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Preparation of Binuclear Complexes Using 2-(Diphenylphosphino)pyridine as a Bridging Ligand. Synthesis of Some Ruthenium Complexes and Their Interaction with Palladium Complexes

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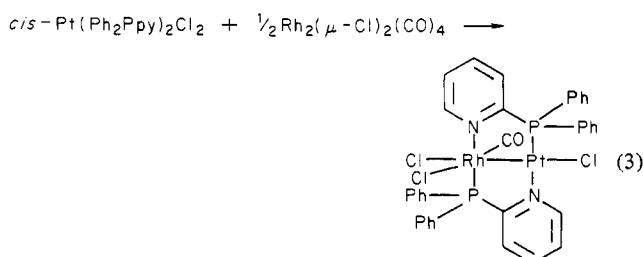
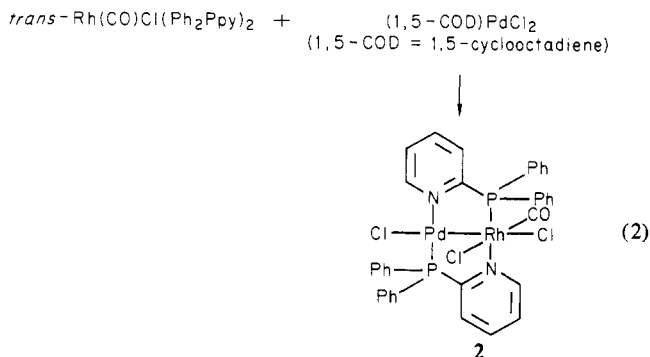
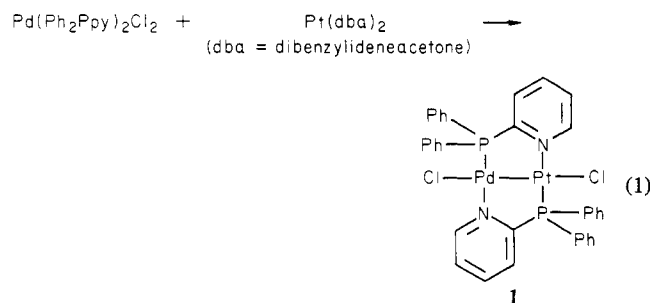
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The reactions between $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$ and $(1,5\text{-cyclooctadiene})\text{PdCl}_2$ and between $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dibenzylideneacetone})_3$ have been examined as routes to binuclear Ru/Pd complexes. The first reaction produces $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$, $\text{Ru}(\text{Ph}_2\text{Ppy})(\text{CO})_2\text{Cl}_2$, and two isomers of $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$, while the second forms predominantly the two binuclear products. Syntheses of $\text{Ru}_3(\text{CO})_9(\text{Ph}_2\text{Ppy})_3$, $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$, and $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ from $\text{Ru}_3(\text{CO})_{12}$ are reported as are the preparations of $\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ and $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$. All new compounds have been characterized by infrared spectroscopy and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The two isomers of $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ interconvert on heating in solution. The structure of one isomer has been determined unambiguously by X-ray crystallography. $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ crystallizes in the space group $P2_1/c$ with cell dimensions (determined at 140 K) of $a = 10.493$ (2) Å, $b = 17.685$ (4) Å, $c = 21.470$ (5) Å, $\beta = 92.07$ (2)°, $Z = 4$, and $V = 3982$ (1) Å³. The structure was refined by blocked cascade least-squares to a conventional R value of 0.043 by using 4605 significant reflections. The compound possesses a Pd-Ru bond with a distance of 2.660 (1) Å. The palladium atom is four-coordinate with a Ru, Cl, P, N donor set, while the ruthenium atom is six-coordinate with a Pd, Cl, P, N, C₂ donor set.

Introduction

The ligand 2-(diphenylphosphino)pyridine (Ph_2Ppy) has been used to prepare bridged heterobinuclear transition-metal complexes in high yield.¹⁻⁴ The basic reaction pattern we have employed has involved sequential binding of the ligand to the first metal by the phosphorus atom followed by complexation to the second metal atom. Some representative reactions that demonstrate the second step are given in eq 1-3.

Here we report our results on using Ph_2Ppy to form some ruthenium complexes. We undertook this work for two reasons. Although there has been extensive study of binuclear, phosphine-bridged complexes of many of the group 8 elements,⁵⁻¹² little has been done with either ruthenium or osmium. For example, bis(diphenylphosphino)methane forms a host of well-characterized binuclear complexes with platinum, palladium, nickel, iridium, rhodium, cobalt, and iron, but with ruthenium its only known compounds are trinuclear substitution products of $\text{Ru}_3(\text{CO})_{12}$ ¹³⁻¹⁵ and chelated ruthenium(II) complexes.¹⁶ Secondly, complexes of ruthenium in its lower oxidation states tend to be coordinatively saturated. We know that this would inhibit access to the metal, and hence



it would slow down the reactions analogous to those given in eq 1-3. Thus it remained to be seen whether any binuclear complexes could be assembled in this fashion.

Results and Discussion

Synthesis of Monomeric Ruthenium Complexes. The syntheses of a variety of ruthenium complexes of Ph_2Ppy are summarized in Scheme I. Beginning with $\text{Ru}_3(\text{CO})_{12}$, we have obtained the monomers $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$, $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$, and $\text{Ru}(\text{Ph}_2\text{Ppy})(\text{CO})_2\text{Cl}_2$, as well as trinuclear

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Scheme 1

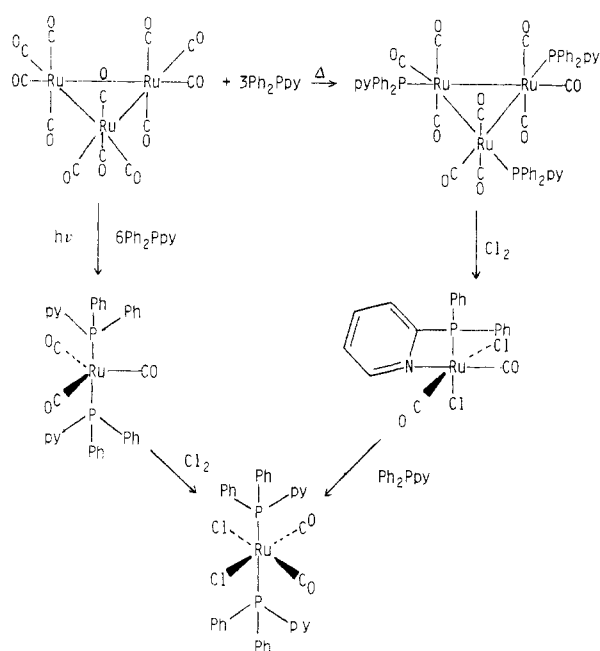


Table I. Spectroscopic Parameters for Ruthenium and Palladium Compounds

compd	³¹ P { ¹ H} NMR, ^a	
	δ (J, Hz)	ν(C≡O), ^a cm ⁻¹
Ru ₃ (CO) ₉ (Ph ₂ Ppy) ₃	37.7	2045 vw, 1975 vs
Ru ₃ (CO) ₉ (PPh ₃) ₃		2044 vs, 1978 sh, 1967 s, br
Ru(Ph ₂ Ppy) ₂ (CO) ₃	57.8	1895 vs
Ru(PPh ₃) ₂ (CO) ₃	55.7	1895 vs
Ru(Ph ₂ Ppy)(CO) ₂ Cl ₂	-6.8	2067 vs, 2007 vs
Ru(Ph ₂ Ppy) ₂ (CO) ₂ Cl ₂	21.5	2062 vs, 2001 vs
Ru(PPh ₃) ₂ (CO) ₂ Cl ₂	17.8	2058 vs, 1996 vs
Pd(Ph ₂ Ppy) ₂ Cl ₂	23.8, 29.3 ^b	none
Pd ₂ (Ph ₂ Ppy) ₂ Cl ₂	4.4	none
RuPd(Ph ₂ Ppy) ₂ (CO) ₂ Cl ₂ , D	38.9 d (7.5), 17.9 d (7.5)	2013 vs, 1954 vs
RuPd(Ph ₂ Ppy) ₂ (CO) ₂ Cl ₂ , E	20.1 d (2), 16.5 d (2)	2025 vs, 1965 vs

^a In dichloromethane solution. ^b Two singlets with an intensity ratio of 1:1.9 are observed. These are believed to arise from the presence of cis and trans isomers.

Ru₃(Ph₂Ppy)₃(CO)₉. Analogues of all of these, with the exception of Ru(Ph₂Ppy)(CO)₂Cl₂, have been made earlier with triphenylphosphine. Our synthetic procedures have been based upon the routes developed to the triphenylphosphine analogues.¹⁷⁻²⁰ The ³¹P{¹H} NMR and infrared spectroscopic data in Table I reveal very close similarities between the two series of materials. Consequently the structures of the two series of compounds can be taken to be similar, and our structural assignments follow those previously made for the triphenylphosphine analogues.

The one unique compound is Ru(Ph₂Ppy)(CO)₂Cl₂. This has no triphenylphosphine analogue because the phosphine ligand here is bonding as a chelate rather than as a monodentate ligand. The geometric details of its structure have been determined from an X-ray crystallographic study that verifies

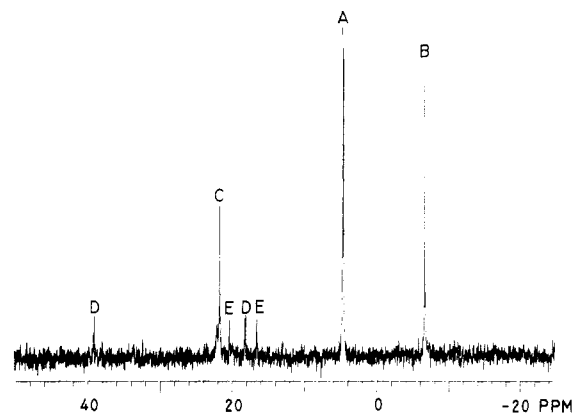


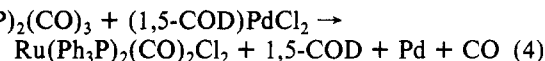
Figure 1. ³¹P{¹H} NMR spectrum of a dichloromethane solution prepared from a 1:1 molar ratio of Ru(Ph₂Ppy)₂(CO)₃ and (1,5-COD)PdCl₂. Compounds present have been identified as follows: A, Pd₂(Ph₂Ppy)₂Cl₂; B, Ru(Ph₂Ppy)(CO)₂Cl₂; C, Ru(Ph₂Ppy)₂(CO)₂Cl₂; D and E, isomers of RuPd(Ph₂Ppy)₂(CO)₂Cl₂.

the presence of the somewhat strained four-membered chelate ring.²¹ This chelated complex is most readily synthesized by the chlorination of Ru₃(CO)₉(Ph₂Ppy)₃ as reported earlier.²¹

Reaction between Ru(Ph₂Ppy)₂(CO)₃ and (1,5-COD)PdCl₂. The first attempt to construct a heterobinuclear or Ru/Pd complex involved the interaction of Ru(Ph₂Ppy)₂(CO)₃ and (1,5-COD)PdCl₂. We felt this would be analogous to the reaction between Rh(Ph₂Ppy)₂(CO)Cl and (1,5-COD)PdCl₂, which produced RhPd(Ph₂Ppy)₂(CO)Cl₃, eq 2. The ³¹P{¹H} NMR spectrum of the products of the reaction in dichloromethane recorded after a reaction time of 5 min is shown in Figure 1. At least five species, labeled A-E, are present in the deep red-brown solution. Three of these produce singlets in the spectrum while the other two give rise to pairs of doublets with small coupling constants (D, 7.5 Hz; E, 2 Hz), which can only be ascribed to phosphorus-phosphorus coupling.

By a process of fractional crystallization and independent synthesis it has been possible to identify the products as follows: A, Pd₂(Ph₂Ppy)₂Cl₂; B, Ru(PPh₂Ppy)(CO)₂Cl₂; C, Ru(Ph₂Ppy)₂(CO)₂Cl₂; D and E, isomers of composition RuPd(Ph₂Ppy)₂(CO)₂Cl₂. They are formed in the following yields (%): A, 38; B, 31; C, 16; D, 8; E, 7. The identification of these components is described in succeeding sections.

Reaction of Ru(Ph₃P)₂(CO)₃ with (1,5-COD)PdCl₂. This reaction was run for comparison with the previous reaction under identical conditions. The reaction rapidly produced a black precipitate of palladium metal, which was removed by filtration. Analysis of the remaining solution by ³¹P{¹H} NMR spectroscopy and by infrared spectroscopy showed that Ru(PPh₃)₂(CO)₂Cl₂ had formed in 78% yield. Thus the predominant reaction is as given in eq 4. As a result of this

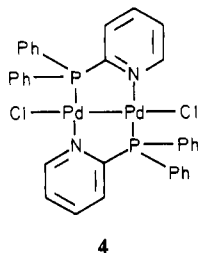


comparison, we can ascribe the formation of Ru(Ph₂Ppy)₂(CO)₂Cl₂ in the preceding section to a natural redox process between Ru(0) and Pd(II), which does not require the presence of the bifunctional phosphinopyridine ligand.

Formation and Attempted Formation of Homobinuclear Compounds. Compound A, the species responsible for the red-brown color that develops when Ru(Ph₂Ppy)₂(CO)₃ reacts with (1,5-COD)PdCl₂, was found to be the Pd(I) complex Pd₂(Ph₂Ppy)₂Cl₂ (4). This species is isoelectronic with the well-studied Pd₂(dpm)₂Cl₂ but lacks the reactivity associated

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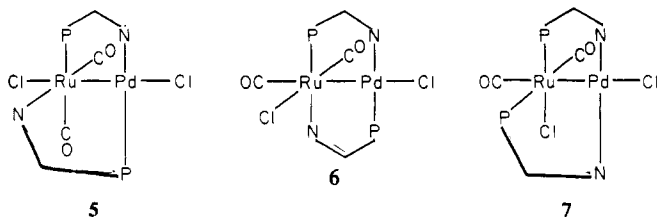


with the Pd-Pd bond of the latter complex.²² Pd₂(Ph₂Ppy)₂Cl₂ has been independently prepared by the comproportionation reaction between Pd(II) and Pd(0) compounds, which is a generally useful method for the preparation of dimeric Pd(I) complexes.^{22,23} Thus treatment of Pd(Ph₂Ppy)₂Cl₂, which was made from (PhCN)₂PdCl₂ and Ph₂Ppy, with Pd₂(dba)₃ in dichloromethane solution produces Pd₂(Ph₂Ppy)₂Cl₂ in 90% yield. While the spectroscopic data do not distinguish between head-to-tail and head-to-head orientations of the Ph₂Ppy ligands, the head-to-tail structure, **4**, is more likely since the heteronuclear PtPd(Ph₂Ppy)₂Cl₂ has been shown to have this structure.³

Because of the facile formation of a number of homonuclear dimers (including dimers of Pd(I), Pt(I), and Rh(II)) by this type of comproportionation reaction,²²⁻²⁶ comproportionation reactions between Ru(0) and Ru(II) compounds were examined. No reaction occurs in mixtures of Ru(Ph₂Ppy)₂(CO)₃ and Ru(Ph₂Ppy)₂(CO)₂Cl₂ or of Ru(Ph₃P)₂(CO)₃ and Ru-(Ph₃P)₂(CO)₂Cl₂ in dichloromethane solution after 2 days, a much longer time than required for any of the other reactions reported here.

Reaction between Ru(Ph₂Ppy)₂(CO)₂Cl₂ and Pd(0). By reversing the oxidation states of ruthenium and palladium in the reaction between their complexes, it is possible to alter the product distribution so that the binuclear complexes become the predominant products. Thus the reaction between Ru-(Ph₂Ppy)₂(CO)₂Cl₂ and the palladium(0) olefin complex Pd₂(dba)₃²⁷ yields the same compounds, D and E, as formed from the reaction of Ru(Ph₂Ppy)₂(CO)₃ with (1,5-COD)PdCl₂. These two compounds may be separated by either fractional crystallization or chromatography on silica gel.

Compounds D and E are isomers of composition RuPd-(Ph₂Ppy)₂(CO)₂Cl₂. Both compounds have similar infrared spectra and therefore similar structural elements. The infrared spectrum of each isomer is consistent with the presence of two cis-carbonyl groups. The ³¹P{¹H} NMR spectra of D and E indicate that in each there are two inequivalent phosphine ligands. These cannot lie trans to one another and be bonded to the same metal. This condition would produce P-P coupling constants much larger than the observed values. Consequently compounds D and E may have any of the isomeric structures **5-7**, if both phosphine ligands are bridging. If only one



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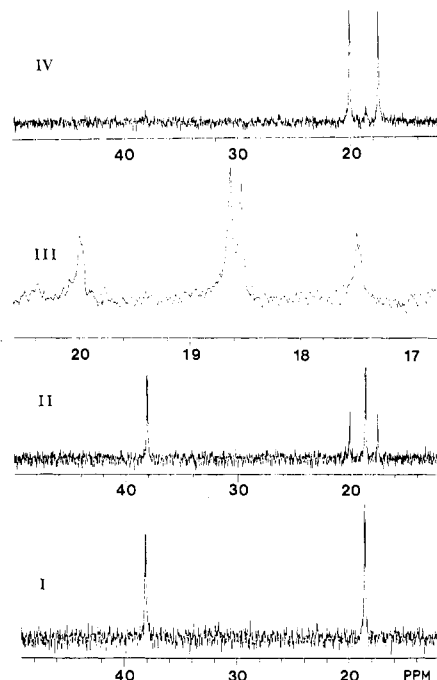


Figure 2. ³¹P{¹H} NMR (chloroform solutions): (I) spectrum of RuPd(Ppy)₂(CO)₂Cl₂, isomer D; (II) spectrum of the same solution as shown in part I after heating to 60 °C for 20 min, showing isomerization D → E; (III) expanded version of part of spectrum II, showing the doublet nature of the spectrum of E; (IV) spectrum of RuPd(Ph₂Ppy)₂(CO)₂Cl₂, isomer E.

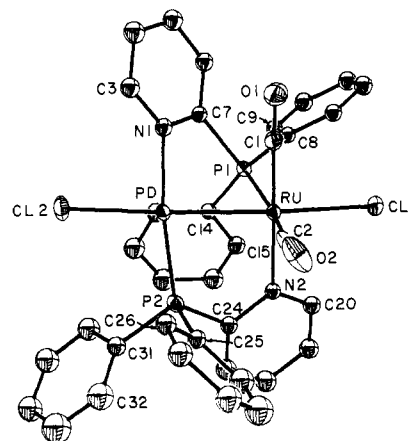


Figure 3. Perspective drawing of the molecular structure of RuPd-(Ph₂Ppy)₂(CO)₂Cl₂, isomer E.

phosphine ligand is bridging, there are 13 other structures that are consistent with the data (with the constraint of a cis Ru-(CO)₂ unit), but we feel this situation is much less likely.

The isomeric compounds D and E can be interconverted thermally. This is shown in Figure 2, which presents in traces I and IV the spectra of D and E, respectively. When a sample of D is heated in chloroform solution to 60 °C, it isomerizes partially to E as shown in trace II. Similarly pure E is converted into a mixture of D and E upon heating. Since this is a reversible conversion (regardless of whether we start with D or E the same mixture results), the equilibrium constant for reaction 5 can be estimated. From integration of the ³¹P NMR spectra, K_{eq} is 2.5 for reaction 5 in chloroform solution.



Crystal and Molecular Structure of E, RuPd(Ph₂Ppy)₂(CO)₂Cl₂. So that the details of the structure of the two binuclear isomers D and E could be determined, attempts were made to obtain suitable samples for X-ray crystallography.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$

atom	x	y	z	U
Ru	3808.0 (4)	-72.2 (3)	1859.9 (2)	14.3 (2) ^a
Pd	2417.4 (4)	1185.6 (3)	1841.0 (2)	16.0 (2) ^a
Cl(1)	5015 (2)	-1271.4 (9)	1793.4 (7)	22.8 (5) ^a
Cl(2)	1345 (2)	2400.9 (9)	1814.8 (8)	32.6 (6) ^a
Cl(3)	5326 (2)	2281 (1)	1777 (1)	51.2 (7) ^a
Cl(4)	4906 (3)	3539 (1)	938 (1)	72 (1) ^a
P(1)	2198 (2)	-265.9 (9)	1055.6 (7)	16.4 (5) ^a
P(2)	2188 (2)	894.6 (9)	2822.2 (8)	18.5 (5) ^a
N(1)	2497 (5)	1219 (3)	853 (2)	19 (1)
N(2)	2591 (5)	-566 (3)	2553 (2)	17 (1)
O(1)	5462 (4)	598 (3)	893 (2)	35 (2) ^a
O(2)	5924 (5)	513 (3)	2724 (3)	47 (2) ^a
C(1)	4803 (6)	351 (4)	1263 (3)	21 (2) ^a
C(2)	5075 (6)	290 (4)	2446 (3)	26 (2) ^a
C(3)	2719 (6)	1846 (4)	533 (3)	23 (1)
C(4)	2855 (6)	1843 (4)	-106 (3)	29 (2)
C(5)	2734 (6)	1172 (4)	-427 (3)	27 (2)
C(6)	2432 (6)	515 (4)	-104 (3)	22 (1)
C(7)	2329 (6)	559 (3)	543 (3)	17 (1)
C(8)	2237 (6)	-1052 (3)	499 (3)	18 (1)
C(9)	1141 (6)	-1293 (4)	175 (3)	21 (1)
C(10)	1214 (6)	-1843 (4)	-272 (3)	26 (2)
C(11)	2384 (6)	-2163 (4)	-401 (3)	26 (2)
C(12)	3465 (6)	-1930 (4)	-86 (3)	25 (2)
C(13)	3405 (6)	-1370 (4)	365 (3)	20 (1)
C(14)	570 (6)	-299 (4)	1324 (3)	18 (1)
C(15)	178 (6)	-964 (4)	1602 (3)	23 (1)
C(16)	-996 (7)	-1009 (4)	1878 (3)	31 (2)
C(17)	-1778 (7)	-385 (4)	1865 (3)	37 (2)
C(18)	-1427 (7)	269 (4)	1583 (3)	34 (2)
C(19)	-236 (6)	323 (4)	1310 (3)	25 (2)
C(20)	2452 (6)	-1326 (4)	2613 (3)	21 (1)
C(21)	1616 (6)	-1643 (4)	3006 (3)	27 (2)
C(22)	851 (7)	-1181 (4)	3360 (3)	31 (2)
C(23)	1002 (7)	-413 (4)	3308 (3)	29 (2)
C(24)	1863 (6)	-120 (4)	2916 (3)	19 (1)
C(25)	3487 (6)	1060 (4)	3393 (3)	18 (1)
C(26)	4093 (6)	1759 (4)	3384 (3)	22 (1)
C(27)	5057 (6)	1913 (4)	3811 (3)	28 (2)
C(28)	5461 (7)	1384 (4)	4244 (3)	33 (2)
C(29)	4866 (7)	682 (5)	4241 (4)	42 (2)
C(30)	3868 (7)	522 (4)	3826 (3)	34 (2)
C(31)	835 (6)	1335 (4)	3201 (3)	21 (1)
C(32)	933 (8)	1605 (4)	3797 (4)	42 (2)
C(33)	-107 (8)	1928 (5)	4077 (4)	53 (2)
C(34)	-1251 (7)	1989 (4)	3759 (4)	39 (2)
C(35)	-1369 (7)	1708 (4)	3158 (4)	38 (2)
C(36)	-327 (7)	1387 (4)	2872 (3)	33 (2)
C(37)	4550 (8)	3151 (5)	1669 (4)	47 (3) ^a
C(38)	-1871 (30)	-18 (17)	4429 (15)	38 (7)
Cl(5)	-1939 (7)	526 (4)	5106 (3)	36 (2)
Cl(6)	-1687 (9)	-847 (6)	4426 (4)	59 (2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensor.

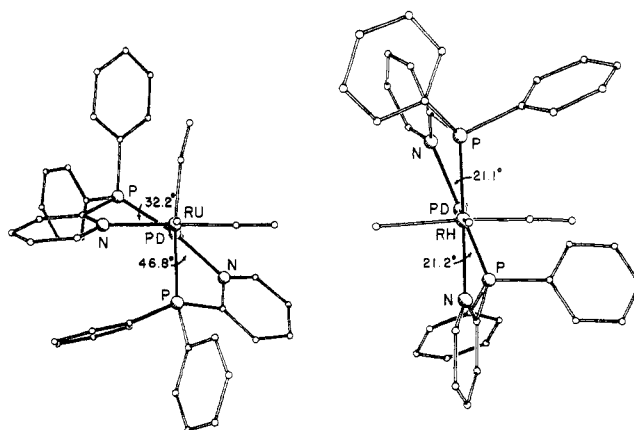
Only compound E gave satisfactory results. Attempts to crystallize D slowly always produced crystals of E along with unsuitable crystals of D.

$\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$, isomer E, crystallizes with one molecule in the asymmetric unit. A perspective drawing with the atom numbering scheme is given in Figure 3. A stereoscopic view of the molecule is shown in Figure 4 (supplementary material). As can be seen from these views, the molecule possesses no symmetry and corresponds to isomeric structure 5. Atomic coordinates and temperature factors are given in Table II. Selected interatomic distances and angles are presented in Tables III and IV.

The palladium atom is four-coordinate with nearly planar coordination while the ruthenium is six-coordinate. The two metal atoms are joined by a metal-metal bond whose length (2.660 (1) Å) is consistent with the presence of a Ru-Pd single bond. In electron-counting terms the ruthenium may be

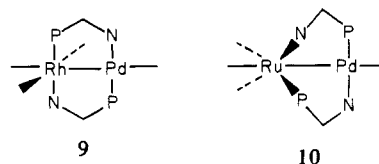
Table III. Bond Lengths (Å) in $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$

Ru-Pd	2.660 (1)	Ru-Cl(1)	2.477 (2)
Ru-P(1)	2.396 (2)	Ru-N(2)	2.178 (5)
Ru-C(1)	1.841 (7)	Ru-C(2)	1.908 (7)
Pd-Cl(2)	2.426 (2)	Pd-P(2)	2.190 (2)
Pd-N(1)	2.126 (5)	Cl(3)-C(37)	1.753 (9)
Cl(4)-C(37)	1.764 (8)	P(1)-C(7)	1.836 (6)
P(1)-C(8)	1.834 (6)	P(1)-C(14)	1.824 (6)
P(2)-C(24)	1.838 (6)	P(2)-C(25)	1.824 (6)
P(2)-C(31)	1.835 (7)	N(1)-C(3)	1.330 (8)
N(1)-C(7)	1.353 (8)	N(2)-C(20)	1.357 (8)
N(2)-C(24)	1.364 (8)	O(1)-C(1)	1.157 (8)
O(2)-C(2)	1.127 (9)	C(3)-C(4)	1.383 (9)
C(4)-C(5)	1.38 (1)	C(5)-C(6)	1.397 (9)
C(6)-C(7)	1.398 (9)	C(8)-C(9)	1.390 (9)
C(8)-C(13)	1.388 (9)	C(9)-C(10)	1.371 (9)
C(10)-C(11)	1.389 (9)	C(11)-C(12)	1.364 (9)
C(12)-C(13)	1.387 (9)	C(14)-C(15)	1.387 (9)
C(14)-C(19)	1.388 (9)	C(15)-C(16)	1.39 (1)
C(16)-C(17)	1.37 (1)	C(17)-C(18)	1.36 (1)
C(18)-C(19)	1.40 (1)	C(20)-C(21)	1.361 (9)
C(21)-C(22)	1.39 (1)	C(22)-C(23)	1.37 (1)
C(23)-C(24)	1.360 (9)	C(25)-C(26)	1.390 (9)
C(25)-C(30)	1.379 (9)	C(26)-C(27)	1.367 (9)
C(27)-C(28)	1.37 (1)	C(28)-C(29)	1.39 (1)
C(29)-C(30)	1.38 (1)	C(31)-C(32)	1.37 (1)
C(31)-C(36)	1.390 (9)	C(32)-C(33)	1.39 (1)
C(33)-C(34)	1.36 (1)	C(34)-C(35)	1.38 (1)
C(35)-C(36)	1.39 (1)	C(38)-Cl(5)	1.75 (3)
C(38)-Cl(6)	1.48 (3)		

**Figure 5.** Projections down the Cl-Ru and Cl-Rh bonds of $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ and $\text{RhPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$ showing the N-M-P dihedral angles.

considered as Ru(I) and the palladium as Pd(I), with the ruthenium atom being a coordinatively saturated, 18-electron center while the palladium is a coordinatively unsaturated, 16-electron center.

The structure of $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ may be compared to that of $\text{RhPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$ (12).¹ The latter contains a four-coordinate, planar palladium atom and a six-coordinate rhodium atom. The two are joined by a Rh-Pd single bond. The metal-metal bond lengths in the two complexes are similar: Ru-Pd, 2.660 (1) Å; Rh-Pd, 2.594 (1) Å. A major difference between the two involves the relative orientation of the two bridging diphosphine ligands. In $\text{RhPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$ these adopt a head-to-tail arrangement and lie trans to one another on each metal as shown in 9. This



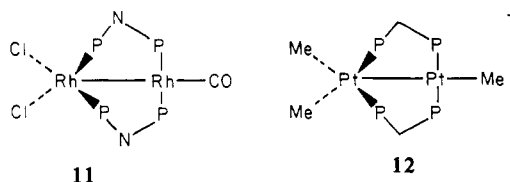
is the most common geometric orientation that is found for

Table IV. Bond Angles (Deg) in RuPd(Ph₂Ppy)₂(CO)₂Cl₂

Pd-Ru-Cl(1)	175.3 (1)	Pd-Ru-P(1)	74.7 (1)
Cl(1)-Ru-P(1)	100.6 (1)	Pd-Ru-N(2)	90.6 (1)
Cl(1)-Ru-N(2)	90.5 (1)	P(1)-Ru-N(2)	91.1 (1)
Pd-Ru-C(1)	88.5 (2)	Cl(1)-Ru-C(1)	90.2 (2)
P(1)-Ru-C(1)	87.7 (2)	N(2)-Ru-C(1)	178.7 (2)
Pd-Ru-C(2)	95.6 (2)	Cl(1)-Ru-C(2)	88.9 (2)
P(1)-Ru-C(2)	168.4 (2)	N(2)-Ru-C(2)	95.5 (2)
C(1)-Ru-C(2)	85.6 (3)	Ru-Pd-Cl(2)	174.3 (1)
Ru-Pd-P(2)	82.4 (1)	Cl(2)-Pd-P(2)	99.4 (1)
Ru-Pd-N(1)	89.8 (1)	Cl(2)-Pd-N(1)	89.3 (1)
P(2)-Pd-N(1)	167.3 (1)	Ru-P(1)-C(7)	104.6 (2)
Ru-P(1)-C(8)	123.1 (2)	C(7)-P(1)-C(8)	101.9 (3)
Ru-P(1)-C(14)	114.9 (2)	C(7)-P(1)-C(14)	107.9 (3)
C(8)-P(1)-C(14)	103.0 (3)	Pd-P(2)-C(24)	111.2 (2)
Pd-P(2)-C(25)	120.2 (2)	C(24)-P(2)-C(25)	102.7 (3)
Pd-P(2)-C(31)	116.1 (2)	C(24)-P(2)-C(31)	102.5 (3)
C(25)-P(2)-C(31)	101.9 (3)	Pd-N(1)-C(3)	123.6 (4)
Pd-N(1)-C(7)	117.3 (4)	C(3)-N(1)-C(7)	119.1 (5)
Ru-N(2)-C(20)	122.0 (4)	Ru-N(2)-C(24)	120.8 (4)
C(20)-N(2)-C(24)	117.1 (5)	Ru-C(1)-O(1)	177.6 (6)
Ru-C(2)-O(2)	170.7 (6)	N(1)-C(3)-C(4)	122.5 (6)
C(3)-C(4)-C(5)	119.3 (6)	C(4)-C(5)-C(6)	119.2 (6)
C(5)-C(6)-C(7)	118.3 (6)	P(1)-C(7)-N(1)	113.6 (4)
P(1)-C(7)-C(6)	124.1 (5)	N(1)-C(7)-C(6)	121.6 (6)
P(1)-C(8)-C(9)	121.4 (6)	P(1)-C(8)-C(13)	118.9 (4)
C(9)-C(8)-C(13)	119.5 (6)	C(8)-C(9)-C(10)	120.1 (6)
C(9)-C(10)-C(11)	120.1 (6)	C(10)-C(11)-C(12)	120.2 (6)
C(11)-C(12)-C(13)	120.3 (6)	C(8)-C(13)-C(12)	119.8 (6)
C(1)-C(14)-C(15)	117.3 (5)	P(1)-C(14)-C(19)	123.0 (5)
C(15)-C(14)-C(19)	119.4 (6)	C(14)-C(14)-C(16)	121.0 (6)
C(15)-C(16)-C(17)	118.8 (7)	C(16)-C(17)-C(18)	121.4 (7)
C(17)-C(18)-C(19)	120.2 (7)	C(14)-C(19)-C(18)	119.3 (6)
N(2)-C(20)-C(21)	122.8 (6)	C(20)-C(21)-C(22)	119.6 (6)
C(21)-C(22)-C(23)	117.8 (7)	C(22)-C(23)-C(24)	120.6 (6)
P(2)-C(24)-N(2)	113.1 (4)	P(2)-C(24)-C(23)	124.8 (5)
N(2)-C(24)-C(23)	122.1 (6)	P(2)-C(25)-C(26)	117.7 (5)
P(2)-C(25)-C(30)	122.2 (5)	C(26)-C(25)-C(30)	120.1 (6)
C(25)-C(26)-C(27)	119.7 (6)	C(26)-C(27)-C(28)	121.4 (6)
C(27)-C(28)-C(29)	118.6 (7)	C(28)-C(29)-C(30)	121.0 (7)
C(25)-C(30)-C(29)	119.2 (7)	P(2)-C(31)-C(32)	122.0 (5)
P(2)-C(31)-C(36)	118.8 (5)	C(32)-C(31)-C(36)	119.2 (6)
C(31)-C(32)-C(33)	121.1 (7)	C(32)-C(33)-C(34)	120.5 (8)
C(33)-C(34)-C(35)	119.1 (8)	C(34)-C(35)-C(36)	120.7 (7)
C(31)-C(36)-C(35)	119.4 (7)	Cl(3)-C(37)-Cl(4)	110.3 (5)
Cl(5)-C(38)-Cl(6)	124 (2)		

binuclear complexes containing two bridging diphosphine ligands. In RuPd(Ph₂Ppy)₂(CO)₂Cl₂, however, while the ligands still have a head-to-tail arrangement and are trans to each other on the palladium atom, they are cis to each other at the ruthenium atom as shown in 10. Thus the PRhN angle in RhPd(Ph₂Ppy)₂(CO)Cl₃ is 178.1 (5)° while the PRuN angle in RuPd(Ph₂Ppy)₂(CO)₂Cl₂, isomer E, is 91.1 (1)°. Similarly the P-M-Pd-N dihedral angles differ. This is best appreciated by referring to Figure 5, which shows projections down the Cl-M-Pd-Cl unit of both structures. The P-Pd-N unit in the RuPd(Ph₂Ppy)₂(CO)₂Cl₂ complex is in a staggered orientation with respect to the Cartesian coordinates of the ruthenium atom and its ligands, while in RhPd(Ph₂Ppy)₂(CO)Cl₃ the P-Pd-N unit is halfway between an eclipsed and a staggered orientation relative to the rhodium atom and its ligands. Only two examples of bridging phosphine ligands adopting the sort of arrangement found in RuPd(Ph₂Ppy)₂(CO)₂Cl₂ are known. They are Rh₂[(Et₂O)₂PNEtP(OEt)₂]₂(CO)Cl₂ (11)²⁸ and [Pt₂(Ph₂PCH₂PPh₂)₂(CH₃)₃]⁺ (12).²⁹

The coordinations about the palladium atoms in RuPd(Ph₂Ppy)₂(CO)₂Cl₂ and RhPd(Ppy)₂(CO)Cl₃ are very similar as shown by their respective parameters: Pd-N, 2.126 (7),



2.13 (1) Å; Pd-Cl, 2.426 (2), 2.393 (4) Å; Pd-P, 2.190 (2), 2.220 (4) Å; P-Pd-Cl, 99.4 (1), 88.4 (1)°; N-Pd-Cl, 89.3 (1), 93.1 (3)°; N-Pd-M, 89.8 (1), 92.4 (3)°; P-Pd-M, 82.4 (1), 86.2 (1)°. The Pd-Cl distance of 2.426 (2) Å is at the long end of the range of known Pd-Cl distances (2.24–2.45 Å)³⁰ and probably reflects the high trans effect of the metal-metal bond.

The coordination about ruthenium is quite regular. Most of the bond angles between cis ligands lie close to the expected 90°. The greatest deviation involves the P(1)-Ru-Pd angle, which is 74.7 (1)°. The bond lengths about ruthenium fall within normal ranges and are similar to those reported for Ru(Ph₂Ppy)(CO)₂Cl₂.²¹ The difference in the two Ru-C distances reflects the greater trans effect of the phosphine ligand, which serves to lengthen the trans Ru-C bond. The Ru-Cl distance of 2.477 (2) Å, like the Pd-Cl distance, is at the long end of the range of known Ru-Cl distances (2.51–2.39 Å).³¹ This may reflect the high trans effect of the metal-metal bond.

With the structure of E (RuPd(Ph₂Ppy)₂(CO)₂Cl₂) known, the structure of isomer D is limited to 6 and 7, but we still feel that there are insufficient data available to distinguish between these two possibilities. The interconversion of structures 5 and 6 could be accomplished by a twist motion and does not require bond breaking. On the other hand, isomerization between 5 and 7 requires reorientation of one Ph₂Ppy ligand. Such a reaction, the conversion of head-to-head RhPd(Ph₂Ppy)₂(CNCH₃)₂Cl₂⁺ to the head-to-tail isomer, has been recently observed.³⁹ Regardless of the structure of E, it is clear that these binuclear complexes have considerable stability and remain intact through the isomerization.

Experimental Section

Preparation of Compounds. Triruthenium dodecacarbonyl was prepared according to the method described by Mantovani and Cenini.³² Pd₂(dba)₃·CHCl₃²⁷ and (1,5-COD)PdCl₂³³ were prepared by established routes.

Ph₂Ppy. A solution of *n*-butyllithium (22.4 mL of a 2.4 M hexane solution, 54 mmol) was added slowly to a solution of diphenylphosphine (10 g, 54 mmol) in tetrahydrofuran (200 mL) at room temperature. The resulting red solution was stirred for 1/2 h. A solution of 2-chloropyridine (5.0 g mL, 54 mmol) in tetrahydrofuran (40 mL) was then added dropwise during 1 h, at room temperature. The red color of the solution dissipated slowly upon addition of 2-chloropyridine. After this the solution was stirred overnight, 50 mL of ethanol was added, and the mixture was stirred for an additional 1/2 h. Then all the solvents were removed in vacuo to give a yellow solid (13.8 g).

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- (38) Definitions are as follows: $R = \sum |F_o| - |F_c| / \sum |F_o|$; the quantity minimized during final refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o) + 0.001F_o^2$. In the initial stages of solution a Hughes weighting scheme was employed.
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The product was extracted by dissolution in hot hexane (800 mL) to give a light yellow solution. After treatment by charcoal, filtration of the resulting colorless solution, and evaporation of the solvent, the pure product was obtained as white crystals having a melting point of 82 °C (lit.³⁴ mp 84–85 °C) (13.25 g, 94% yield based on PPh₃H). The identity of the product was confirmed by comparison of the infrared spectrum and the ³¹P{¹H} NMR spectrum with those of an authentic sample.

[Ru(CO)₃(Ph₂Ppy)]₃. This was prepared according to the method described for the triphenylphosphine analogue.¹⁷ Triruthenium dodecacarbonyl (0.46 g, 0.72 mmol) was dissolved in methanol (20 mL) and a threefold excess of 2-(diphenylphosphino)pyridine (0.64 g, 2.4 mmol) added. Upon reflux for 5 h, a dark violet precipitate was formed. This precipitate was collected, washed with methanol, and dried in vacuo (0.70 g, 73% yield). It may be recrystallized from dichloromethane/diethyl ether. Anal. Calcd for C₆₀H₄₂N₃O₃P₃Ru₃: C, 53.57; H, 3.15; N, 3.12. Found: C, 53.55; H, 3.21; N, 3.11.

(Ph₂Ppy)₂Ru(CO)₃. This was prepared by an adaptation of reported procedures for the PPh₃ analogue.^{18,19} Triruthenium dodecacarbonyl (0.40 g, 0.63 mmol) was dissolved in dioxigen-free hexane (400 mL), and an excess of Ph₂Ppy (0.99 g, 3.8 mmol) was added under an inert atmosphere. After irradiation of the orange solution at 25 °C with a UV lamp at λ > 390 nm (2 M NaNO₂ filter) for 5 h, a pale yellow precipitate had formed. This precipitate was collected, washed with hexane, and dried in vacuo (1.02 g, 76% yield). It was recrystallized from dichloromethane/ethyl ether to give pale yellow crystals. Anal. Calcd for C₃₇H₂₈N₂O₃P₂Ru: C, 62.48; H, 3.97; N, 3.94. Found: C, 62.47; H, 3.92; N, 3.90.

Ru(Ph₂Ppy)₂(CO)₂Cl₂. This follows the work of Collman and Roper.²⁰ A stream of dichlorine was bubble for a few seconds through a yellow solution of Ru(CO)₃(PPh₂py)₂ (0.71 g) in dichloromethane (35 mL) at room temperature. The infrared spectrum (ν_{CO} 2143 w, 2085 vs, 2052 s cm⁻¹) of the resulting pale yellow solution indicated the complete transformation of the starting material into the ionic species [Ru(CO)₃Cl(PPh₂py)₂]⁺Cl⁻ (identified by analogy with the infrared spectrum of [Os(CO)₃Br(Ph₂P)₂]⁺Br⁻ in the CO stretching region³⁵). Upon reflux for 6 h, decarbonylation of the cation occurred to give the title compound quantitatively as indicated by the evolution of its infrared spectrum. The solvent was then evaporated, and the solid residue was crystallized from dichloromethane/ethyl ether. White crystals (0.57 g, 76% yield) of Ru(Ph₂Ppy)₂(CO)₂Cl₂ were obtained. The compound crystallizes in the space group *Pbca* (No. 61) with *a* = 16.44 (1), *b* = 21.05 (1), and *c* = 19.60 (1) Å. Anal. Calcd for C₃₆H₂₈N₂B₂Cl₂P₂Ru: C, 57.30; H, 3.75; N, 3.71; Cl, 9.40. Found: C, 57.06; H, 3.82; N, 3.63; Cl, 9.71.

Reaction of Ru(Ph₂Ppy)₂(CO)₃ with (1,5-COD)PdCl₂. Treatment of a colorless solution of Ru(Ph₂Ppy)₂(CO)₃ (0.498 g, 0.70 mmol) in dichloromethane (25 mL) with an excess of yellow (1,5-COD)PdCl₂ (0.244 g, 0.86 mmol) in dichloromethane (20 mL) produced, within a few seconds, a deep red-brown solution. The infrared spectrum of this solution exhibited carbon monoxide stretching absorptions at 2065 vs, 2005 vs, br, and 1955 m cm⁻¹ while the ³¹P{¹H} NMR spectrum showed resonances due to five compounds: A, 4.44 ppm, singlet, 38% yield; B, -6.84 ppm, singlet, 31%; C, 21.49 ppm, singlet, 16%; D, 38.88 ppm, doublet, 17.95 ppm, doublet, *J*(P,P) = 7.5 Hz, 8%; E, 20.14 ppm, doublet; 16.54 ppm, doublet, *J*(P,P) = 2 Hz, 7%. The solution was filtered and the solvent was removed in vacuo to give a red-brown solid (0.56 g). Fractional crystallization of the crude product from dichloromethane by the gradual addition of ethyl ether gave successively a crop of red crystals and a crop of white crystals. The red crystals, which showed no infrared absorption in the carbonyl region (2200–1600 cm⁻¹), were identified as A by the presence of a ³¹P NMR resonance at 4.4 ppm. The white crystals had infrared absorptions at 2067 vs and 2007 vs cm⁻¹ in dichloromethane solution and were identified as B by a ³¹P NMR resonance at -6.84 ppm. The solution that remained after the removal of these two species was evaporated to dryness, and the orange residue was dissolved in a minimum volume of methanol to give an orange solution and a white solid. This white solid was identified as C by ³¹P NMR spectroscopy (singlet at 21.5 ppm) and had carbonyl absorptions at 2062 s and 2002 vs cm⁻¹ in dichloromethane solution. The remaining methanolic solution was cooled and stored at -5 °C. Yellow needles (ν_{CO} 2013 vs, 1954 vs cm⁻¹; ³¹P NMR 38.8 ppm (doublet, *J* = 7.5 Hz), 17.9 ppm (doublet, *J* = 7.5 Hz)) were deposited and identified as compound D. Further concentration and cooling of the remaining solution gave orange crystals of compound E (ν_{CO} 2025 vs, 1965 vs; ³¹P NMR 20.1 ppm

(doublet, *J* = 2 Hz), 16.5 ppm (doublet, *J* = 2 Hz)).

Pd(Ph₂Ppy)₂Cl₂·1.7CH₂Cl₂. A solution containing 0.505 g (1.3 mmol) of Pd(C₇H₅N)₂Cl₂ in 10 mL of dichloromethane was added dropwise to a solution containing 0.74 g (2.8 mmol) of Ph₂Ppy also in dichloromethane. Yellow crystals were precipitated by the dropwise addition of ethyl ether. The crystals were collected by filtration, washed with ethyl ether, and vacuum dried; yield 0.916 g, 99%. The presence of dichloromethane was confirmed by ¹H NMR in CDCl₃. Integration of the CH₂Cl₂ peak vs. the phenyl region gave a ratio of 3.4:28. Anal. Calcd for C₃₄H₂₈Cl₂N₂P₂Pd·1.7CH₂Cl₂: C, 50.5; H, 3.73; N, 3.30; Cl, 22.57. Found: C, 50.45; H, 3.87; N, 3.19; Cl, 22.71.

Pd₂(Ph₂Ppy)₂Cl₂. A deep violet solution of Pd₂(dba)₃·CHCl₃ (0.094 g, 0.09 mmol) in dichloromethane (20 mL) was added to a stirred suspension of Pd(Ph₂Ppy)₂Cl₂ (0.128 g, 0.18 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the dark red solution was filtered. The solution was concentrated under vacuum to ca. 5 mL, and ethyl ether was added dropwise to the solution. The dark red crystals of the product that deposited were collected by filtration, washed with ethyl ether, and dried under vacuum (yield 90%). Anal. Calcd for C₃₄H₂₈N₂Cl₂P₂Pd₂: C, 50.39; H, 3.49; N, 3.46. Found: C, 49.23; H, 3.54; N, 3.30.

RuPd(Ph₂Ppy)₂(CO)₂Cl₂. A solution of Ru(Ph₂Ppy)₂(CO)₂Cl₂ (0.413 g, 0.55 mmol) and Pd₂(dba)₃·CHCl₃ (0.284 g, 0.27 mmol) in dichloromethane (60 mL) was heated under reflux for 2 h. The solution was filtered, and the filtrate was evaporated to dryness under vacuum. The solid was redissolved in a minimum volume of dichloromethane and transferred onto a wet-packed 27 × 2 cm silica gel chromatography column. Elution of the column with a 5:1 v/v mixture of dichloromethane/acetone produced five bands with the following characteristics: first band, yellow, contains Ru(Ph₂Ppy)(CO)₂Cl₂ and RuPd(Ph₂Ppy)₂(CO)₂Cl₂; second band red, contains RuPd(Ph₂Ppy)₂(CO)₂Cl₂, isomer E; third band, yellow, contains RuPd(Ph₂Ppy)₂(CO)₂Cl₂, isomers D and E; fourth band, orange, contains RuPd(Ph₂Ppy)₂(CO)₂Cl₂, isomer D; fifth band, yellow contains RuPd(Ph₂Ppy)₂(CO)₂Cl₂, isomer D. Band composition was determined by infrared and ³¹P NMR spectroscopy. Bands 4 and 5 were combined, and their volume was reduced to 5 mL. The dropwise addition ethyl ether produced 0.11 g (23%) of ochre crystals of RuPd(Ph₂Ppy)₂(CO)₂Cl₂·0.5CH₂Cl₂, isomer D. Anal. Calcd for C_{36.5}H₂₉N₂O₂Cl_{1.5}P₂RuPd: C, 48.52; H, 3.24; N, 3.10; Cl, 11.77. Found: C, 47.92; H, 3.42; N, 3.05; Cl, 11.45. Band 2 was evaporated to 3 mL. The dropwise addition of ethyl ether produced orange crystals of isomer E, which were collected by filtration, washed with ether, and vacuum dried (yield 0.2 g, 4.2%). The composition of isomer E was confirmed by the X-ray crystallographic study reported in the next section.

RuPd(Ph₂Ppy)₂(CO)₂Cl₂·1.25CH₂Cl₂. X-ray Data Collection. A dark yellow crystal of isomer E of dimensions 0.12 × 0.20 × 0.20 mm was found to be suitable for X-ray data collection. The crystal was mounted on the goniometer head of a Syntex P2₁ diffractometer in a cold stream of N₂(g), which maintained the crystal temperature at 140 K. The radiation used was graphite-monochromated Mo Kα (λ 0.71069 Å). A typical reflection, located by using a rotation photograph, had a width at half-height of 0.4° on an ω scan. With use of procedures described elsewhere²¹ the space group was found to be *P2*₁/c (No. 14) and the density 1.61 g cm⁻³, indicating *Z* = 4 (fw 967.14). A least-squares fit of 16 reflections with 30° < 2θ < 43° yielded cell dimensions *a* = 10.493 (2) Å, *b* = 17.685 (4) Å, *c* = 21.470 (5) Å, β = 92.07 (2)°, and *V* = 3982 (1) Å³.

Data were collected with use of an ω scan of 1° range and speed ranging from 2 to 60°/min. Stationary-background counts were collected with a 1° offset from the center of the peak. Two check reflections were monitored throughout and showed only a random fluctuation. Reflections were collected to 2θ = 45°, yielding 5387 unique data. The data were corrected for Lorentz and polarization effects but not for absorption (μ(Mo Kα) = 12.3 cm⁻¹). For a crystal of the dimensions given the absorption correction factors range from 1.28 to 1.51. Reduction of the data to *F*_o and σ(*F*_o) were as previously described.³⁶

Solution and Refinement of the Structure. The structure was solved by finding two metal atoms on a Patterson map.³⁷ Four chlorine atoms (two of these were from a molecule of crystallization of CH₂Cl₂), two phosphorus atoms, and one nitrogen atom were located on a first Fourier map. Full-matrix least-squares refinement of these atoms brought *R* to 0.26.³⁸ The remaining atoms were located on a second Fourier map except for a partially occupied second CH₂Cl₂ molecule,

which was assigned an estimated occupancy of 0.25 on the basis of its intensity in a difference Fourier map. Full-matrix least-squares refinement of all non-hydrogen atoms using isotropic thermal parameters yielded an R of 0.060. The final stage of refinement made use of the blocked-cascade least-squares method and a riding model for hydrogen atoms in which a hydrogen atom was given a computed position and assigned a thermal parameter 1.2 times that of the carbon atom to which it was bonded. In addition, the atoms Ru, Pd, Cl(1), Cl(2), P(1), P(2), C(1), C(2), O(1), and O(2) of the title compound, as well as the fully occupied molecule of dichloromethane, were given anisotropic thermal parameters. This brought the number of parameters to 274, yielding R of 0.043, $R_w = 0.049$, by using 4605 reflections ($I > 3\sigma(I)$). Neutral-atom scattering factors and corrections for anomalous dispersion for Pd, Ru, Cl, and P were from ref 40. Positional and isotropic thermal parameters, hydrogen atom coordinates, anisotropic thermal parameters, and structure factor tables

are available as supplementary material.

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Registry No. A, 78055-58-0; B, 78790-90-6; C, 78790-91-7; D, 82648-72-4; E, 82690-70-8; $[\text{Ru}(\text{CO})_3(\text{Ph}_2\text{Ppy})]_3$, 82690-69-5; $(\text{Ph}_2\text{Ppy})_2\text{Ru}(\text{CO})_3$, 82648-71-3; $\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$, 78088-45-6; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $(1,5\text{-COD})\text{PdCl}_2$, 12107-56-1; $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, 14220-64-5; $\text{Pd}_2(\text{dba})_3$, 51364-51-3; Ru, 7440-18-8; Pd, 7440-05-3.

Supplementary Material Available: Anisotropic temperature factors (Table V), hydrogen coordinates (Table VI), a stereoscopic view of $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$, isomer E (Figure 4), and a table of structure factors for $\text{RuPd}(\text{Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_2$ (31 pages). Ordering information is given on any current masthead page.

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Concerning the Absorption Spectra of the Ions $\text{M}(\text{bpy})_3^{2+}$ ($\text{M} = \text{Fe, Ru, Os}$; $\text{bpy} = 2,2'$ -Bipyridine)

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An electronic structural model, which includes spin-orbit coupling, is developed for the absorption spectra of the ions $\text{M}(\text{bpy})_3^{2+}$ ($\text{M} = \text{Fe, Ru, Os}$; $\text{bpy} = 2,2'$ -bipyridine). It is found that, even for Os, the excited states can be classified as "singlets" and "triplets" although there is considerable mixing between the pure spin states. Consequently, the luminescent excited states of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Os}(\text{bpy})_3^{2+}$ are assigned as being states largely "triplet" in character. Explicit assignments of the absorption spectra for the complexes are proposed. The implications of the present treatment relative to other theoretical analyses are discussed.

Introduction

Polypyridyl complexes of the type $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Os}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) have been studied intensively¹ in part because of possible applications of their metal to ligand charge transfer (MLCT) excited states in energy conversion processes.² Despite their importance, the electronic structures of the MLCT excited states have not been clearly delineated. In particular, three rather fundamental questions have not been totally resolved: (1) Is the promoted electron localized in the π^* levels of a single bpy ligand or is it delocalized over the π^* orbitals of all three bpy ligands?³⁻⁵ (2) Can the lower lying excited states be characterized as being triplet states or is such a description meaningless?^{5,6} (3) Why is the excited-state lifetime of $\text{Os}(\text{bpy})_3^{2+}$ so much shorter than that of $\text{Ru}(\text{bpy})_3^{2+}$?^{5,7,8}

Pertinent information concerning each of the three questions is obtainable from an analysis of electronic absorption spectra. Recently, the polarized absorption spectra (at 8 K) of the $\text{M}(\text{bpy})_3^{2+}$ ions ($\text{M} = \text{Fe, Ru, Os}$) doped into single crystals of $\text{Zn}(\text{bpy})_3^{2+}$ salts have been reported.⁶ It was noted that the intensity of the lowest lying MLCT transitions relative to the strongest MLCT transitions increased dramatically in the series $\text{Fe} < \text{Ru} < \text{Os}$. The increase was found to be proportional to λ^2 , where λ is the spin-orbit coupling constant of the metal, and it was inferred that lowest energy bands were transitions to "triplet" states into which appreciable singlet

character was mixed via spin-orbit coupling. It was also found that the absorption spectrum of $\text{Os}(\text{bpy})_3^{2+}$ was much more complex than that of the other ions, and it has been suggested that spin-orbit coupling could be responsible for the increased complexity as well.^{6,9} Neither of these latter two points was

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