this type of reaction have recently been discussed by Ortiz, Havlas, and Hoffmann,[8] who proposed that aryl shifts should be particularly facile.



(1)

To explore the generality of the process we sought further examples of reaction 1 by varying both the triarylphosphine and the bridging amidato ligand. In this paper we report the syntheses and molecular structures of two new diruthenium(III) complexes, $Ru_2(C_6H_5)_2(3,5\text{-}(OCH_3)_2C_6H_3CONH)_2[(C_6H_5)_2POC(3,5\text{-}(OCH_3)_2C_6H_3)N]_2$ (**1**) and $Ru_2(p\text{-}C_6H_4CH_3)_2(C_6H_5CONH)_2[(p\text{-}C_6H_4CH_3)_2POC(C_6H_5)N]_2$ (**2**).

Experimental Section

$Ru_2Cl(O_2CCH_3)_4$ was prepared by following a literature procedure.[9] Benzamide, 3,5-dimethoxybenzamide, triphenylphosphine, and tri-*p*-tolylphosphine were purchased from Aldrich Chemical Co. The preparative method for $Ru_2Cl(PhCONH)_4$ is available in our previous report[7] on $Ru_2(C_6H_5)_2(C_6H_5CONH)_2[(C_6H_5)_2POC(C_6H_5)N]_2$.

Synthesis of $Ru_2Cl(3,5\text{-}(OCH_3)_2C_6H_3CONH)_4$. A mixture of 0.1 g of $Ru_2Cl(O_2CCH_3)_4$ and 1 g of $3,5\text{-}(OCH_3)_2C_6H_3CONH_2$ was heated to 148 °C and stirred for 48 h under dinitrogen atmosphere. Excess ligand was removed by sublimation under reduced pressure at 148 °C. The residue was orange-brown. The compound was washed several times with methanol and finally with diethyl ether to remove any trace of unreacted ligand or starting acetate complex. The yield is quantitative. The compound is soluble in Me_2SO but insoluble in many other solvents tested.

Synthesis of $Ru_2(C_6H_5)_2[3,5\text{-}(OCH_3)_2C_6H_3CONH]_2[(C_6H_5)_2POC(3,5\text{-}(OCH_3)_2C_6H_3)N]_2$ (1). A 0.05-g sample of $Ru_2Cl(3,5\text{-}(OCH_3)_2C_6H_3CONH)_4$ was added to 15 mL of Me_2SO. The mixture was stirred for 24 h. The resulting brown solution was then filtered. A 7-mL portion of this solution was placed in a test tube, and 10 mL of a methanol solution containing 0.05 g of $P(C_6H_5)_3$ and 0.1 g of $[N(C_2H_5)_4]ClO_4$ was layered carefully on the top of the brown solution. After several days red-brown crystals suitable for X-ray study were obtained in ca. 20% yield. The crystalline compound is insoluble in all solvents tested.

Synthesis of $Ru_2(p\text{-}C_6H_4CH_3)_2(C_6H_5CONH)_2[(p\text{-}C_6H_4CH_3)_2POC(C_6H_5)N]_2$ (2). This compound was prepared in a similar way. A 5-mL quantity of a saturated Me_2SO solution of $Ru_2Cl(PhCONH)_4$ was layered with 10 mL of a methanol solution containing 0.05 g of $P(p\text{-}C_6H_4CH_3)_3$ and 0.1 g of $[N(C_2H_5)_4]ClO_4$. The crystals obtained after slow diffusion of solvents and electrolytes were yellow-brown. The solubility, nature, and yield of the complex are similar to the case of compound **1**.

X-ray Crystallographic Procedures. The molecular structures of **1** and **2** were determined by using general procedures reported in the literature.[10] A detailed description of the crystal structure determinations is

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Table I. Crystallographic Data

formula	$Ru_2P_2O_{12}N_4C_{72}H_{70}$ (**1**)	$Ru_2P_2O_4N_4C_{70}H_{66}$ (**2**)
fw	1447.47	1291.42
space group	$P\bar{1}$	$P\bar{1}$
syst abs	none	none
a, Å	12.716 (3)	11.855 (4)
b, Å	15.301 (3)	13.134 (5)
c, Å	18.003 (4)	11.603 (4)
α, deg	90.67 (2)	113.28 (2)
β, deg	98.47 (2)	90.25 (3)
γ, deg	105.50 (2)	114.42 (3)
V, Å^3	3334 (1)	1480 (2)
Z	2	1
d_{calcd}, g/cm^3	1.442	1.449
cryst size, mm	0.6 × 0.5 × 0.5	0.2 × 0.2 × 0.1
μ(Mo Kα), cm^{-1}	5.533	6.049
data collcn instrum	Nicolet P3	Enraf-Nonius CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
no. of orientation reflcns; range (2θ), deg	25; $20 < 2\theta < 30$	25; $4 < 2\theta < 36$
temp, °C	22 ± 1	22 [illegible] 1
scan method	$\omega-2\theta$	$\omega-2\theta$
data collcn range (2θ), deg	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 50$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	11815, 6598	4923, 2311
no. of params refined	808	365
transmission factors, %: max, min	99.99, 92.46	99.30, 88.51
R^a	0.0566	0.0600
$R_w{}^b$	0.0720	0.0700
quality-of-fit indicator^c	1.409	1.584
largest shift/esd, final cycle	0.18	0.33
largest peak, e/Å^3	0.851	0.802

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

Both compounds crystallize in the triclinic system with the space group $P\bar{1}$. In **1**, there are two independent dimers at $^1/_2$, 0, 0 and 0, $^1/_2$, $^1/_2$. The methoxy groups of the 3,5-dimethoxybenzamide ligands tend to be slightly disordered. The isotropic thermal parameters of O48, O95, and O98 atoms are high compared to those of other oxygen atoms in the molecules. The difference Fourier map showed two peaks near O48, and both peaks were refined as carbon atoms C48 and C(48), each with a site occupancy factor of 0.5. The carbon atoms bonded to O95 and O98 were successfully refined as single atoms with site occupancy factors of 1.0, but their high thermal parameter values do suggest slight disorder. The atoms having high thermal parameters were refined isotropically along with the disordered C48 and C(48) carbon atoms. There were no problems during refinement of compound **2** except that the methyl carbon atom of the migrated tolyl group became nonpositive definite when made anisotropic; that carbon atom was therefore refined isotropically. Both crystals were of very good quality, and the last difference Fourier map in each case had no peak greater than 0.85 e/Å^3.

Results and Discussion

Synthetic Aspects and Plausible Mechanism. The capacity of tertiary monophosphines to assist in stabilizing the lower oxidation states of metals has been utilized in the syntheses of dimeric complexes having metal–metal multiple bonds.[1] The effect of the presence of such unidentate phosphines on the axial or equatorial sites of the M–M core has been studied on Cr_2, Mo_2, Rh_2, and Re_2. The only earlier work, done by Wilkinson and co-workers,[11] on compounds containing ruthenium, carboxyl groups, and triphenylphosphine was structurally inconclusive. We earlier examined[12] a reaction between $Ru_2Cl(O_2CPh)_4$ and PPh_3 in methanol. The product isolated was a yellow solid slightly soluble in common organic solvents. The analytical, infrared, and X-ray structural studies showed[13] this to be a mononuclear species, $RuCl(CO)(O_2CPh)(PPh_3)_2$,[13-15] in which the CO is believed to have been generated from a bridging benzoate group. Other attempts to prepare phosphine adducts of tetrakis(acetato)diruthenium were shown[16] to yield μ-oxo-bridged trinuclear species $Ru_3O(O_2CCH_3)_6(PPh_3)_3$.

Recent syntheses of tetrakis(amidato)diruthenium(II,III) species provide us an opportunity to study the reaction chemistry of such complexes toward tertiary monophosphines. The carboxylato O–C–O and amidato HN–C–O functionalities are isoelectronic in nature, the difference being that the first one is symmetric while the second one is asymmetric. Studies by Bear and co-workers have shown[17,18] that $Ru_2Cl(HNOCCF_3)_4$ and $Ru_2Cl(HNOCCH_3)_4$ compounds, which are polymeric solids with Ru–Cl–Ru bridges, will dissolve in sufficiently polar solvents. In Me_2SO, there is an equilibrium between $[Ru_2(HNOCR)_4Cl]$ and $[Ru_2(HNOCR)_4(Me_2SO)_2]^+$. The benzamidato compound, $Ru_2Cl(C_6H_5CONH)_4$, reported by us is soluble only in Me_2SO.

When we reacted $Ru_2Cl(PhCONH)_4$ in Me_2SO with PPh_3, the product expected was a simple phosphine adduct, since formation of such adducts is known to occur in the cases of $Rh_2(O_2CCH_3)_4(PPh_3)_2$[19] and $Rh_2(PhCONH)_4(PPh_3)_2$.[20] However, as we reported earlier,[7] this reaction in Me_2SO–MeOH produces, in low yield, $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$. We have subsequently shown that the preparation, though always in low yield, is reproducible and follows the same course whether carried out in room light or in the dark. In the presence of $[N(C_2H_5)_4]ClO_4$, the reaction seems to be faster. To find out if the process is fairly general, we have investigated several reactions in which the starting amidato species and the phosphine have been changed, and we have been able to isolate complexes **1** and **2**, the structures of which were determined by X-ray crystallography. These will be discussed in detail presently.

Comparable P–C bond cleavages are known[21-30] to occur in the

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(12) The compound $Ru_2Cl(O_2CPh)_4$ was prepared in quantitative yield by refluxing a mixture of $Ru_2Cl(O_2CCH_3)_4$ and $PhCO_2H$ in 1:4 molar proportions in water. The product was brown and insoluble in common organic solvents. The composition was established from analytical and infrared data. Anal. Calcd: C, 46.56; H, 2.77. Found: C, 46.71; H, 3.64.

(13) Anal. Calcd: C, 65.22; H, 4.32. Found: C, 65.85; H, 4.55. IR (KBr): ν(CO) 1915 cm^{-1} (vs). The X-ray structure, which shows a trans disposition of PPh_3 ligands, is identical with the reported structure of this compound by another group.[15]

(14) This compound can also be obtained from the reaction between $RuHCl(CO)(PPh_3)_3$ and carboxylic acids: Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.

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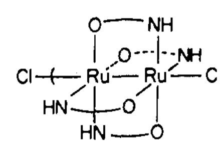
reactions between PPh_3 and a variety of low-valent transition-metal complexes. $Pt(PPh_3)_3$ and $Pt(PPh_3)_2(C_2H_4)$ are known[22] to react with RCNO to give $Pt(OPPh_2)(RCN)(Ph)(PPh_3)$. The molecular structure of this compound was established by X-ray study. Work of Kikukawa and co-workers has shown[31] that a cleavage occurs in the reaction between PPh_3 and $[Pd(O_2CCH_3)_2]_3$ involving a nucleophilic 1,2-migration process as a key step, but there is no structural information available and the assumption of the intermediate is a pure speculation. A nitrogen-assisted migration of a phenyl group from a tertiary phosphine to the metal is reported[32] by Riess and co-workers. In the reaction between a strong base and $Cp(CO)Fe[PhP(OCH_2CH_2)_2NH]^+$, the product is known to be $Cp(CO)Fe(Ph)[P(OCH_2CH_2)_2N]$. This process has some similarity to the one we have studied. In the formation of $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$, as well as **1** and **2**, the migration of the aryl group from PAr_3 takes place along with the formation of a bond from P to the amidato oxygen atom. The process is also accompanied by the loss of the NH proton and the formation of a $Ru(\mu\text{-}N)_2Ru$ core.

While the mechanism of the reaction is of obvious interest, we have not yet been able to learn much about it. We have been unable to isolate single crystals of $Ru_2Cl(PhCONH)_4$ or $Ru_2Cl(3,5\text{-}(OCH_3)_2C_6H_3CONH)_4$, but our recent structural study of the analogous compound $Ru_2Cl(4\text{-}ClC_6H_4CONH)_4$ has shown[33] it to be polymeric, with a 2:2 type of ligand arrangement, **3**, around the diruthenium unit. The crystal structure consists of $Ru_2(ArCONH)_4$ units linked together by Cl atoms in infinite zigzag chains. A similar type of 2:2 arrangement of ligands is also observed[20] in dirhodium tetrakis(amidato) species. We assume that in Me_2SO solvent a cleavage of the Ru–Cl bond takes place to give disolvated discrete dimeric species $[Ru_2(ArCONH)_4(Me_2SO)_2]^+$. The addition of PPh_3 causes a displacement of Me_2SO from the axial sites to produce an intermediate **4**, which then undergoes the rearrangements necessary to give the final product, **5**. During the process one-electron oxidation of the $Ru^{II}Ru^{III}$ to $Ru^{III}{}_2$ as well as loss of two hydrogen atoms also takes place. We have no experimental data bearing on how the oxidation occurs, but we can suggest that the process of P–C bond cleavage might be an oxidative addition of PPh_3 to the metal, as proposed in several other cases. Another possibility is the disproportionation of $Ru^{II}Ru^{III}$ to $Ru^{III}{}_2$ and $Ru^{II}{}_2$ species. A recent report by Wilkinson and co-workers shows[34] that the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Bu^tCH_2MgCl under anaerobic conditions forms the diruthenium(III) complex $Ru_2(CH_2Bu^t)_6$.



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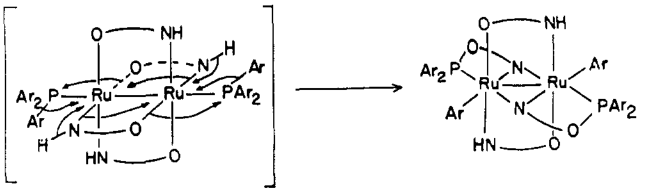

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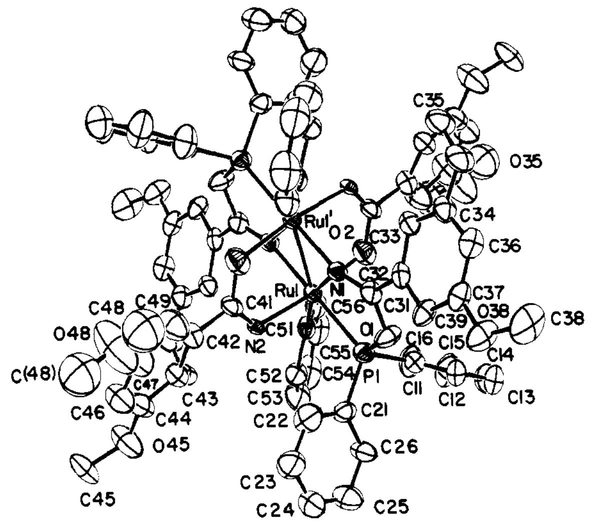

Figure 1. ORTEP drawing of the first of the independent centrosymmetric molecules of $Ru_2(C_6H_5)_2(3,5\text{-}(OCH_3)_2C_6H_3CONH)_2[(C_6H_5)_2POC(3,5\text{-}(OCH_3)_2C_6H_3)N]_2$ (**1**) along with the atom-labeling scheme. Vibrational ellipsoids are at the 50% level. Atoms C48 and C(48), connected to O48, were refined with half-occupancy.

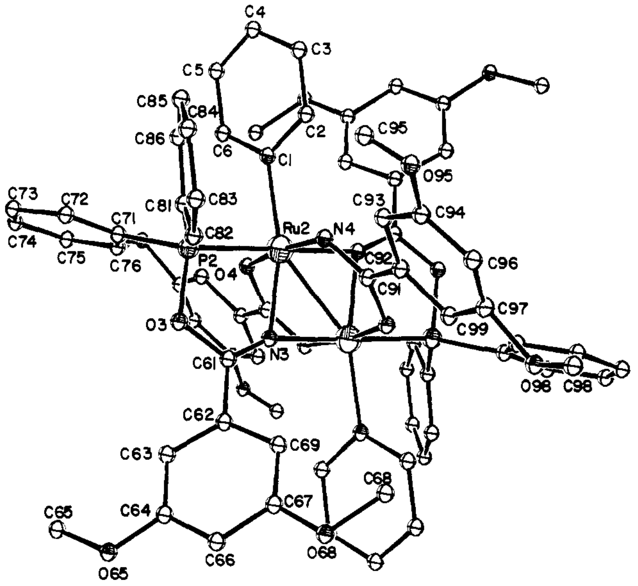

Figure 2. ORTEP drawing of the second independent centrosymmetric molecule of $Ru_2(C_6H_5)_2(3,5\text{-}(OCH_3)_2C_6H_3CONH)_2[(C_6H_5)_2POC(3,5\text{-}(OCH_3)_2C_6H_3)N]_2$ (**1**) showing the atomic numbering scheme. To get a clear view of the molecule, the vibrational ellipsoids were reduced in size.

Matsuda and co-workers, in their study[27] of the arylation reaction of substituted olefins by lead(II) acetate and triphenylphosphine, proposed a reaction pathway involving a nucleophilic attack on phosphorus, eq 2. It is not clear from their study which

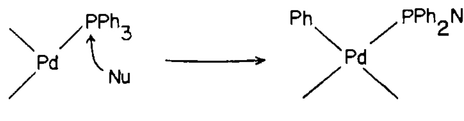

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Table II. Positional Parameters and Their Estimated Standard Deviations for **1**

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Ru1	0.46115 (5)	0.06921 (4)	−0.00630 (4)	2.52 (1)	C41	0.4502 (6)	−0.0387 (5)	−0.1489 (5)	3.2 (2)
Ru2	0.04603 (5)	0.45970 (4)	0.45663 (4)	2.91 (1)	C42	0.4259 (7)	−0.0572 (6)	−0.2338 (5)	3.8 (2)
P1	0.2811 (2)	0.0719 (1)	−0.0034 (1)	3.15 (5)	C43	0.5857 (7)	0.1454 (6)	0.2606 (5)	4.2 (2)
P2	−0.0221 (2)	0.4049 (1)	0.3344 (1)	3.11 (5)	C44	0.3980 (8)	−0.1621 (6)	−0.3387 (5)	4.8 (2)
O1	0.2139 (4)	−0.0354 (3)	0.0032 (4)	4.1 (1)	C45	0.349 (1)	−0.2755 (8)	−0.4404 (6)	6.7 (3)
O2	0.4273 (5)	0.0328 (4)	−0.1214 (4)	4.5 (2)	C46	0.3954 (9)	−0.0960 (7)	−0.3883 (6)	5.4 (3)
O3	−0.1420 (4)	0.4307 (4)	0.3159 (3)	3.6 (1)	C47	0.409 (1)	−0.0083 (7)	−0.3580 (6)	6.3 (3)
O4	−0.0194 (5)	0.3385 (4)	0.5094 (3)	3.6 (1)	C48	0.478 (3)	0.151 (2)	−0.394 (2)	9.7 (8)*
O35	0.1802 (5)	−0.4116 (4)	−0.0962 (4)	5.0 (2)	C49	0.423 (1)	0.0112 (7)	−0.2804 (6)	5.6 (3)
O38	−0.0608 (5)	−0.3084 (4)	0.0393 (4)	4.8 (2)	C51	0.4890 (6)	0.2069 (5)	−0.0282 (5)	3.0 (2)
O45	0.3837 (7)	−0.2520 (5)	−0.3606 (4)	7.0 (2)	C52	0.4600 (7)	0.2680 (5)	0.0193 (6)	4.4 (2)
O48	0.406 (1)	0.0612 (6)	−0.4062 (5)	11.5 (4)	C53	0.4659 (9)	0.3564 (7)	−0.0011 (7)	6.1 (3)
O65	0.5322 (5)	0.5392 (6)	0.7664 (5)	7.0 (2)	C54	0.504 (1)	0.3871 (7)	−0.0682 (8)	6.8 (3)
O68	−0.3216 (7)	0.7378 (5)	0.3557 (6)	8.9 (3)	C55	0.537 (1)	0.3291 (7)	−0.1131 (7)	6.3 (3)
O95	−0.281 (1)	0.131 (1)	0.734 (1)	19.0 (6)*	C56	0.5301 (7)	0.2392 (6)	−0.0926 (5)	4.1 (2)
O98	−0.091 (1)	0.0228 (8)	0.5595 (7)	12.7 (4)*	C61	−0.1645 (6)	0.4787 (5)	0.3742 (4)	3.2 (2)
N1	0.3825 (5)	−0.0648 (4)	0.0080 (4)	2.7 (1)	C62	0.2583 (7)	0.4825 (6)	0.6488 (5)	3.6 (2)
N2	0.5108 (4)	0.0941 (3)	0.1104 (3)	1.9 (1)	C63	0.3531 (7)	0.5367 (6)	0.6951 (5)	3.9 (2)
N3	0.1038 (5)	0.5125 (4)	0.5619 (4)	2.9 (1)	C64	0.4351 (8)	0.4941 (7)	0.7192 (6)	4.9 (2)
N4	0.1057 (6)	0.5870 (4)	0.4169 (4)	3.4 (2)	C65	−0.5519 (9)	0.3658 (9)	0.2165 (8)	7.0 (3)
C1	0.1871 (7)	0.4216 (6)	0.4386 (5)	3.9 (2)	C66	−0.4256 (8)	0.5963 (7)	0.2989 (7)	5.7 (3)
C2	0.2879 (7)	0.4903 (7)	0.4376 (5)	4.8 (2)	C67	−0.3270 (9)	0.6477 (6)	0.3429 (6)	5.8 (3)
C3	0.3857 (9)	0.4652 (8)	0.4270 (7)	6.4 (3)	C68	−0.215 (1)	0.7984 (9)	0.3929 (9)	9.5 (5)
C4	0.3829 (9)	0.3743 (9)	0.4155 (7)	6.9 (3)	C69	0.2437 (8)	0.3920 (6)	0.6275 (5)	4.6 (2)
C5	0.2844 (9)	0.3058 (8)	0.4172 (7)	6.5 (3)	C71	−0.0629 (6)	0.2861 (6)	0.3025 (5)	3.3 (2)
C6	0.1866 (8)	0.3300 (6)	0.4291 (5)	4.9 (2)	C72	−0.0701 (8)	0.2601 (6)	0.2270 (5)	4.6 (2)
C11	0.1951 (7)	0.1007 (6)	−0.0846 (5)	4.1 (2)	C73	−0.1079 (9)	0.1669 (7)	0.2040 (6)	5.3 (3)
C12	0.0837 (7)	0.0473 (7)	−0.1012 (6)	5.3 (2)	C74	−0.1384 (8)	0.1034 (7)	0.2558 (6)	5.7 (3)
C13	0.0175 (8)	0.0733 (8)	−0.1652 (7)	6.6 (3)	C75	−0.1293 (9)	0.1298 (7)	0.3324 (6)	5.5 (3)
C14	0.060 (1)	0.1481 (8)	−0.2052 (6)	6.6 (3)	C76	−0.0930 (8)	0.2225 (7)	0.3551 (6)	4.9 (2)
C15	0.1704 (9)	0.2007 (9)	−0.1860 (7)	6.8 (3)	C81	0.0507 (7)	0.4655 (6)	0.2624 (4)	3.3 (2)
C16	0.2375 (8)	0.1754 (7)	−0.1244 (6)	5.3 (3)	C82	0.0150 (8)	0.5364 (6)	0.2278 (5)	4.3 (2)
C21	0.2424 (6)	0.1210 (5)	0.0770 (5)	3.4 (2)	C83	0.0756 (8)	0.5879 (7)	0.1778 (6)	5.2 (3)
C22	0.2818 (8)	0.0993 (7)	0.1492 (6)	5.4 (3)	C84	0.1718 (9)	0.5708 (8)	0.1610 (6)	5.6 (3)
C23	0.2549 (8)	0.1354 (8)	0.2123 (6)	5.9 (3)	C85	0.2093 (8)	0.5025 (8)	0.1982 (6)	5.6 (3)
C24	0.1877 (8)	0.1916 (7)	0.2044 (6)	5.3 (3)	C86	0.1496 (7)	0.4493 (7)	0.2491 (5)	4.5 (2)
C25	0.1477 (9)	0.2144 (6)	0.1334 (6)	5.4 (3)	C91	−0.0808 (7)	0.3396 (6)	0.5606 (4)	3.3 (2)
C26	0.1753 (8)	0.1790 (6)	0.0692 (5)	4.4 (2)	C92	−0.1240 (7)	0.2498 (6)	0.5930 (5)	4.0 (2)
C31	0.2789 (7)	−0.0944 (5)	0.0045 (5)	3.2 (2)	C93	−0.187 (1)	0.2425 (8)	0.6501 (6)	6.4 (3)
C32	0.2087 (7)	−0.1906 (5)	−0.0014 (5)	3.3 (2)	C94	−0.221 (1)	0.153 (1)	0.6750 (7)	10.0 (4)
C33	0.2410 (7)	−0.2567 (5)	−0.0415 (5)	3.3 (2)	C95	−0.290 (2)	0.184 (2)	0.767 (1)	15.0 (7)*
C34	0.1639 (7)	−0.3417 (5)	−0.0540 (5)	3.5 (2)	C96	−0.196 (1)	0.0770 (9)	0.6489 (8)	9.0 (4)
C35	0.2763 (8)	−0.3948 (7)	−0.1317 (6)	5.3 (2)	C97	−0.135 (1)	0.0910 (8)	0.5950 (8)	7.3 (4)
C36	0.0619 (7)	−0.3637 (6)	−0.0293 (5)	3.9 (2)	C98	−0.120 (2)	−0.061 (2)	0.589 (2)	17.8 (9)*
C37	0.0358 (7)	−0.2960 (6)	0.0113 (5)	3.6 (2)	C99	−0.092 (1)	0.1760 (7)	0.5650 (7)	5.9 (3)
C38	−0.1479 (9)	−0.3921 (7)	0.0179 (8)	7.2 (3)	C(48)	0.395 (3)	0.060 (2)	−0.479 (2)	10.2 (9)*
C39	0.1077 (6)	−0.2085 (5)	0.0256 (5)	3.6 (2)					

[a] Starred values indicate the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Ru1	0.00829 (9)	0.08700 (7)	−0.02962 (8)	3.35 (2)	C22	0.278 (1)	0.3667 (9)	−0.066 (1)	4.9 (3)
P1	0.1173 (3)	0.2969 (2)	0.0925 (3)	3.83 (7)	C23	0.365 (1)	0.4551 (9)	−0.101 (1)	5.6 (4)
O1	0.2114 (7)	0.3142 (5)	0.2150 (6)	4.8 (2)	C24	0.406 (1)	0.5845 (9)	−0.031 (1)	4.9 (3)
O2	−0.1619 (6)	−0.0700 (5)	0.1169 (6)	4.4 (2)	C25	0.494 (1)	0.677 (1)	−0.074 (1)	7.1 (4)
N1	0.0976 (7)	0.1012 (6)	0.1330 (8)	3.9 (2)	C26	0.357 (1)	0.6211 (9)	0.080 (1)	5.7 (4)
N2	−0.1461 (7)	0.0808 (6)	0.0542 (7)	3.4 (2)	C27	0.270 (1)	0.5387 (9)	0.122 (1)	5.6 (4)
C1	−0.0421 (9)	0.1389 (7)	−0.1634 (9)	3.7 (3)	C31	0.0222 (9)	0.3699 (8)	0.1770 (9)	3.9 (3)
C2	0.144 (1)	−0.1683 (8)	0.160 (1)	5.2 (3)	C32	−0.0252 (9)	0.4278 (8)	0.126 (1)	4.4 (3)
C3	−0.179 (1)	0.1987 (9)	−0.255 (1)	6.0 (4)	C33	−0.106 (1)	0.4748 (9)	0.189 (1)	5.6 (4)
C4	−0.112 (1)	0.2020 (9)	−0.353 (1)	5.7 (4)	C34	−0.139 (1)	0.4624 (9)	0.299 (1)	5.2 (3)
C5	−0.147 (1)	0.238 (1)	−0.454 (1)	7.2 (4)*	C35	−0.225 (1)	0.517 (1)	0.371 (1)	7.2 (4)
C6	−0.013 (1)	0.173 (1)	−0.360 (1)	6.1 (4)	C36	−0.095 (1)	0.4031 (8)	0.348 (1)	5.0 (3)
C7	0.026 (1)	0.1434 (9)	−0.264 (1)	5.8 (4)	C37	−0.013 (1)	0.3559 (9)	0.287 (1)	5.2 (3)
C11	0.1806 (9)	0.2003 (7)	0.2187 (9)	3.5 (3)	C41	−0.1984 (8)	0.0092 (7)	0.1079 (9)	3.5 (3)
C12	0.255 (1)	0.2202 (8)	0.3337 (9)	4.3 (3)	C42	−0.3058 (9)	0.0161 (8)	0.1744 (9)	4.0 (3)
C13	0.201 (1)	0.1409 (9)	0.393 (1)	5.9 (4)	C43	−0.373 (1)	0.073 (1)	0.150 (1)	7.4 (4)
C14	0.280 (1)	0.162 (1)	0.503 (1)	7.0 (4)	C44	−0.470 (1)	0.077 (1)	0.214 (2)	9.5 (5)
C15	0.404 (1)	0.261 (1)	0.551 (1)	7.1 (4)	C45	−0.505 (1)	0.024 (1)	0.297 (1)	7.4 (5)
C16	0.453 (1)	0.336 (1)	0.495 (1)	6.8 (4)	C46	−0.442 (1)	−0.035 (1)	0.319 (1)	7.0 (4)
C17	0.380 (1)	0.318 (1)	0.382 (1)	6.2 (4)	C47	−0.343 (1)	−0.0388 (9)	0.257 (1)	5.2 (3)
C21	0.2297 (9)	0.4086 (7)	0.0446 (9)	4.0 (3)					

[a] Starred values indicate the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Important Bond Distances and Angles in **1**[a]

	Distances, Å		
Ru1-Ru1′	2.565 (1)	Ru2-Ru2′	2.568 (1)
-P1	2.309 (2)	-P2	2.302 (2)
-N1	2.064 (5), 2.012 (6)	-N3	2.006 (6), 2.043 (6)
-N2	2.103 (5)	-N4	2.069 (6)
-O2	2.091 (5)	-O4	2.118 (5)
-C51	2.093 (7)	-C1	2.096 (8)
P1-O1	1.651 (5)	P2-O3	1.663 (5)
-C11	1.823 (8)	-C71	1.813 (8)
-C21	1.813 (7)	-C81	1.822 (7)
O1-C31	1.375 (8)	O3-C61	1.381 (8)
O2-C41	1.315 (8)	O4-C91	1.295 (8)
N1-C31	1.266 (9)	N3-C61	1.271 (9)
N2-C41	1.256 (8)	N4-C91	1.321 (9)
	Angles, deg		
Ru1′-Ru1-P1	127.13 (6)	Ru2′-Ru2-P2	127.09 (6)
-O2	85.1 (2)	-O4	87.5 (1)
-N1	50.1 (2), 51.9 (2)	-N3	51.3 (2), 50.0 (2)
-N2	87.1 (1)	-N4	85.3 (2)
-C51	147.5 (2)	-C1	147.8 (2)
P1-Ru1-O2	92.1 (2)	P2-Ru2-O4	97.3 (1)
-N1	77.0 (2), 179.0 (2)	-N3	77.1 (2), 177.5 (2)
P1-Ru1-N2	94.7 (2)	P2-Ru2-N4	88.8 (2)
-C51	85.2 (2)	-C1	84.8 (2)
O2-Ru1-N1	85.8 (2), 88.2 (2)	O4-Ru2-N3	84.6 (2), 92.1 (2)
-N2	171.8 (2)	-N4	172.5 (2)
-C51	91.1 (3)	-C1	93.3 (3)
N1-Ru1-N1	102.0 (2)	N3-Ru2-N3	101.3 (2)
-N2	91.2 (2), 85.1 (2)	-N4	89.2 (2)
-C51	161.8 (3), 95.7 (3)	-C1	161.6 (3), 96.7 (3)
N2-Ru1-C51	94.1 (2)	N4-Ru2-C1	91.7 (3)
Ru1-N1-Ru1	78.0 (2)	Ru2-N3-Ru2′	78.7 (2)
-C31	123.1 (5), 157.8 (5)	-C61	124.3 (5), 154.9 (5)
N1-C31-O1	120.6 (6)	N3-C61-O3	119.4 (7)
Ru1-P1-O1	104.4 (2)	Ru2-P2-O3	104.3 (2)
P1-O1-C31	114.1 (4)	P2-O3-C61	113.8 (4)
O1-C31-C32	110.3 (6)	O3-C61-C62	112.6 (6)
N1-C31-C32	129.0 (6)	N3-C61-C62	128.0 (7)
Ru1-P1-C11	122.2 (3)	Ru2-P2-C71	125.2 (3)
-C21	121.5 (3)	-C81	116.0 (2)
Ru1-N2-C41	120.4 (4)	Ru2-N4-C91	123.8 (5)
Ru1-O2-C41	122.0 (5)	Ru2-O4-C91	119.6 (5)
N2-C41-O2	125.1 (7)	N4-C91-O4	123.8 (7)

[a] In parentheses are estimated standard deviations in the least significant digits.

reagent acts as the nucleophile in the key step of arylation, but the authors believed[27] that acetate ion could act as the nucleophile. The process observed by us incorporates a nucleophilic attack by the amidato oxygen on the phosphorus atom, since the resulting P–O bonds are found in the products, **1**, **2**, and $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$.

Molecular Structures. The atomic positional coordinates of **1** and **2** are presented in Tables II and III, respectively. Significant bond distances and angles of **1** and **2** are listed in Tables IV and V, respectively. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two independent dimers in the crystallographic asymmetric unit. The molecules are shown in Figures 1 and 2 along with atom-labeling schemes. Molecule **2** also crystallizes in the triclinic space group $P\bar{1}$, and the ORTEP diagram of the molecule is shown in Figure 3.

The molecular structures of **1** and **2** are similar to that of $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$.[7] The centrosymmetric molecules consist of a dimetallic unit, and the immediate coordination spheres around the metal atoms are distorted octahedra. The pairs of metal atoms are held together by two bridging amidato ligands and by two μ_2-imido nitrogen atoms. Each metal atom is bonded to an aryl group that has migrated from the triarylphosphine to the metal. The transfer of the amidato oxygen atom to the phosphorus atom gives rise to a new ligand system, $R_2POC(R')N$, which exhibits both chelating (through P and N) and bridging (through μ_2-N modes). The chelate ring is essentially planar. The bridging nitrogen atoms form a common edge of the two octahedra. Structure **2**, as shown in Figures 3 and 4, clearly demonstrates the migration of the P–C bond onto the metal atom.

The Ru–Ru distances of 2.567 [1] and 2.570 (2) Å found in **1** and **2**, respectively, are very similar to that observed[7] in $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$. The Ru–P, Ru–N, Ru–O, and Ru–C distances in **1** and **2** lie in the ranges 2.287 (3)–2.309 (2), 2.006 (6)–2.103 (5), 2.091 (5)–2.137 (6), and 2.093 (7)–2.097 (8) Å, respectively. Earlier, in $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$, we found that the oxygen atoms of the amidato as well as $Ph_2POC(Ph)N$ ligands were slightly disordered, but this does not appear to be the case in the structures of **1** and **2**. In both **1** and **2**, the sums of the Ru–N–Ru, Ru–N–C, and Ru′–N–C angles are ca. 360°. The bridging nitrogen atom thus has sp^2

Table V. Important Bond Distances and Angles in **2**[a]

	Distances, Å		
Ru1-Ru1	2.570 (2)	P1-O1	1.684 (7)
-P1	2.287 (3)	-C21	1.809 (9)
-O2	2.137 (6)	-C31	1.821 (9)
Ru1-N1	2.064 (8), 2.050 (8)	O1-C11	1.405 (10)
-N2	2.064 (7)	O2-C41	1.318 (10)
-C1	2.097 (8)	N1-C11	1.249 (10)
		N2-C41	1.281 (10)
	Angles, deg		
Ru1′-Ru1-P1	127.87 (9)	Ru1-P1-O1	105.0 (2)
-O2	86.9 (2)	-C21	126.5 (3)
-N1	51.1 (2), 51.6 (2)	-C31	114.8 (3)
-N2	85.8 (2)	O1-P1-C21	100.4 (4)
-C1	148.7 (3)	-C31	101.4 (4)
P1-Ru1-O2	95.0 (2)	C21-P1-C31	105.0 (4)
-N1	76.9 (2), 176.7 (2)	P1-O1-C11	111.8 (6)
-N2	91.1 (2)	Ru1-N1-Ru1′	77.3 (3)
-C1	83.4 (3)	-C11	124.4 (6), 157.5 (7)
O2-Ru1-N1	87.9 (3), 88.2 (3)	O1-C11-N1	120.5 (9)
-N2	172.4 (3)	-C12	110.3 (9)
-C1	91.2 (3)	N1-C11-C12	129.1 (9)
N1-Ru1-N1	102.7 (3)	Ru1-O2-C41	118.2 (6)
-N2	89.2 (3), 85.6 (3)	Ru1-N2-C41	123.8 (6)
-C1	160.1 (3), 97.1 (3)	O2-C41-N2	125.2 (8)
N2-Ru1-C1	93.9 (3)		

[a] In parentheses are estimated standard deviations in the least significant digits.

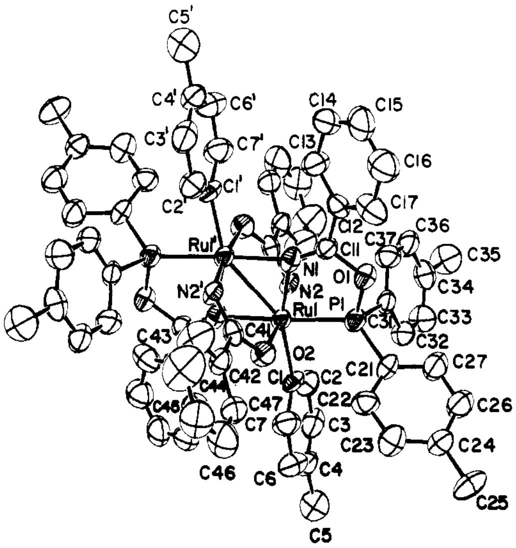

Figure 3. ORTEP drawing of the centrosymmetric molecule of $Ru_2(p\text{-}C_6H_4CH_3)_2(C_6H_5CONH)_2[(p\text{-}C_6H_4CH_3)_2POC(C_6H_5)N]_2$ (**2**) showing the thermal ellipsoids at the 50% probability level and the atom-labeling scheme.

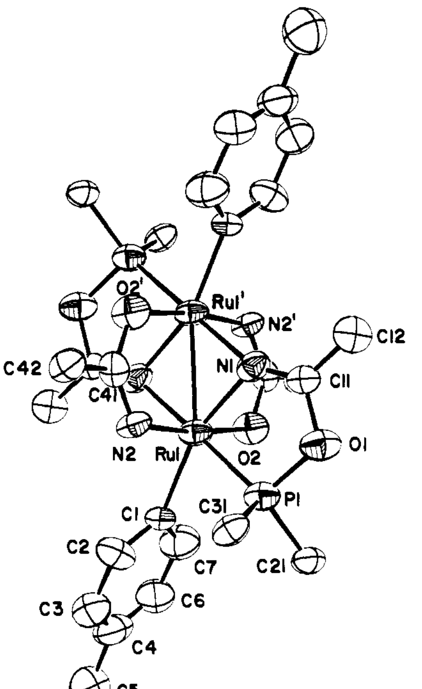

Figure 4. View of the coordination sphere of **2** showing the edge-shared bioctahedral coordination sphere.

hybridization, and the existence of C=N bonds is also evidenced from the short C–N distances. The Ru–N–Ru angle, ca. 78°, deviates considerably from the ideal sp^2 angle of 120°, and this is offset by a considerable increase in one of the other two angles to ca. 160°. These distortions may be attributed to (i) the presence of a strong metal–metal interaction (vide infra) and (ii) the formation of a five-membered chelate ring. The difference of ca. 0.015 Å between two Ru–(μ-N) bond lengths is presumed to be due to the requirements of the chelate ring.

With the two metal atoms in oxidation state III, having $t_{2g}{}^5$ electronic configurations, the formation of a net Ru–Ru single bond may be postulated. Examples of such a bond have been previously seen in $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$ as well as in $[Ru_2(\mu\text{-}NH_2)_2(NH_3)_8]Cl_4\cdot 4H_2O$[35] and $Ru_2(ap)_6(PMe_2Ph)_2$,[36] where ap represents the anion of 2-aminopyridine.

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Registry No. **1**, 98216-98-9; **2**, 98194-59-3; $Ru_2Cl(O_2CCH_3)_4$, 38833-34-0; 3,5-$(OCH_3)_2C_6H_3CONH_2$, 17213-58-0; $Ru_2Cl(3,5\text{-}(OCH_3)_2C_6H_3CONH)_4$, 98194-57-1; PPh_3, 603-35-0; $Ru_2Cl(PhCONH)_4$, 98194-58-2; $P(p\text{-}C_6H_4CH_3)_3$, 1038-95-5; $Ru_3Cl(O_2CPh)_4$, 38832-60-9; $PhCO_2H$, 65-85-0; $RuCl(CO)(O_2CPh)(PPh_3)_2$, 50661-68-2.

Supplementary Material Available: Details of crystal structure determinations and tables of structure factors, anisotropic thermal parameters, complete bond distances and angles, and root-mean-square amplitudes of thermal vibration (75 pages). Ordering information is given on any current masthead page.

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Palladium–Palladium σ-Bonds Supported by Bis(dimethylphosphino)methane (dmpm). Synthetic, Structural, and Raman Studies of $Pd_2X_2(dmpm)_2$ (X = Cl, Br, OH)

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The reaction of bis(dimethylphosphino)methane (dmpm) with $[Pd(CO)Cl]_n$ leads to the formation of the bridged binuclear complex $Pd_2Cl_2(dmpm)_2$ (**1**). The chloride ligands of **1** are labile and may be substituted by X^- (X = Br, OH). The crystal and molecular structure of the Br derivative, $Pd_2Br_2(dmpm)_2$ (**2**), has been determined. Complex **2** crystallizes in the monoclinic space group $C2/c$ with $a = 19.623$ (5) Å, $b = 8.684$ (3) Å, $c = 16.902$ (6) Å, $\beta = 132.25$ (2)°, $V = 2132$ (3) Å^3, and $Z = 4$. The structure was refined to convergence, leading to R and R_w of 0.052 and 0.057, respectively, for 1245 observations in the range $2° < 2\theta < 50°$ with $I \geq 2\sigma(I)$. Complex **2** possesses crystallographic 2-fold symmetry. The Pd–Pd separation is 2.603 (1) Å, consistent with a Pd–Pd bond. The molecular structure of **2** is markedly distorted from planarity of the Pd_2P_4 unit and exhibits a P(1)–Pd–Pd′–P(2) torsion angle of 50.5°. The complexes $Pd_2X_2(dmpm)_2$ are stable and soluble in H_2O. Substitution of hydroxide for the chloride ligands of **1** occurs in water to form $Pd_2(OH)_2(dmpm)_2$. Raman and IR data have been employed in the characterization of the Pd–Pd and Pd–X bonds of the $Pd_2X_2(dmpm)_2$ species. The Raman spectra of **1** and **2** in CH_2Cl_2 show ν(Pd–Pd) to be 140 and 123 cm^{-1}, respectively. Complex **1** in aqueous solution exhibits ν(Pd–Pd) = 140 cm^{-1} and ν(Pd–OH) = 351 cm^{-1}.

Introduction

We report studies of complexes that formally contain a Pd–Pd bond supported by the diphosphine bis(dimethylphosphino)methane (dmpm). Over the past several years, there has been considerable interest in the chemistry of binuclear complexes bridged by diphosphines. The range of structures exhibited by these complexes include (i) face-to-face bi-square-planar $M_2(\widehat{PP})_2L_4$,[1b-f] (ii) diphosphine-supported M–M-bonded $M_2(\widehat{PP})_2L_2$,[2] (iii) molecular A-frame $M_2(\mu\text{-}B)(\widehat{PP})_2L_2$,[3] and (iv) *endo* and *exo* A-frame adducts, $M_2(\mu\text{-}B)(\widehat{PP})_2L_2L'$.[4] An in-

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