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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

REACTIVITY OF THE DIPHOSPHINE $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ WITH $[(\eta^6\text{-}i\text{-C}_6\text{H}_4\text{Pr})\text{RuCl}_2]_2$. CRYSTAL STRUCTURES OF RUTHENIUM COMPLEXES CONTAINING MONODENTATE AND SINGLY-BRIDGING DIPHOSPHINE LIGANDS

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To cite this Article Coleman, Anthony W. , Zhang, Hongming , Bott, Simon G. , Atwood, Jerry L. and Dixneuf, Pierre H.(1987) 'REACTIVITY OF THE DIPHOSPHINE $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ WITH $[(\eta^6\text{-}i\text{-C}_6\text{H}_4\text{Pr})\text{RuCl}_2]_2$. CRYSTAL STRUCTURES OF RUTHENIUM COMPLEXES CONTAINING MONODENTATE AND SINGLY-BRIDGING DIPHOSPHINE LIGANDS', *Journal of Coordination Chemistry*, 16: 1, 9 – 17

To link to this Article: DOI: 10.1080/00958978708079801

URL: <http://dx.doi.org/10.1080/00958978708079801>

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REACTIVITY OF THE DIPHOSPHINE $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ WITH $[(\eta^6\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$. CRYSTAL STRUCTURES OF RUTHENIUM COMPLEXES CONTAINING MONODENTATE AND SINGLY- BRIDGING DIPHOSPHINE LIGANDS

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(Received July 28, 1986)

The reaction of $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ with dpm in refluxing benzene or heptane (molar ratio, 1:2) leads to the formation of two products, the major one of which is the monodentate dpm complex $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2\cdot\text{dpm}]$, **1**. A small amount (5-15%) of *trans*- $\text{RuCl}_2\cdot\text{dpm}_2$ is also formed. Complex **1** will react further with the starting dimer under the same conditions to yield the singly dpm bridged complex $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2\cdot\text{dpmCl}_2\cdot\text{Ru}(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)]$, **2**. **1** as the CH_2Cl_2 adduct crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.981(6)$, $b = 19.603(5)$, $c = 11.525(5)$ Å, $\beta = 96.08(5)^\circ$, and $Z = 4$ for $D_c = 1.43$ g cm $^{-3}$. **2** as the CH_2Cl_2 adduct crystallizes in the orthorhombic space group $Pcca$ with $a = 38.633(8)$, $b = 12.062(4)$, $c = 21.196(6)$ Å, and $Z = 8$ for $D_c = 1.45$ g cm $^{-3}$. **1** was refined to $R = 0.028$ based on 3398 observed reflections, and **2**, 0.077 based on 1900 observed.

Keywords: Ruthenium, diphosphines, arene, syntheses, structures.

INTRODUCTION

Bis(diphenylphosphino)methane, dpm, can bind to metal atoms in a number of ways: chelating,¹ doubly bridging,² singly bridging,^{3,4} or monodentate.^{5,6,7} An extensive chemistry has evolved around the first two, and whilst the dinuclear chemistry of some platinum metals (Rh,⁸ Ir,⁹ Pd,^{9,10} and Pt^{9,11}) has undergone extensive exploration, little attention has been paid to the chemistry of similar ruthenium complexes.^{12,13} This lack of interest has been attributed to a dearth of suitable starting materials, and indeed only two other dinuclear dpm complexes have been reported with the exception of carbonyl clusters.^{4,14}

We report here the facile synthesis of a binuclear dpm complex of ruthenium of the type $\{[(\text{arene})\text{RuCl}_2]_2\text{dpm}\}$, which has been previously shown to be an excellent starting material for the preparation of carbonyl clusters of ruthenium containing bridging dpm ligands. The molecular structure of the complex $\{[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]\text{dpm}\}$ has been determined, as has been that of $\{[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]\text{dpm}\}$ which contains a monodentate dpm ligand offering possibilities for the synthesis of heterometallic dinuclear complexes of dpm.

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EXPERIMENTAL

All procedures were conducted using standard Schlenk techniques.

Synthesis of 1

The compound was prepared according to the method of Dixneuf *et al.*,¹⁵ using commercially available dpm and $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^f)\text{RuCl}_2]_2$. Recrystallization of the red solid from dichloromethane/diethyl ether produced crystals suitable for X-ray analysis.

Synthesis of 2

2 was prepared using the method of Dixneuf *et al.*,¹⁵ with $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^f)\text{RuCl}_2 \cdot \text{dpm}]$ and $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^f)\text{RuCl}_2]_2$. Recrystallization of the red solid from dichloromethane/hexane afforded crystals suitable for the X-ray work.

X-ray Structure Determination for 1

Single crystals were mounted in thin-walled glass capillaries. One, exhibiting excellent faces, was placed on the goniometer. Final lattice parameters as determined from the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 25 reflections ($2\theta > 36^\circ$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Data were collected by the θ - 2θ scan technique as described previously.¹⁶ A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization and absorption effects. Calculations were carried out using the SHELX system of computer programs.¹⁷ Neutral atom scattering factors for Ru, Cl, P, and C were taken from Cromer and Waber.¹⁸ The scattering for all atoms was corrected for the

TABLE I
Crystal data and summary of intensity data collection and structure refinement

| Compound | 1 | 2 |
|-----------------------------------|------------------------|-----------------------------|
| mol. wt. | 773.5 | 1081.7 |
| space group | $P2_1/n$ | $Pcca$ |
| cell constants | | |
| <i>a</i> , Å | 15.981(6) | 38.633(8) |
| <i>b</i> , Å | 19.603(5) | 12.062(4) |
| <i>c</i> , Å | 11.525(5) | 21.196(6) |
| β , deg | 96.08(5) | 90 |
| cell vol., Å ³ | 3590 | 9877 |
| molecules/unit cell | 4 | 8 |
| ρ (calc), g cm ⁻³ | 1.43 | 1.45 |
| μ (calc), cm ⁻¹ | 8.35 | 10.11 |
| radiation | $\text{MoK}\alpha$ | $\text{MoK}\alpha$ |
| scan width, deg | $0.8 + 0.2 \tan\theta$ | $0.8 \times 0.2 \tan\theta$ |
| std. reflections | 100, 016, 001 | 800, 080, 002 |
| variation of stds. | < 5% | < 2% |
| 2θ range | 2-44 | 2-40 |
| obsd. reflections | 3398 | 4972 |
| no. of parameters varied | 388 | 275 |
| GOF | 1.05 | 4.14 |
| <i>R</i> | 0.028 | 0.077 |
| <i>R_w</i> | 0.031 | 0.079 |

TABLE II
Final fractional coordinates for **1** (as the CH₂Cl₂ adduct).

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|-------------|------------|-------------|
| Ru | 0.01568(2) | 0.12952(2) | -0.10438(3) |
| Cl(1) | 0.10614(7) | 0.12828(7) | 0.0771(1) |
| Cl(2) | -0.10402(7) | 0.14505(6) | 0.0052(1) |
| Cl(3) | -0.0177(2) | 0.0740(1) | 0.4222(2) |
| Cl(4) | 0.0368(1) | 0.2103(1) | 0.3923(2) |
| P(1) | 0.03349(7) | 0.24872(6) | -0.0920(1) |
| P(2) | 0.01969(8) | 0.37539(7) | 0.0713(1) |
| C(1) | 0.0275(3) | 0.2816(2) | 0.0557(4) |
| C(2) | 0.0234(5) | 0.1294(4) | 0.3292(6) |
| C(11) | 0.1361(3) | 0.2736(2) | -0.1344(4) |
| C(12) | 0.1458(3) | 0.2805(3) | -0.2530(5) |
| C(13) | 0.2246(4) | 0.2904(3) | -0.2884(6) |
| C(14) | 0.2939(4) | 0.2926(3) | -0.2089(7) |
| C(15) | 0.2861(4) | 0.2865(4) | -0.0915(7) |
| C(16) | 0.2064(3) | 0.2772(3) | -0.0541(5) |
| C(21) | -0.0399(3) | 0.3017(2) | -0.1839(4) |
| C(22) | -0.1230(3) | 0.2793(3) | -0.2109(5) |
| C(23) | -0.1822(4) | 0.3213(4) | -0.2714(6) |
| C(24) | -0.1605(5) | 0.3869(4) | -0.3028(6) |
| C(25) | -0.0800(5) | 0.4099(3) | -0.02759(5) |
| C(26) | -0.0187(3) | 0.3680(3) | -0.2169(4) |
| C(31) | 0.0418(3) | 0.3824(2) | 0.2299(4) |
| C(32) | -0.0174(3) | 0.3847(4) | 0.3073(5) |
| C(33) | 0.0056(4) | 0.3925(5) | 0.4256(6) |
| C(34) | 0.0878(4) | 0.3973(4) | 0.4691(5) |
| C(35) | 0.1475(4) | 0.3950(4) | 0.3947(6) |
| C(36) | 0.1248(3) | 0.3873(4) | 0.2763(5) |
| C(41) | -0.0935(3) | 0.3934(2) | 0.0506(4) |
| C(42) | -0.1584(3) | 0.3458(3) | 0.0433(5) |
| C(43) | -0.2410(3) | 0.3659(4) | 0.0239(6) |
| C(44) | -0.2605(4) | 0.4352(4) | 0.0121(6) |
| C(45) | -0.1978(4) | 0.4824(3) | 0.0206(6) |
| C(46) | -0.1146(3) | 0.4622(3) | 0.0382(5) |
| C(50) | 0.1068(3) | 0.0586(2) | -0.1753(4) |
| C(51) | 0.0379(3) | 0.0185(2) | -0.1423(4) |
| C(52) | -0.0438(3) | 0.0351(2) | -0.1841(4) |
| C(53) | -0.0631(3) | 0.0909(3) | -0.2598(4) |
| C(54) | 0.0051(3) | 0.1298(3) | -0.2934(4) |
| C(55) | 0.0891(3) | 0.1132(2) | -0.2529(4) |
| C(56) | -0.1528(3) | 0.1058(3) | -0.3043(6) |
| C(57) | 0.1941(3) | 0.0371(3) | -0.1256(5) |
| C(58) | 0.2191(4) | -0.0252(3) | -0.1935(6) |
| C(59) | 0.2604(4) | 0.0949(4) | -0.1331(6) |

real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.¹⁹ Structure solution was accomplished by means of Patterson techniques, which gave the location of the Ru atom. Difference Fourier maps phased on the metal readily revealed the positions of the remaining non-hydrogen atoms. All atoms were treated with anisotropic thermal parameters. A final $R = \sum | |F_o| - |F_c| | / \sum |F_o| = 0.028$ ($R_w = 0.031$) was obtained. A final difference Fourier showed no feature greater than $0.5e/\text{\AA}^3$. The weighting scheme was based upon unit weights and no systematic variation of $w(|F_o| - |F_c|)^2$ vs $|F_o|$ or $(\sin\theta/\lambda)$ was observed. The final values of the positional parameters are given in Table II. Tables of anisotropic thermal parameters and structure factors are available as supplementary material from the Editor.

TABLE III
Final Fractional Coordinates for **2** (as the CH₂Cl₂ adduct).

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|------------|------------|------------|
| Ru(1) | 0.05198(6) | 0.4113(2) | 0.0739(1) |
| Ru(2) | 0.21671(6) | 0.2937(2) | 0.0513(1) |
| Cl(1) | 0.0032(2) | 0.2875(6) | 0.0654(4) |
| Cl(2) | 0.0687(2) | 0.3675(6) | -0.0335(4) |
| Cl(3) | 0.1818(2) | 0.4055(7) | -0.0178(4) |
| Cl(4) | 0.1972(2) | 0.4056(6) | 0.1395(4) |
| Cl(5) | 0.1070(6) | 0.682(2) | 0.2904(8) |
| Cl(6) | 0.1658(5) | 0.544(1) | 0.2858(9) |
| P(1) | 0.0841(2) | 0.2533(6) | 0.1050(4) |
| P(2) | 0.1662(2) | 0.1883(6) | 0.0696(4) |
| C(1) | 0.1281(6) | 0.282(2) | 0.074(1) |
| (2) | 0.134(1) | 0.592(5) | 0.339(3) |
| C(11) | 0.0849(7) | 0.565(2) | 0.079(1) |
| C(12) | 0.0840(7) | 0.513(3) | 0.137(1) |
| C(13) | 0.0516(7) | 0.491(2) | 0.167(1) |
| C(14) | 0.0196(8) | 0.516(2) | 0.135(1) |
| C(15) | 0.0206(6) | 0.568(2) | 0.076(1) |
| C(16) | 0.0522(9) | 0.593(3) | 0.043(1) |
| C(17) | 0.1202(8) | 0.595(2) | 0.046(1) |
| C(18) | 0.1337(8) | 0.693(3) | 0.090(2) |
| C(19) | 0.1184(9) | 0.626(3) | -0.021(2) |
| C(20) | -0.0151(8) | 0.491(3) | 0.168(2) |
| C(21) | 0.2712(7) | 0.344(2) | 0.068(1) |
| C(22) | 0.2652(8) | 0.349(2) | 0.002(2) |
| C(23) | 0.2502(9) | 0.258(3) | -0.033(1) |
| C(24) | 0.2444(9) | 0.160(3) | 0.005(2) |
| C(25) | 0.2521(7) | 0.157(2) | 0.072(1) |
| C(26) | 0.2652(8) | 0.253(3) | 0.106(2) |
| C(27) | 0.245(1) | 0.278(3) | -0.099(2) |
| C(28) | 0.228(1) | 0.179(5) | -0.125(2) |
| C(29) | 0.276(1) | 0.301(4) | -0.134(2) |
| C(30) | 0.2734(9) | 0.249(3) | 0.176(2) |
| C(31) | 0.0697(7) | 0.115(2) | 0.078(1) |
| C(32) | 0.0686(9) | 0.030(3) | 0.125(2) |
| C(33) | 0.056(1) | -0.077(3) | 0.102(2) |
| C(34) | 0.0451(8) | -0.089(3) | 0.038(2) |
| C(35) | 0.0485(9) | -0.004(3) | -0.002(2) |
| C(36) | 0.0608(7) | 0.100(2) | 0.019(1) |
| C(41) | 0.0850(8) | 0.246(2) | 0.188(1) |
| C(42) | 0.1140(8) | 0.275(2) | 0.224(1) |
| C(43) | 0.112(1) | 0.279(3) | 0.289(2) |
| C(44) | 0.081(1) | 0.246(3) | 0.322(2) |
| C(45) | 0.0528(9) | 0.218(3) | 0.287(1) |
| C(46) | 0.0545(8) | 0.217(2) | 0.221(1) |
| C(51) | 0.1689(6) | 0.099(2) | 0.137(1) |
| C(52) | 0.1478(7) | 0.003(3) | 0.142(1) |
| C(53) | 0.1507(7) | -0.067(2) | 0.197(1) |
| C(54) | 0.1701(9) | -0.037(3) | 0.247(2) |
| C(55) | 0.1893(9) | 0.065(3) | 0.241(2) |
| C(56) | 0.1866(7) | 0.128(2) | 0.188(1) |
| C(61) | 0.1559(6) | 0.097(2) | 0.004(1) |
| C(62) | 0.1376(8) | 0.130(2) | -0.046(2) |
| C(63) | 0.1300(9) | 0.062(3) | -0.099(2) |
| C(64) | 0.142(1) | -0.048(3) | -0.097(2) |
| C(65) | 0.1634(8) | -0.078(2) | -0.049(2) |
| C(66) | 0.1716(7) | -0.011(2) | 0.004(1) |

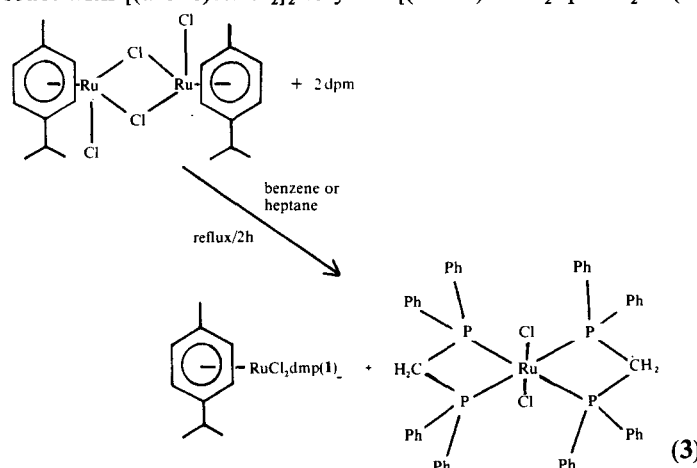
X-ray Structure Determination for 2

A summary of data collection parameters are given in Table I. The methods were as

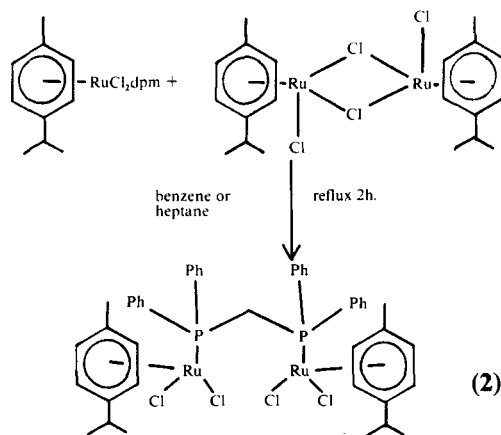
described for **1**, except that only the Ru, Cl, and P atoms were refined with anisotropic thermal parameters. The final R values were $R = 0.077$ and $R_w = 0.079$. The positional parameters are given in Table III. Supplementary data are available from the Editor.

RESULTS AND DISCUSSION

It has been previously shown that the reaction of dpm with $[(\text{arene})\text{RuCl}_2]_2$ leads to the formation of $[(\text{arene})\text{RuCl}_2(\text{dpm})]$, **1**, in which the dpm was believed to be monodentate.²⁰ In the course of an investigation of the chemistry of $[(\text{arene})\text{RuCl}_2\text{L}]$ complexes in the formation of mixed metal clusters it was found that $[(\text{arene})\text{RuCl}_2\text{dpm}]$ will further react with $[(\text{arene})\text{RuCl}_2]_2$ to yield $[(\text{arene})\text{RuCl}_2\text{dpmCl}_2\text{Ru}(\text{arene})]$, **2**.¹⁵



The reaction of $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ with dpm in refluxing benzene or heptane, in the molar ratio 1:2, leads as shown above to the formation of two products. The major product is the monodentate dpm complex **1**. However, a variable amount (5–15%) of the complex *trans*- $\text{RuCl}_2\text{dpm}_2$, **3**, is also formed, resulting from the displacement of the arene ring by dpm. The structure of **3** has been determined by Cotton and coworkers²¹ showing the 2 Cl atoms to be *trans*. Complex **1** will react further with $[(p\text{-CH}_3\text{C}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ under the same conditions to yield the singly bridged complex **2**.



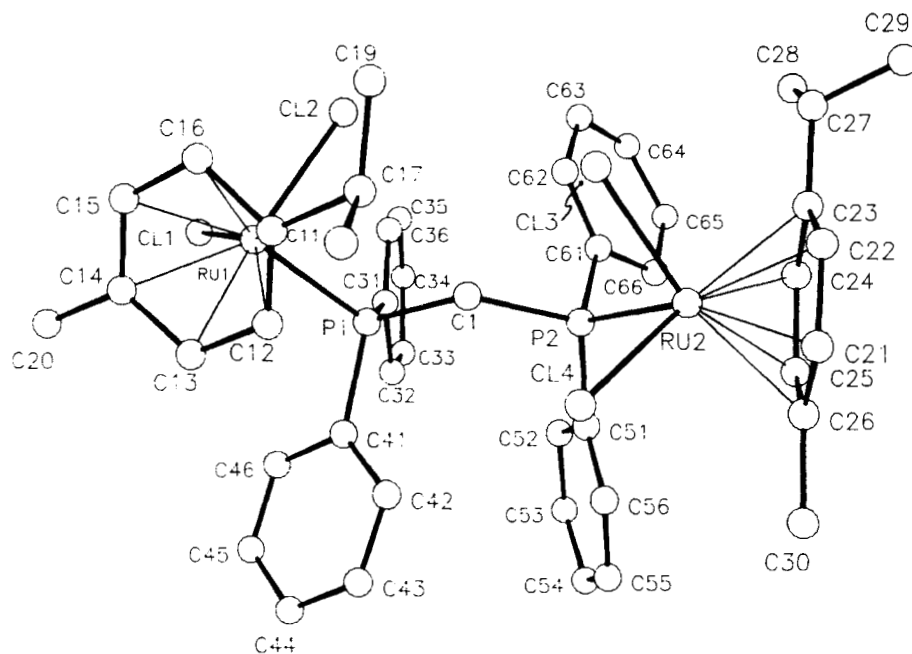


FIGURE 1 Molecular structure of $[\eta^6\text{-}(p\text{-CH}_3\text{C}_6\text{H}_4)\text{PrRuCl}_2 \cdot \text{dpm}]$, **1**.

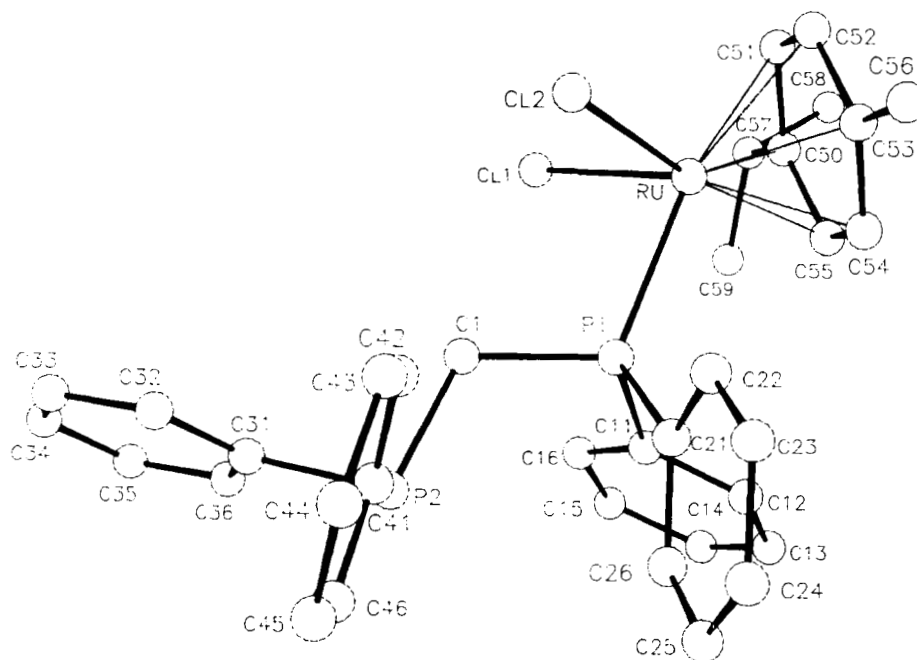


FIGURE 2 Molecular structure of $[\eta^6\text{-}(p\text{-CH}_3\text{C}_6\text{H}_4)\text{PrRuCl}_2]_2\text{dpm}$, **2**.

For complex **1** the ^{31}P nmr spectrum consists of two doublets ($^3J_{\text{PP}}$ 31.7 Hz) centered at 25.47 and -28.03 ppm, relative to H_3PO_4 , which is in agreement with ^{31}P nmr measurements obtained for similar monodentate complexes.⁵ Whilst crystal structures of complexes containing monodentate dpm ligands have been obtained, the crystal structure of **1** is only the second structural example of a complex containing dpm ligands coordinating only in a monodentate mode. The structure of **1** is shown in Figure 1, with a pseudo-octahedral arrangement about the Ru atom and the non-coordinating P atom directed away from the central metal atom. Structurally, monodentate dpm complexes are of two types: type *A* in which there is a relatively short non-bonding distance between the metal atom and the uncoordinated P atom,⁶ and type *B* in which the uncoordinated P atom has no interaction with the metal atom.⁷ Complex **1** is of type *B*. The P-C-P angle of 116.8° (Table IV) is similar to that of 116° found in the type *B* complex $[\text{MoCl}_2(\text{CO})_2(\text{dpm})_2]$ ⁷ as opposed to that of 111.7° in the type *A* complex $[\text{Pd}(t\text{-C}_4\text{H}_9\text{NC})_2(\text{dpm})_2]^{2+}$.⁶ As a result of this wider angle, the non-bonding P...P distance, 3.14 Å, is longer than the value of 3.05 Å found in the Pd complex. The metal-arene carbon bond distance of 2.22 Å (av) is similar to that found in other η^6 -arene Ru complexes (2.25 Å).²²

TABLE IV
Selected Bond Lengths (Å) and Angles ($^\circ$) for **1**.

| Atoms | | Distance | Atoms | | Distance |
|-------|---------|----------|-------|---------|----------|
| Ru | - Cl(1) | 2.414(1) | Ru | - Cl(2) | 2.421(1) |
| Ru | - P(1) | 2.357(1) | Ru | - C(50) | 2.230(4) |
| Ru | - C(51) | 2.255(5) | Ru | - C(52) | 2.234(5) |
| Ru | - C(53) | 2.211(5) | Ru | - C(54) | 2.167(4) |
| Ru | - C(55) | 2.198(4) | Cl(3) | - C(2) | 1.706(7) |
| Cl(4) | - C(2) | 1.747(8) | P(1) | - C(1) | 1.832(5) |
| P(1) | - C(11) | 1.826(5) | P(1) | - C(2i) | 1.820(5) |
| P(2) | - C(1) | 1.852(5) | P(2) | - C(31) | 1.830(5) |
| P(2) | - C(41) | 1.834(5) | C(11) | - C(12) | 1.399(7) |
| C(11) | - C(16) | 1.378(7) | C(12) | - C(13) | 1.379(7) |
| C(13) | - C(14) | 1.361(8) | C(14) | - C(15) | 1.377(9) |
| C(15) | - C(16) | 1.400(8) | C(21) | - C(22) | 1.402(7) |
| C(21) | - C(26) | 1.407(7) | C(22) | - C(23) | 1.385(7) |
| C(23) | - C(24) | 1.39(1) | C(24) | - C(25) | 1.368(9) |
| C(25) | - C(26) | 1.398(8) | C(31) | - C(32) | 1.366(7) |
| C(31) | - C(36) | 1.381(7) | C(32) | - C(33) | 1.383(8) |
| C(33) | - C(34) | 1.359(8) | C(34) | - C(35) | 1.349(8) |
| C(35) | - C(36) | 1.382(8) | C(41) | - C(42) | 1.390(7) |
| C(41) | - C(46) | 1.393(7) | C(42) | - C(43) | 1.373(7) |
| C(43) | - C(44) | 1.397(9) | C(44) | - C(45) | 1.360(9) |
| C(45) | - C(46) | 1.380(7) | C(50) | - C(51) | 1.437(6) |
| C(50) | - C(55) | 1.404(6) | C(50) | - C(57) | 1.510(6) |
| C(51) | - C(52) | 1.382(7) | C(52) | - C(53) | 1.413(7) |
| C(53) | - C(54) | 1.418(7) | C(53) | - C(56) | 1.500(7) |
| C(54) | - C(55) | 1.411(6) | C(57) | - C(58) | 1.527(8) |
| C(57) | - C(59) | 1.560(8) | | | |

| Atoms | | | Angle | Atoms | | | Angle |
|-------|--------|---------|----------|-------|--------|---------|----------|
| Cl(1) | - Ru | - Cl(2) | 89.02(4) | Cl(1) | - Ru | - P(1) | 84.27(4) |
| Cl(2) | - Ru | - P(1) | 86.61(4) | Ru | - P(1) | - C(1) | 112.8(2) |
| Ru | - P(1) | - C(11) | 110.8(2) | C(1) | - P(1) | - C(11) | 106.9(2) |
| Ru | - P(1) | - C(21) | 117.7(2) | C(1) | - P(1) | - C(21) | 104.2(2) |
| C(11) | - P(1) | - C(21) | 103.6(2) | C(1) | - P(2) | - C(31) | 99.4(2) |
| C(1) | - P(2) | - C(41) | 104.7(2) | C(31) | - P(2) | - C(41) | 101.5(2) |
| P(1) | - C(1) | - P(2) | 116.8(2) | Cl(3) | - C(2) | - Cl(4) | 110.8(4) |

Complex **2** is the second example of a noncarbonyl dinuclear ruthenium complex of dpm, and is the first structural example of a dpm ligand bridging two metal centers in which there are neither other bridging ligands nor direct bonds connecting the two metal atoms. This form of coordination for dpm is rare, being represented by only two other examples, $\{[\text{Fe}(\text{CO})_4]_2\text{dpm}\}^3$ and $\{[(\text{bipy})_2\text{ClRu}]_2\text{dpm}\}^{3+}$.

The structure of **2**, as shown in Figure 2, contains two Ru atoms symmetrically bridged by the dpm ligand (in agreement with the ^{31}P nmr spectrum of **2** which consists of a singlet at 23.81 ppm). The geometry about the Ru atoms is pseudo-octahedral with the two arene groups twisted away from each other to minimize steric interactions. The Ru-C_{arene} average distance is 2.23 Å (Table V). The two Ru atoms are coordinated to the dpm ligand in a *cis* type arrangement, although in contrast to other bridging dpm ligand complexes the central methylene group is bent towards the metal centers, again minimizing steric interactions in the complex.

The P...P non-bonding distance of 3.35 Å is long, with a P-C-P angle of 129° which is consistent with an opening of the dpm ligand from the monodentate coordination mode in order to minimize non-bonding atom contacts. Whilst the non-bonding Ru...Ru of 6.53 Å is extremely long, implying no direct metal-metal interaction, in the reaction of **2** with $\text{Fe}_2(\text{CO})_9$ only mixed-metal clusters containing Ru-Ru bonded species are formed suggesting that some form of co-operative reactivity exists for the Ru atoms in complex **2**.¹⁵

ACKNOWLEDGEMENTS

We thank the National Science Foundation for support of this work.

TABLE V
Selected Bond Lengths (Å) and Angles (°) for **2**.

| Atoms | Distance | Atoms | Distance |
|---------------|----------|---------------|----------|
| Ru(1) - Cl(1) | 2.413(7) | Ru(1) - Cl(2) | 2.423(8) |
| Ru(1) - P(1) | 2.368(7) | Ru(1) - C(11) | 2.25(3) |
| Ru(1) - C(12) | 2.19(3) | Ru(1) - C(13) | 2.20(2) |
| Ru(1) - C(14) | 2.20(3) | Ru(1) - C(15) | 2.24(2) |
| Ru(1) - C(16) | 2.29(3) | Ru(2) - Cl(3) | 2.407(7) |
| Ru(2) - Cl(4) | 2.425(8) | Ru(2) - P(2) | 2.361(7) |
| Ru(2) - C(21) | 2.22(2) | Ru(2) - C(22) | 2.25(3) |
| Ru(2) - C(23) | 2.25(3) | Ru(2) - C(24) | 2.17(3) |
| Ru(2) - C(25) | 2.18(3) | Ru(2) - C(26) | 2.26(3) |
| Cl(5) - C(2) | 1.81(5) | Cl(6) - C(2) | 1.78(5) |
| P(1) - C(1) | 1.86(2) | P(1) - C(31) | 1.85(2) |
| P(1) - C(41) | 1.77(3) | P(2) - C(1) | 1.86(2) |
| P(2) - C(51) | 1.79(2) | P(2) - C(61) | 1.81(2) |

| Atoms | Angle | Atoms | Angle |
|-----------------------|----------|-----------------------|----------|
| Cl(1) - Ru(1) - Cl(2) | 90.2(3) | Cl(1) - Ru(1) - P(1) | 86.1(2) |
| Cl(2) - Ru(1) - P(1) | 86.9(3) | Cl(3) - Ru(2) - Cl(4) | 89.0(3) |
| Cl(3) - Ru(2) - P(2) | 86.5(3) | Cl(4) - Ru(2) - P(2) | 85.2(2) |
| Ru(1) - P(1) - C(1) | 103.2(8) | Ru(1) - P(1) - C(31) | 118.8(8) |
| C(1) - P(1) - C(31) | 109(1) | Ru(1) - P(1) - C(41) | 109.3(9) |
| C(1) - P(1) - C(41) | 110(1) | C(31) - P(1) - C(41) | 106(1) |
| Ru(2) - P(2) - C(1) | 109.5(7) | Ru(2) - P(2) - C(51) | 113.9(8) |
| C(1) - P(2) - C(51) | 112(1) | Ru(2) - P(2) - C(61) | 112.6(8) |
| C(1) - P(2) - C(61) | 103(1) | C(51) - P(2) - C(61) | 105(1) |
| P(1) - C(1) - P(2) | 129(1) | Cl(5) - C(2) - Cl(6) | 103(3) |

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