# Displacive Transfer of a Phenyl Group from Triphenylphosphine to a Metal Atom: Synthesis and Molecular Structure of Ru₂Ph₂(PhCONH)₂[Ph₂POC(Ph)N]₂

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**Abstract:** The reaction of $Ru_2(O_2CCH_3)_4Cl$ with excess molten benzamide, $PhCONH_2$, affords $Ru_2(PhCONH)_4Cl$ (**1**). This reacts with triphenylphosphine in $Me_2SO-MeOH$ to generate the title compound, **2**, as a brown crystalline solid, insoluble in common solvents. Compound **2** was identified by X-ray crystallography. It forms triclinic crystals belonging to space group $P\bar{1}$ with one molecule in the unit cell, which has the following dimensions: $a = 11.800$ (6) Å, $b = 12.164$ (3) Å, $c = 10.316$ (2) Å, $\alpha = 108.09$ (2)°, $\beta = 97.89$ (3)°, $\gamma = 101.33$ (4)°, $V = 1349$ (1) Å³. The molecule consists of two equivalent ruthenium(III) atoms each surrounded by a distorted octahedron of ligand atoms; the two octahedra share an edge. The $Ph_2POC(Ph)N^-$ ligand coordinates through its P and N atoms to form a five-membered chelate ring. The nitrogen atom also serves as a bridge to the other ruthenium atom so that an essentially planar $P-Ru(\mu-N)_2Ru-P$ unit is formed. The remaining coordination positions in this plane are occupied by the carbon atoms of the phenyl groups. Above and below this plane are bridging $PhCONH^-$ ligands, whose O and N atoms complete the octahedra about each metal atom. The Ru–Ru distance of 2.566 (1) Å and the distortions of the octahedra (e.g., N–Ru–N angles of 101.7 (3)°) imply that a Ru–Ru bond is formed. Ru–P and Ru–O distances are 2.305 (2) Å and 2.093 (5) Å, respectively. The Ru–N distances are in the range 2.024–2.127 Å and the Ru–C distances are 2.104 (6) Å. The chelating ligand is (at least formally) the product of attack of a $PhCONH^-$ oxygen atom on $Ph_3P$ with concomitant shift of a phenyl group to Ru and loss of H. The compound $Ru_2(PhCONH)_4Cl$ has been characterized by elemental analysis, IR, electronic spectral, and electrochemical data. In $Me_2SO$ it displays two CV reductions at potentials −0.655 V ($\Delta E_p = 70$ mV) and −1.085 V ($\Delta E_p = 90$ mV) at 100 mV s⁻¹, and it exhibits a strong absorption band at 445 nm ($\epsilon = 9800$ M⁻¹ cm⁻¹) in the visible spectrum.

In the rapidly developing chemistry of multiply bonded metal–metal species, the tetracarboxylates play an important role as starting materials in synthesizing various other multiply bonded transition-metal complexes.[1] The extensive studies already reported employing the tetracarboxylato $Cr_2$, $Mo_2$, $Re_2$, and $Rh_2$ compounds strongly suggest the possibility of developing parallel chemistry of ruthenium and osmium. Such development would be highly welcome since at present, apart from the carboxylates, the only well-known multiply bonded $M_2$ compounds of these elements are the hydroxypyridinato compounds,[2] $Ru_2(mhp)_4$· $2CH_2Cl_2$ and $Os_2(hp)_4Cl_2$, and some recently reported porphyrin compounds of the type $M_2(porph)_2$.[3] We recently reported the molecular structures of two products, $Ru(ap)_6(PMe_2Ph)_2$⁴ (ap⁻ = the anion of 2-aminopyridine) and $Os_2(MeCOO)_2$-$(Ph_2PC_6H_4)_2Cl_2$,[5] both of which were obtained from the dinuclear carboxylates. From our studies it soon became apparent that many anionic three-atom bridging ligands[1] can easily replace the bridging carboxyl groups of $Ru_2(O_2CR)_4Cl$ and $Os_2(O_2CR)_4Cl_2$ in much the same way as is observed in other dinuclear transition-metal carboxylates. Amides of the carboxylic acids with –NH-CO– functionalities were one of our first choices as three atom-bridging ligands.

This paper reports first the synthesis, spectral, and electrochemical properties of a new diruthenium(II,III) complex, $Ru_2(PhCONH)_4Cl$, (**1**). Crystals of this compound suitable for X-ray crystallography were not obtainable because of its insolubility, which in turn is, presumably, due to polymerization through bridging chloride ions. With the idea of breaking up the polymer and obtaining a crystalline derivative with axially coordinated phosphines, $Ru_2(PhCONH)_4Cl$ was reacted with $PPh_3$. However,

instead of isolating a $Ru_2(PhCONH)_4(PPh_3)_2^{n+}$ ($n = 0$ or 1) type compound we obtained a far more elaborate and interesting metal–metal bonded ruthenium(III) compound, $Ru_2(Ph)_2$-$(PhCONH)_2(NC(Ph)OPPh_2)_2$ (**2**). The molecular structure of this compound was solved by X-ray crystallography and will be reported here.

## Experimental Section

$Ru_2(O_2CCH_3)_4Cl$ was prepared by using a literature method.[6] Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from the Aldrich Chemical Co. Solvents used in the preparations for spectroscopic and electrochemical measurements were of analytical grade and were used without any further purification.

**Synthesis of $Ru_2(PhCONH)_4Cl$ (1).** A 10-g quantity of $PhCONH_2$ was added to 0.1 g of $Ru_2(O_2CCH_3)_4Cl$ under dinitrogen atmosphere. The mixture was heated to 140 °C and stirred for 72 h. Excess ligand was then removed by sublimation under reduced pressure. The product, which is yellow-brown in color, is almost insoluble in all solvents other than dimethyl sulfoxide. The product was washed several times with methanol and finally with diethyl ether. It was then dried under vacuum in the presence of $P_4O_{10}$. The yield is quantitative. Anal. Calcd for $Ru_2(PhCONH)_4Cl$: C, 46.83; H, 3.34; N, 7.80. Found: C, 46.6; H, 3.52; N, 7.72. IR (Nujol): 3385, 3310, 3290, 1595, 1580, 1505, 1480, 1442, 1425, 1205, 1110, 1025, 835, 790, 680, 650 cm⁻¹.

**Synthesis of $Ru_2(Ph)_2(PhCONH)_2(\mu-NC(Ph)OPPh_2)_2$ (2).** A 0.04-g sample of $Ru_2(PhCONH)_4Cl$ was dissolved in 5 mL of dimethyl sulfoxide ($Me_2SO$). The solution was then filtered, and a 2-mL volume of the yellow solution was placed in a test tube (diameter 15 mm). A 3-mL volume of methanol containing 0.06 g of $PPh_3$ and 0.1 g of tetrabutyl-ammonium perchlorate (TBAP) was added slowly on the top of the $Me_2SO$ solution maintaining as much as possible a distinct interface between the two solvents. The color of the solution changed gradually from yellow to pink and back to yellow. Slow diffusion of the solvents as well as electrolytes gave brown crystals in about 30% yield. The compound is insoluble in all common organic solvents as well as in water.

**Measurements.** The elemental analysis of *1* was obtained from Galbraith Lab., Inc. The infrared spectrum was taken with a Perkin-Elmer 785 spectrophotometer. Visible spectra were obtained from $Me_2SO$ solutions of the compound by using a Cary 17D spectrophotometer. Electrochemical measurements were made with use of a Bioanalytical

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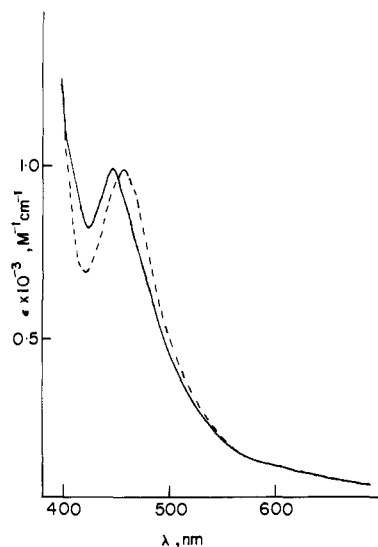
**Figure 1.** The visible absorption spectra of $Ru_2(PhCONH)_4Cl$ in $Me_2SO$ (0.1 M $N(C_4H_9)_4ClO_4$) in the absence of $Cl^-$ (—) and in the presence of 0.1 M $N(C_2H_5)_4Cl$ (---).
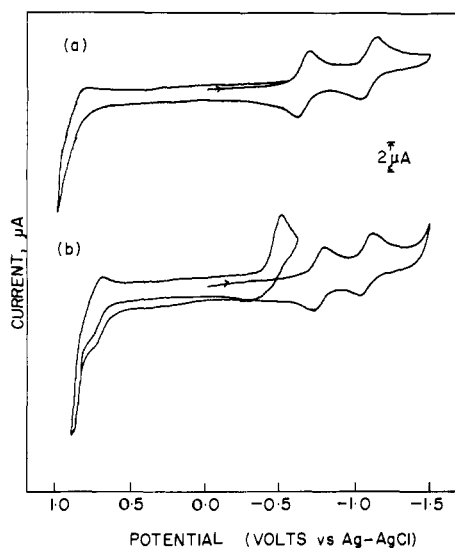


**Figure 2.** Cyclic voltammograms of $Ru_2(PhCONH)_4Cl$ in (a) $Me_2SO$ (0.1 M $N(C_4H_9)_4ClO_4$) and (b) $Me_2SO$ (0.1 M $N(C_4H_9)_4ClO_4$ + 0.1 M $N(C_2H_5)_4Cl$). Scan rate = 100 mV s$^{-1}$. Concentration = 1.0 × 10$^{-3}$ M.

Systems, Inc. Model BAS100 Electrochemical Analyser instrument in connection with a Bausch and Lomb, Houston Instruments Model DMP 40 digital plotter. All experiments were done on $Me_2SO$ solutions containing 0.1 M TBAP. In a three-electrode cell system, a platinum disk, Model BAS MF 2032, and a platinum wire were used as working and auxiliary electrodes and a BAS MF 2020 Ag–AgCl cell was used as the reference electrode (against which ferrocene is oxidized at $E_{1/2}$ = +0.515 V). All potentials are referenced to the Ag–AgCl electrode at 22 ± 2 °C and are uncorrected for junction potentials. All voltammetric measurements were made under a dry argon atmosphere.

**X-ray Crystallographic Procedures.** The structure of the single crystal of **2** was determined by applying the general procedures which are described elsewhere.[7,8] A detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Table II lists the atomic coordinates of **2**. Tables III and IV list important bond distances and angles for **2**. Complete tables of bond lengths and angles as well as anisotropic thermal parameters and structure factor data are available as supplementary material. Figures 3, 4, and 5 show the complete molecule, the coordination sphere, and only the atoms forming the bridged, edge-sharing bioctahedra, respectively, with atom numbering schemes. The compound crystallizes in the triclinic space group, $P\bar{1}$, with one-half of a molecule constituting the asymmetric unit. The whole molecule resides on a crystallographic inversion center. The position of the ruthenium atom was obtained by the direct methods program MULTAN,[7] and the remainder of the structure was solved by
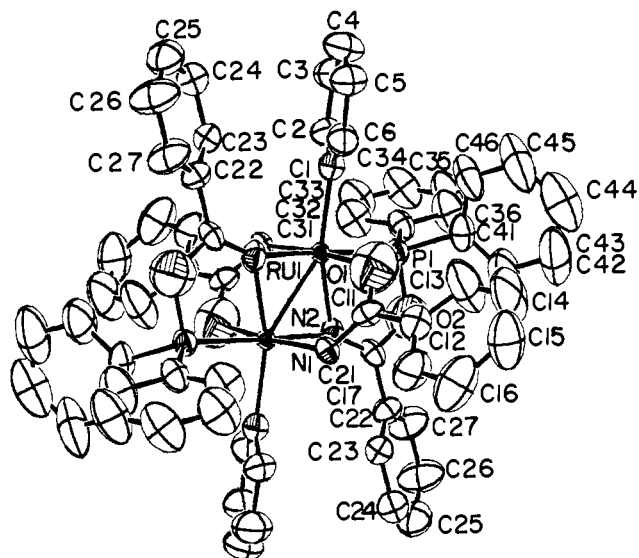


**Figure 3.** An ORTEP drawing of the entire $Ru_2(Ph)_2(PhCONH)_2(\mu-NC-(Ph)OPPh_2)_2$ molecule. Atoms are reprsented by thermal vibration ellisoids at the 50% level, and the atomic labeling scheme in this centrosymmetric molecule is defined.
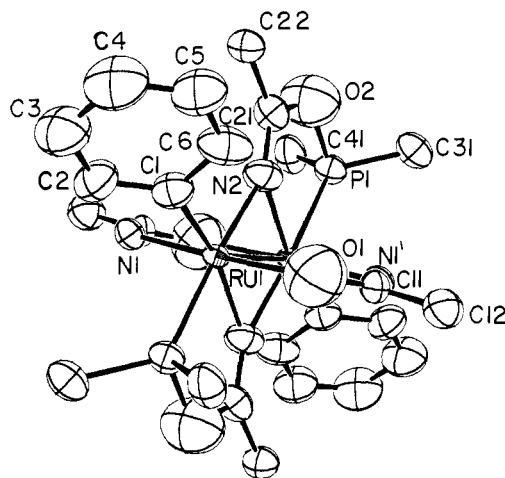


**Figure 4.** An ORTEP drawing in which all phenyl groups except those bonded directly to the metal atoms removed, except for their 1-carbon atoms.
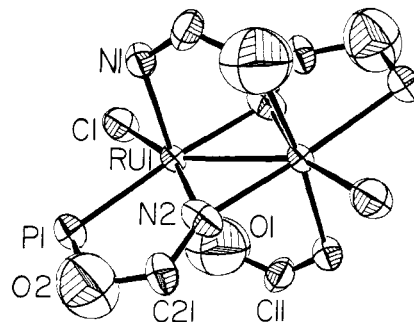


**Figure 5.** An ORTEP drawing showing only the metal atoms and the immediately adjacent ligand atoms.

using least-squares refinement and difference Fourier maps. The oxygen atoms O(1) and O(2) have high thermal parameters which may be due to some sort of disorder. In the last difference Fourier map, there were only two significant peaks, with electron densities 1.42 and 1.33 e Å$^{-3}$ which are 1.1 and 1.0 Å away from the ruthenium atom. All remaining

(7) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with a VAX-SDP software package.

*Structure of Ru$_2$Ph$_2$(PhCONH)$_2$[Ph$_2$POC(Ph)N]$_2$*

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**Table I.** Crystallographic Data

| | |
|---|---|
| formula | Ru$_2$P$_2$O$_4$N$_4$C$_{64}$H$_{54}$ |
| formula wt | 1207.3 |
| space group | P$\bar{1}$ (No. 2) |
| systematic absences | none |
| $a$, Å | 11.800 (6) |
| $b$, Å | 12.164 (3) |
| $c$, Å | 10.316 (2) |
| $\alpha$, degrees | 108.09 (2) |
| $\beta$, degrees | 97.89 (3) |
| $\gamma$, degrees | 101.33 (4) |
| $V$, Å$^3$ | 1348.5 (1) |
| $Z$ | 1 |
| $d_{calcd}$, g/cm$^3$ | 1.487 |
| crystal size, mm | 0.4 × 0.2 × 0.1 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 6.588 |
| data collection instrument | CAD-4 |
| radiation (monochromated in incident beam) | Mo |
| orientation reflections: no., range (2$\theta$) | 25, 13–38 |
| temp, °C | 25 |
| scan method | $\omega$–2$\theta$ |
| data collection range, 2$\theta$, deg | 5–50 |
| no. of unique data, total | 4453 |
| with $F_o^2 > 3\sigma(F_o^2)$ | 3157 |
| no. of parameters refined | 343 |
| trans. factors: max., min. | 99.70, 96.17 |
| $R^a$ | 0.066 |
| $R_w{}^b$ | 0.081 |
| quality-of-fit indicator$^c$ | 2.03 |
| largest shift/esd, final cycle | 0.20 |
| largest peak, e/Å$^3$ | 1.42 |

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

peaks were below 0.75 e Å$^3$. Each oxygen atom has one satellite peak (below 0.7 e Å$^{-3}$) in the last difference Fourier map. The peaks are 0.1 to 0.2 Å from the oxygen atoms. The presence of these peaks is a further indication that there is some disorder in the crystal packing.

## Results and Discussion

**Synthesis.** The first attempts to carry out a reaction between Ru$_2$(O$_2$CCH$_3$)$_4$Cl and PhCONH$_2$ were conducted in a boiling mixture of methanol and water. Under these conditions the benzamide failed to displace the bridging acetate groups. Following a lead given by the work of Bear et al.,$^9$ we then tried the reaction in an excess of molten benzamide and found that at 140 °C it proceeds smoothly to give an essentially quantitative yield of Ru$_2$(PhCONH)$_4$Cl. Excess benzamide is easily removed by sublimation. Unfortunately, however, the product so obtained is amorphous or microcrystalline. It is but sparingly soluble in common solvents except for Me$_2$SO.

Efforts were made to obtain a crystalline product from the yellow solution in Me$_2$SO. A layer of a methanol solution containing a halide ion (Cl$^-$, Br$^-$, or I$^-$) was carefully placed over the solution. With chloride ion small red crystals, possibly containing either Ru$_2$(C$_6$H$_5$CONH)$_4$Cl(Me$_2$SO) or [Ru$_2$(C$_6$H$_5$CONH)$_4$-Cl$_2$]$^-$, were obtained, but none of these crystals was suitable for X-ray analysis. We have not investigated these crystals further and do not know their composition nor why they are red while the solution from which they formed is yellow.

We next introduced triphenylphosphine with the hope that it would occupy one or both axial positions and be conducive to the formation of a suitably crystalline compound containing the Ru$_2$(C$_6$H$_5$CONH)$_4^+$ ion. The addition of PPh$_3$ gave a transient pink color to the solution. On storing the solution, dark brown crystals that were insoluble in all common solvents were obtained.

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**Table II.** Positional Parameters and Their Estimated Standard Deviations in Ru$_2$(Ph)$_2$(PhCONH)$_2$($\mu$-NC(Ph)OPPh$_2$)$_2$ (2)

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Ru1 | -0.10221 (6) | -0.07206 (6) | -0.05930 (7) | 1.84 (1) |
| P1 | -0.2016 (2) | -0.2175 (2) | 0.0132 (2) | 3.08 (5) |
| O1 | -0.0077 (6) | -0.1932 (5) | -0.1513 (6) | 11.3 (2) |
| O2 | 0.8865 (5) | 0.7969 (5) | 0.1603 (6) | 10.3 (2) |
| N1 | 0.8228 (5) | 0.0688 (5) | 0.0400 (6) | 2.8 (1) |
| N2 | 0.0058 (6) | -0.0499 (5) | 0.1238 (7) | 3.9 (2) |
| C1 | -0.2413 (7) | -0.1413 (7) | -0.2366 (9) | 3.9 (2) |
| C2 | -0.3562 (8) | -0.1349 (8) | -0.233 (1) | 4.8 (2) |
| C3 | -0.448 (1) | -0.181 (1) | -0.353 (1) | 6.7 (3) |
| C4 | -0.419 (1) | -0.230 (1) | -0.487 (1) | 7.3 (3) |
| C5 | -0.3022 (9) | -0.2356 (9) | -0.493 (1) | 6.0 (3) |
| C6 | -0.2144 (9) | -0.1923 (8) | -0.3708 (9) | 5.2 (3) |
| C11 | 0.1079 (6) | -0.1687 (7) | -0.1194 (8) | 3.5 (2) |
| C12 | 0.1622 (8) | -0.2689 (8) | -0.1814 (9) | 4.6 (2) |
| C13 | -0.093 (1) | 0.386 (1) | 0.263 (2) | 10.0 (5) |
| C14 | -0.148 (1) | 0.473 (1) | 0.322 (2) | 11.1 (5) |
| C15 | -0.264 (1) | 0.453 (1) | 0.303 (2) | 9.1 (4) |
| C16 | -0.340 (1) | 0.336 (1) | 0.213 (1) | 8.9 (4) |
| C17 | 0.2839 (8) | -0.2478 (9) | -0.160 (1) | 6.3 (3) |
| C21 | -0.0083 (7) | -0.1167 (7) | 0.1948 (8) | 3.6 (2) |
| C22 | 0.0723 (7) | -0.1151 (7) | 0.3184 (8) | 3.9 (2) |
| C23 | 0.1901 (8) | -0.0894 (7) | 0.3258 (9) | 4.5 (2) |
| C24 | 0.2701 (9) | -0.0874 (8) | 0.443 (1) | 5.7 (3) |
| C25 | 0.227 (1) | -0.1117 (9) | 0.552 (1) | 6.3 (3) |
| C26 | 0.105 (1) | -0.136 (1) | 0.541 (1) | 7.8 (3) |
| C27 | 0.027 (1) | -0.139 (1) | 0.4257 (9) | 6.4 (3) |
| C31 | -0.3398 (7) | -0.2229 (7) | 0.0697 (9) | 4.2 (2) |
| C32 | -0.3749 (8) | -0.1163 (9) | 0.115 (1) | 6.0 (3) |
| C33 | -0.481 (1) | -0.117 (1) | 0.160 (1) | 7.3 (3) |
| C34 | -0.551 (1) | -0.220 (1) | 0.166 (1) | 7.7 (4) |
| C35 | -0.514 (1) | -0.327 (1) | 0.120 (1) | 8.6 (4) |
| C36 | -0.4103 (9) | -0.329 (1) | 0.071 (1) | 7.0 (3) |
| C41 | -0.2123 (8) | -0.3712 (7) | -0.091 (1) | 4.6 (2) |
| C42 | -0.152 (1) | -0.4391 (9) | -0.036 (1) | 8.0 (4) |
| C43 | -0.156 (1) | -0.558 (1) | -0.122 (2) | 11.4 (5) |
| C44 | 0.214 (1) | 0.601 (1) | 0.264 (2) | 10.9 (5) |
| C45 | -0.275 (2) | -0.530 (1) | -0.314 (1) | 10.9 (5) |
| C46 | -0.277 (1) | -0.4165 (9) | -0.229 (1) | 8.0 (4) |

$^a$ 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.** Some Important Bond Distances (Å) in Ru$_2$(Ph)$_2$(PhCONH)$_2$($\mu$-NC(Ph)OPPh$_2$)$_2$ (2)

| | |
|---|---|
| Ru(1)–Ru(1) | 2.566 (1) |
| Ru(1)–P(1) | 2.305 (2) |
| Ru(1)–O(1) | 2.093 (5) |
| Ru(1)–N(1) | 2.127 (4) |
| Ru(1)–N(2) | 2.038 (5), 2.024 (5) |
| Ru(1)–C(1) | 2.104 (6) |
| P(1)–O(2) | 1.657 (5) |
| P(1)–C(31) | 1.801 (7) |
| P(1)–C(41) | 1.815 (7) |
| O(1)–C(11) | 1.310 (7) |
| N(1)–C(11) | 1.274 (7) |
| N(2)–C(21) | 1.254 (7) |
| O(2)–C(21) | 1.380 (7) |
| C(21)–C(22) | 1.475 (9) |
| C(11)–C(12) | 1.496 (9) |

These were shown by X-ray crystallography to be compound **2**.

The overall reaction leading from **1** to **2** is clearly a complex one, including oxidation of the Ru$_2^{5+}$ unit to Ru$_2^{6+}$ as well as the making and breaking of several chemical bonds. We shall return to a discussion of this reaction after the properties of **1** and the structure of **2** have been presented and discussed.

**Characterization of Ru$_2$(PhCONH)$_4$Cl (1).** The visible absorption spectrum of **1** in Me$_2$SO (with or without 0.1 M N-(C$_4$H$_9$)$_4$ClO$_4$) has an intense band at 445 nm ($\epsilon$ = 9800 M$^{-1}$ cm$^{-1}$), as shown in Figure 1. This spectrum may be attributable to either [Ru$_2$(PhCONH)$_4$Cl(Me$_2$SO)] or the [Ru$_2$(PhCONH)$_4$-(Me$_2$SO)$_2$]$^+$ ion. Addition of Cl$^-$ ion, in the form of 0.1 M N(C$_2$H$_5$)$_4$Cl, causes a slight red shift, placing the band maximum

**Table IV.** Some Important Bond Angles (in deg) in
Ru$_2$(Ph)$_2$(PhCONH)$_2$($\mu$-NC(Ph)OPPh$_2$)$_2$ (2)

| | |
|---|---|
| Ru(1)-Ru(1)-P(1) | 127.01 (6) |
| Ru(1)-Ru(1)-O(1) | 85.0 (2) |
| Ru(1)-Ru(1)-N(1) | 87.7 (1) |
| Ru(1)-Ru(1)-N(2) | 50.6 (1), 51.1 (2) |
| Ru(1)-Ru(1)-C(1) | 146.7 (2) |
| P(1)-Ru(1)-C(1) | 85.9 (2) |
| P(1)-Ru(1)-O(1) | 87.8 (2) |
| P(1)-Ru(1)-N(1) | 98.4 (1) |
| P(1)-Ru(1)-N(2) | 76.5 (2), 176.0 (2) |
| C(1)-Ru(1)-O(1) | 92.1 (2) |
| C(1)-Ru(1)-N(1) | 92.7 (2) |
| C(1)-Ru(1)-N(2) | 95.8 (2), 162.3 (2) |
| N(1)-Ru(1)-O(1) | 172.4 (2) |
| N(1)-Ru(1)-N(2) | 92.0 (2), 85.1 (2) |
| N(2)-Ru(1)-N(2) | 101.6 (2) |
| O(1)-Ru(1)-N(2) | 85.2 (2), 88.6 (2) |
| N(1)-C(11)-O(1) | 126.1 (6) |
| N(1)-C(11)-C(12) | 117.8 (5) |
| O(1)-C(11)-C(12) | 116.2 (6) |
| Ru(1)-N(1)-C(11) | 118.6 (4) |
| Ru(1)-O(1)-C(11) | 122.3 (5) |
| Ru(1)-N(2)-Ru(1) | 78.4 (2) |
| P(1)-O(2)-C(21) | 114.1 (4) |
| Ru(1)-P(1)-O(2) | 104.2 (2) |
| Ru(1)-P(1)-C(31) | 126.7 (2) |
| Ru(1)-P(1)-C(41) | 116.3 (2) |
| O(2)-C(21)-N(2) | 118.8 (6) |
| O(2)-C(21)-C(22) | 112.3 (5) |
| N(2)-C(21)-C(22) | 128.9 (6) |

at 455 nm. This presumably signifies replacement of axial Me$_2$SO molecules by Cl$^-$ ions. In the case of Ru$_2$(CF$_3$CONH)$_4$Cl, the absorption band in Me$_2$SO solution is at 459 nm and was not shifted by addition of Cl$^-$, although there was such a shift when Cl$^-$ was added to a solution in MeCN.[9]

Solutions of Ru$_2$(PhCONH)$_4$Cl in Me$_2$SO were studied by cyclic voltammetry. In a solution containing N(C$_4$H$_9$)$_4$ClO$_4$ as supporting electrolyte and no additional Cl$^-$ ion, there are two well-defined cyclic voltammetric responses in the potential scan range between +1.5 and -1.5V as shown in Figure 2a. All potentials were measured vs. an Ag/AgCl reference electrode at room temperature under an argon atmosphere. The responses appear between -0.6 and -1.2 V and are due to reduction. No oxidations were observed on the positive side of the Ag/AgCl electrode in the range that is available in this solvent.

The first reduction was observed at the formal potential -0.655 V. The peak-to-peak separation ($\Delta E_p$) is 70 mV at a scan rate ($v$) of 100 mV s$^{-1}$. The anodic and cathodic peak current ratio, $i_{pa}/i_{pc}$, was unity at all scan rates. The second response, at -1.085 V, has a peak-to-peak separation of 90 mV at $v$ = 100 mV s$^{-1}$ and $i_{pa}/i_{pc} \approx 1.0$. This electron transfer process thus appears to be quasireversible. The peak currents of the two responses are essentially the same. By using coulometry, it was found that each of the above CV responses corresponds to a one-electron process, based on total molarity of the diruthenium species. We believe that the first reduction can be attributed to the process [Ru$^{II}$Ru$^{III}$] + e$^-$ → [Ru$^{II}$Ru$^{II}$]. In their study[9] of Ru (CF$_2$CONH)$_3$Cl in Me$_2$SO, Bear and Kadish observed only one reduction (at -0.19 V), and they proposed this assignment for it. They found that on addition of Cl$^-$ there was a shift of 0.15 V to more negative potential. Similarly, we find that in the presence of excess Cl$^-$ there is a shift of ca. -0.12 V. Such shifts are reasonable, as Bear and Kadish proposed, if we assume that in (CH$_3$)$_2$SO we are dealing with a (CH$_3$)$_2$SO[Ru$^{II}$Ru$^{III}$](CH$_3$)$_2$SO$^+$ species which is converted by excess Cl$^-$ ion to a (CH$_3$)$_2$SO[Ru$^{II}$Ru$^{III}$]Cl or Cl-[Ru$^{II}$Ru$^{III}$]Cl species, which would be expected to be more difficult to reduce. It is also reasonable that our compound **1** should have a more negative potential for the [Ru$^{II}$Ru$^{III}$] to [Ru$^{II}$Ru$^{II}$] reduction than the CF$_3$CONH complex.

We cannot suggest a process to account for the second reduction (which is relatively insensitive to Cl$^-$ concentration). It may be ligand centered rather than metal centered. One other notable

feature of the electrochemical behavior is seen in Figure 2. In the presence of excess Cl$^-$ we see a new oxidation at ca. +0.7 V and a new reduction at ca. -0.45 V, the latter being definitely irreversible. Evidently, with the excess Cl$^-$ present an oxidation process that otherwise lies outside the solvent limit (i.e., >+0.85 V) becomes accessible. This might be a [Ru$^{II}$Ru$^{III}$] → [Ru$^{III}$Ru$^{III}$] process. The product of this oxidation process is then subject to irreversible reduction at ca. -0.45 V. As Bear and Kadish have shown,[9] the electrochemistry of these diruthenium(II,III) complexes can be extremely complex and difficult to assign with certainty. We do not plan any further studies of our compound **1**.

**Molecular Structure of Ru$_2$(Ph)$_2$(PhCONH)$_2$($\mu$-NC(Ph)-OPPh$_2$)$_2$ (2).** The structure of this compound was solved by three-dimensional X-ray crystallographic procedures. The atomic coordinates and equivalent isotropic thermal vibration parameters are listed in Table II. The molecule, which resides on a crystallographic center of inversion, is shown in Figure 3 where the complete atom labeling scheme is also shown. Important bond lengths and bond angles are listed in Tables III and IV.

Figures 4 and 5 show progressively stripped down views of the molecule which make it easier to perceive the nature of the ligands and their relationship to the metal atoms, as well as the relationship of the metal atoms to each other. The two metal atoms are equivalent and related by an inversion center midway between them. Each metal atom is at the center of a distorted octahedron of ligand atoms, and the two octahedra are fused on a common edge, which is defined by the two nitrogen atoms N(2) and N(2)'. The two octahedra are also linked by the bridging NCO portions of the C$_6$H$_5$C(O)NH$^-$ anions. Let us consider now individual elements of this structure.

The simplest ligands present are the phenyl groups. The Ru-C distances are 2.104 (6) Å, which seems reasonable for a single bond.

The bridging C$_6$H$_5$C(O)NH$^-$ ligands, benzamidato anions, are also a familiar type of ligand, many bridging amidato ligands having been found across pairs of multiply bonded metal atoms.[10-12] The configuration about the amido carbon atom is planar (the sum of the bond angles is 360° within experimental error). The relatively long Ru-Ru distance here results in Ru-Ru-N and Ru-Ru-O angles that are slightly acute, 87.7 (1)° and 85.0 (2)°, respectively, and a N-C-O angle that is rather larger, at 126.1 (6)°, than those found in compounds with shorter metal-metal distances, namely 120-121° in Cr$_2^{4+}$ and Mo$_2^{4+}$ compounds.[10-12] The thermal ellipsoids of the N and O atoms in this ligand appear to be, respectively, too small and too large. On the other hand, if the assignments of N and O are reversed, an even worse situation develops in the opposite sense, and a higher $R$ value is obtained. We suggest that there is a disorder in these ligands such that the arrangement shown is more highly populated than the alternative. While further refinement in which occupation numbers for these two atoms are varied would be possible, we do not think the benefits would justify the effort.

The most complex and distinctly unusual ligand in this compound is the Ph$_2$POC(Ph)N$^-$ ligand, which is both chelating and bridging. The five-membered chelate ring had the expected effect of making one of the angles in the "octahedron" about the ruthenium atom quite acute; the P(1)-Ru-N(2) angle is only 76.5 (2)°. The P-O, O-C, C-N series of distances, 1.657 (5), 1.380 (7), and 1.254 (7) Å, is consistent with bond orders of approximately 1, 1, and 2. The bridging nitrogen atom forms bonds to the ruthenium atoms that are nearly identical in length, viz., 2.024 (5) and 2.038 (5) Å. In fact, these cannot be regarded as different in a statistically significant sense. They are slightly shorter than those found for the bridging nitrogen atom in Ru$_2$(ap)$_6$(PMe$_2$Ph)$_2$, where they are[4] 2.085 (9) and 2.104 (9) Å. The five-membered chelate ring is nearly planar, but the thermal ellipsoid of the oxygen atom is somewhat larger than those of its neighbors. Probably

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the ring is slightly puckered at the oxygen atom. It may also be noted that the set of bonds about N(2) is essentially coplanar, the sum of the angles being 358.4 (6)°. This is in agreement with the proposal that it is part of a C=N⁻ unit and bears no hydrogen atom.

We turn now to the relationship of the two halves of the molecule. As may be seen most clearly in Figure 5, we are dealing here with an edge-sharing bioctahedron. All the structural features as well as other considerations lead to the conclusion that there is a bond between the ruthenium atoms. The ruthenium atoms are in oxidation state III and thus each one in its own isolated octahedron would have a $t_{2g}^5$ configuration. At a distance of 2.566 Å, overlap of d orbitals to give a $\sigma$ bond seems very likely. This draws the metal atoms together and leads to expansion of the N(2)–Ru–N(2)′ angles to 101.7 (3)° and contraction of the Ru–N(2)–Ru′ angles to 78.4 (2)°. The Ru–Ru distance here is very similar to that in Ru₂(ap)₆(PMe₂Ph)₂, where it is 2.573 (2) Å.

**The Conversion of 1 to 2.** The most important and astonishing aspect of this work is the transformation of compound 1 to compound 2. One aspect of this conversion is the oxidation of the multiply bonded Ru₂⁵⁺ core to a pair of Ru^III atoms joined by a single bond. We have no evidence as to what is the oxidizing agent, and in view of the less than 50% yield, a disproportionation cannot be ruled out.

However, the really interesting process that has occurred is the conversion represented schematically in eq 1. Whether this is



(1)
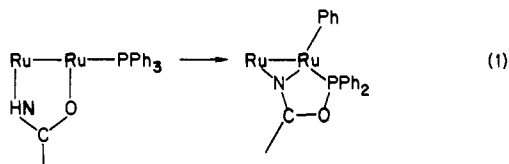
a concerted process (though it is certainly not likely to be a syncronous one[13]) in which adjacent ligands react as in eq 2 is at present speculative, but it does not seem unlikely.



(2)
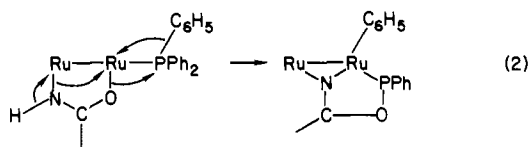
The process by which 1 is converted to 2 may be compared with some previously reported chemistry in which triphenylphosphine undergoes P–C bond breaking in the presence of a transition-metal compound. For the sake of completeness, let us note first that the literature records a number of observations concerning oxidative addition of Ph₃P to a metal atom.[14–17] In most cases a
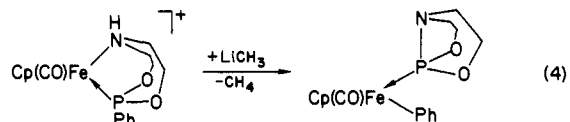
$\mu$-Ph₂P group is found in the product. Such reactions characteristically occur with zero-valent metal atoms, e.g., with Os₃(C-O)₁₂,[14] Pt(0),[15,16] or Ni(0)[17] although in the latter case the product of such an oxidative addition was not isolated but only postulated to be an intermediate. We do not consider these oxidative additions to be the same type of reaction as the one featured in this paper.

Somewhat more related to our reaction is one reported by Beck and co-workers[18] where RCNO attacks Pt(PPh₃)₃ to give a product [Pt(PPh₂O)(Ph)(RCN)(PPh₃)] in which a phenyl group has been transferred from the phosphorus atom to a metal atom and a new P–O bond has been formed. However, the PO(Ph)₂ ligand is, presumably, to be regarded as a radical-containing P^V rather than, as in our case, a substituted phosphine of the type ROPPh₂.

Quite recently it was suggested, without proof, that the process in eq 3 might occur as an intermediate step in a complex reaction.[19] This is rather like what we have observed, but it is, in contrast to our work, pure speculation.



(3)
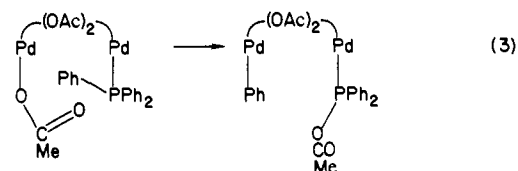
We are aware of one previous report that provides a *documented* example of a process with some genuine similarity to the one reported here. This reaction, reported by Riess and co-workers,[20] is shown in eq 4. This, however, involves a considerably more exotic ligand than PPh₃.



(4)

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